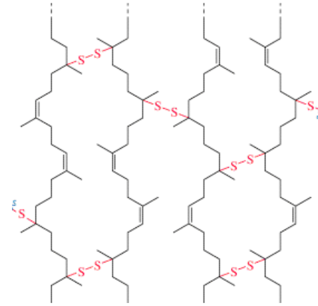


Organic Chemistry, 7th Edition
L. G. Wade, Jr.

Chapter 26

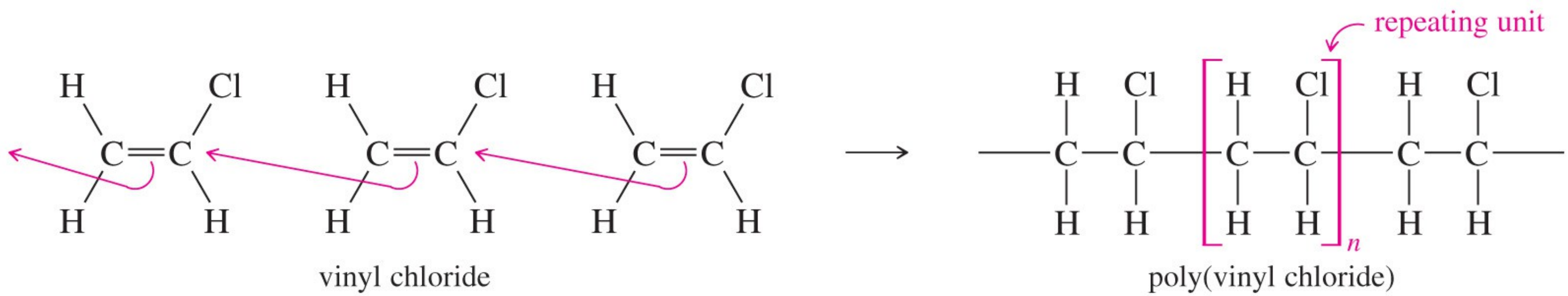
Synthetic Polymers

Introduction

- A ***polymer*** is a large molecule composed of many smaller repeating units.
- First synthetic polymers:
  - Poly(vinyl chloride) in 1838.
  - Polystyrene in 1839.
- Now, 250 billion pounds are produced annually, worldwide.

Classes of Polymers

- Addition, or chain-growth, polymers.



- Condensation, or step-growth, polymers.

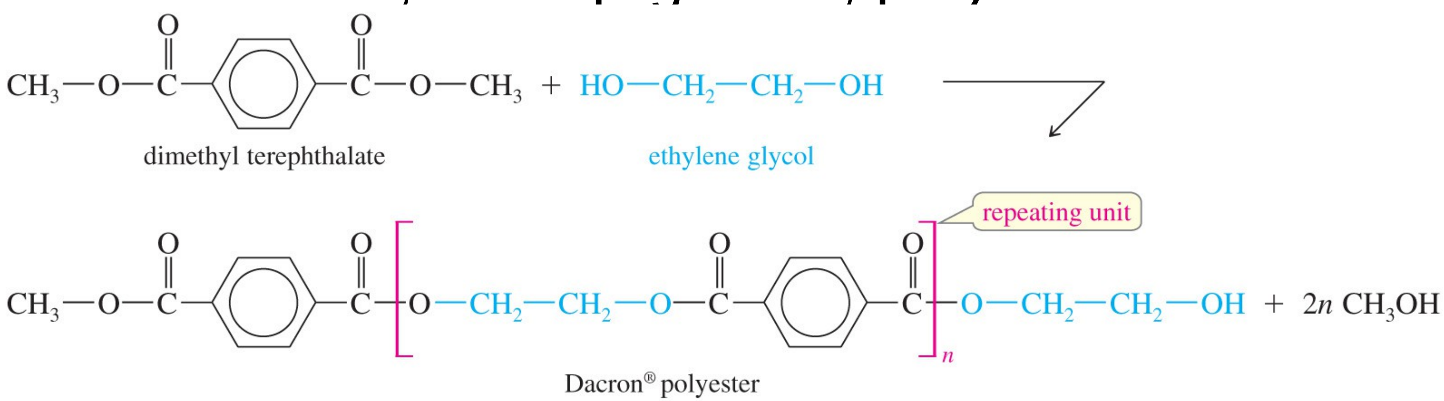


TABLE 26-1

Some of the Most Important Addition Polymers

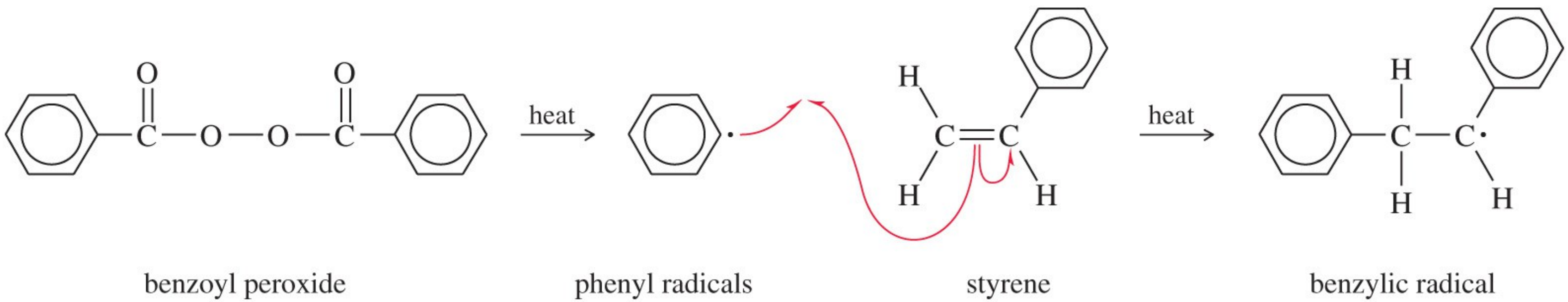
Polymer	Polymer Uses	Monomer Formula	Polymer Repeating Unit
polyethylene	bottles, bags, films	$H_2C{=}CH_2$	$-[CH_2-CH_2]_n-$
polypropylene	plastics, olefin fibers	$H_2C{=}CH(CH_3)$	$-[CH_2-CH(CH_3)]_n-$
polystyrene	plastics, foam insulation	$H_2C{=}CH(C_6H_5)$	$-[CH_2-CH(C_6H_5)]_n-$
poly(isobutylene)	specialized rubbers	$H_2C{=}C(CH_3)_2$	$-[CH_2-C(CH_3)_2]_n-$
poly(vinyl chloride)	vinyl plastics, films, water pipes	$H_2C{=}CHCl$	$-[CH_2-CHCl]_n-$
poly(acrylonitrile)	Orlon®, Acrilan® fibers	$H_2C{=}CH-C{\equiv}N$	$-[CH_2-CH(CN)]_n-$
poly(methyl α-methacrylate)	acrylic fibers, Plexiglas®, Lucite® paints	$H_2C{=}C(CH_3)-C(=O)-OCH_3$	$-[CH_2-C(CH_3)(COOCH_3)]_n-$
poly(methyl α-cyanoacrylate)	"super" glues	$H_2C{=}C(C{\equiv}N)-C(=O)-OCH_3$	$-[CH_2-C(CN)(COOCH_3)]_n-$
poly(tetrafluoroethylene)	Teflon® coatings, PTFE plastics	$F_2C{=}CF_2$	$-[CF_2-CF_2]_n-$

Addition Polymers

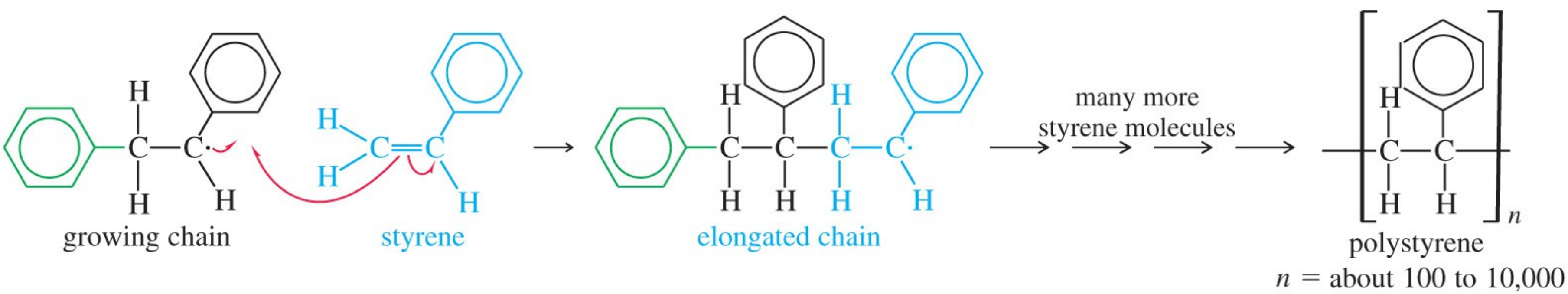
- Three kinds of intermediates:
  - Free radicals
  - Carbocations
  - Carbanions
- Examples of addition polymers:
  - Polypropylene plastics
  - Polystyrene foam insulation
  - Poly(acrylonitrile), Orlon® fiber
  - Poly(methyl -methacrylate), Plexiglas®

Free-Radical Polymerization

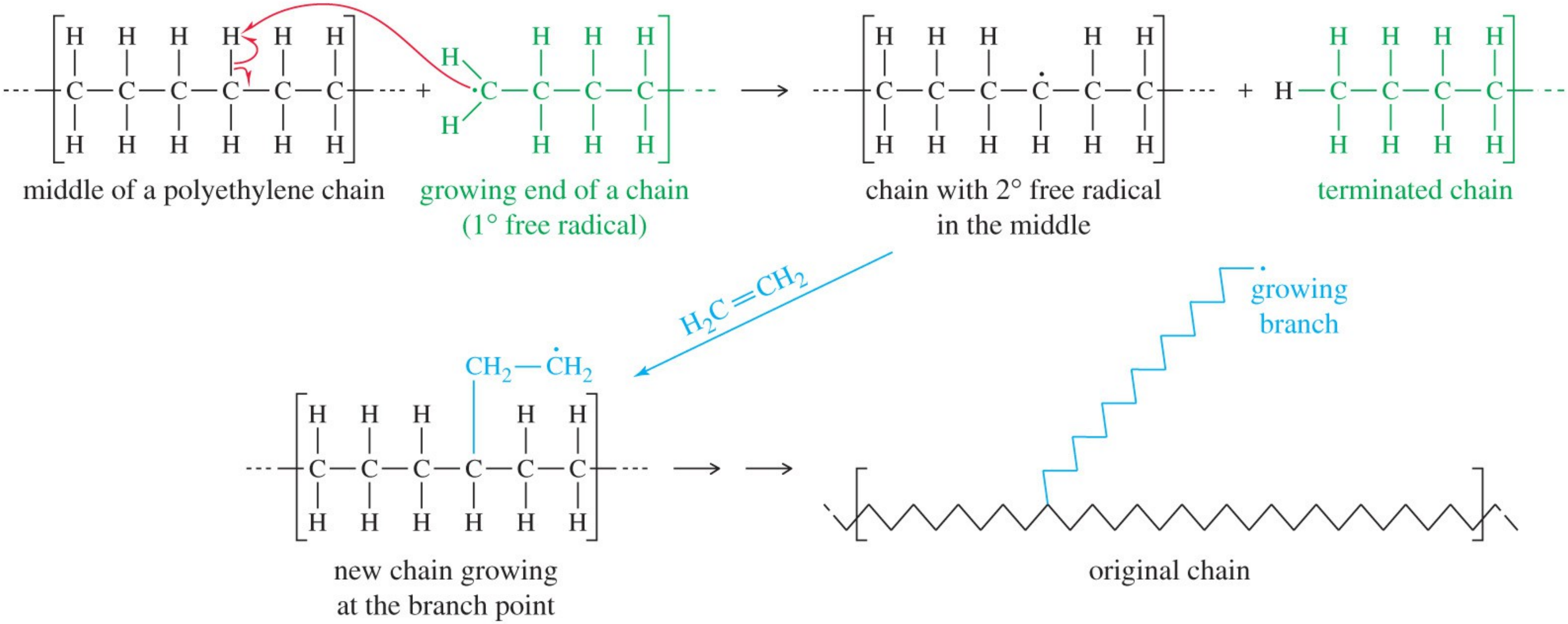
Initiation step:



Propagation step:



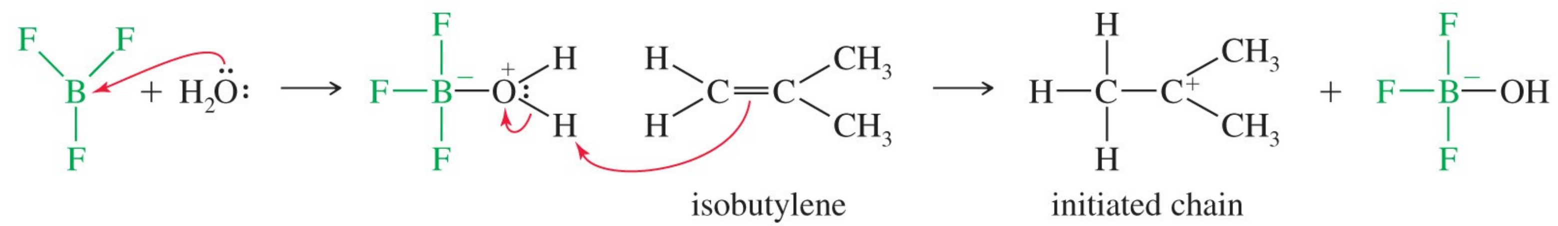
Chain Branching



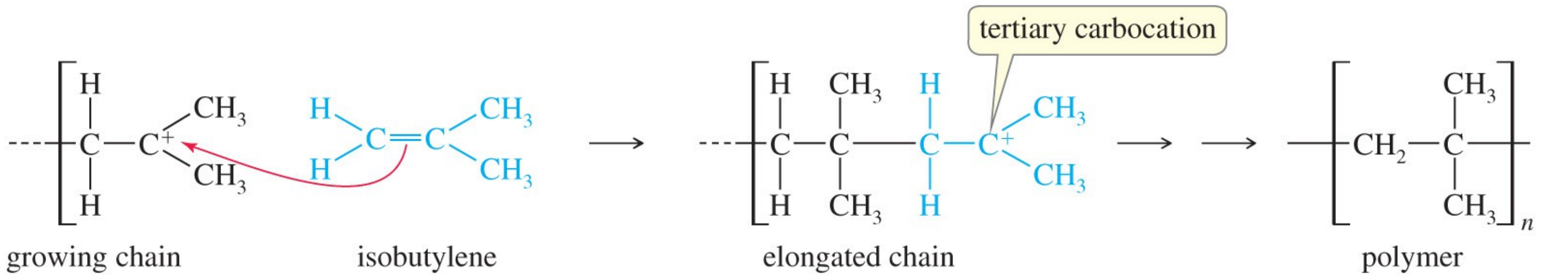
- ***Chain branching*** occurs when the growing end of a chain abstracts a hydrogen atom from the middle of a chain. A new branch grows off the chain at that point.
- Chain branching makes the polymer soft.

Cationic Polymerization

Initiation steps: The catalyst protonates the monomer, starting the chain.

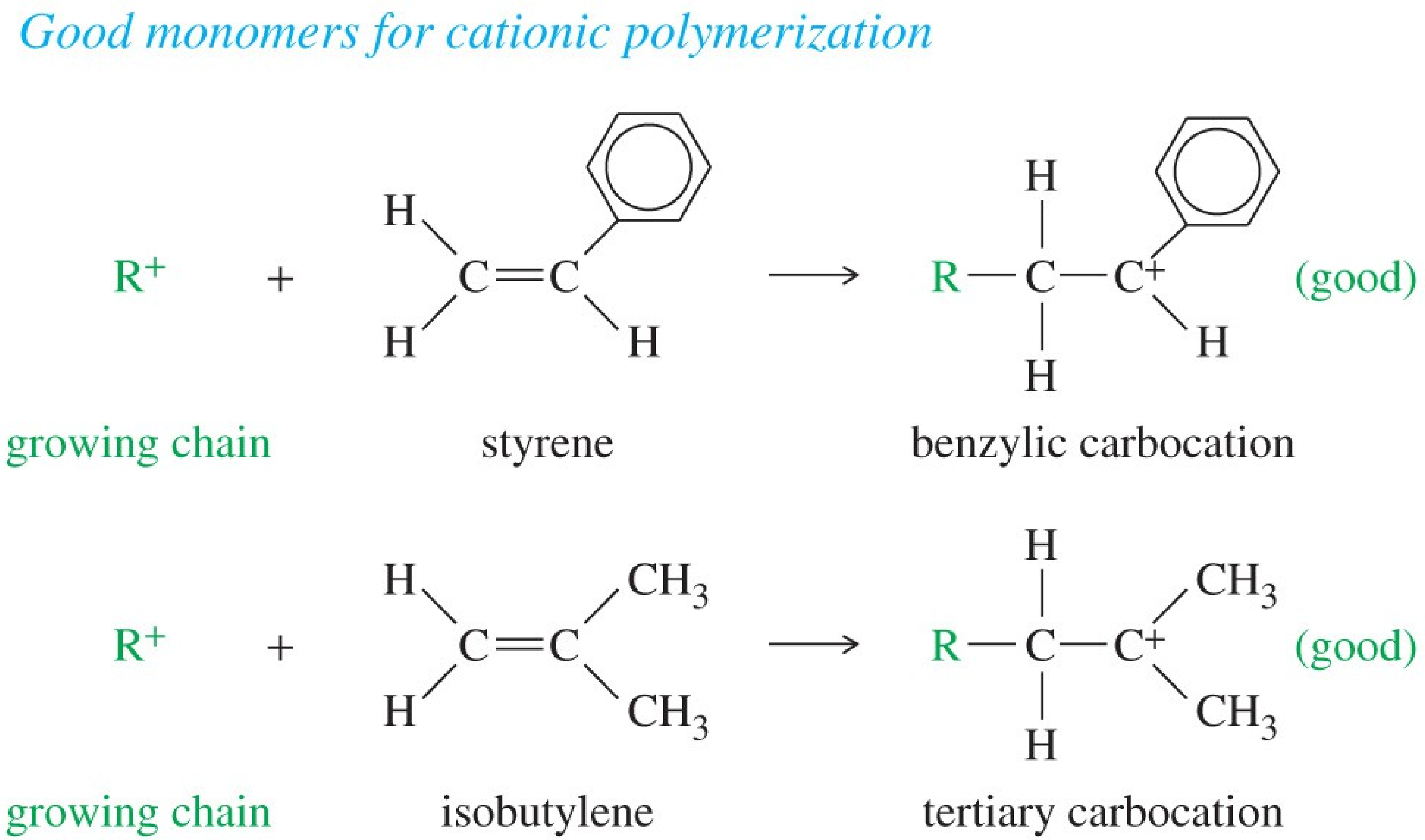


Propagation step: Another molecule of monomer adds to the chain.



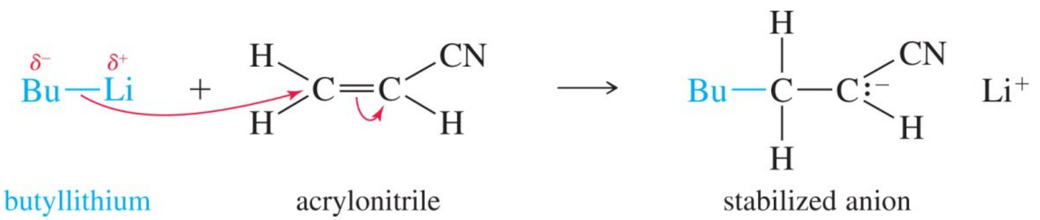
- Strongly acidic catalysts are used to initiate cationic polymerization.
- BF_3 is a particularly effective catalyst, requiring a trace of water or methanol as a co-catalyst. Intermediate must be a stable carbocation.

Good Monomers for Cationic Polymerization

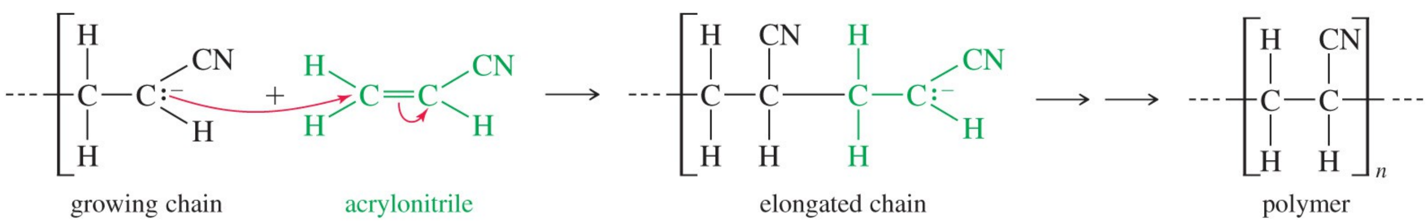


Anionic Polymerization

Initiation step: The initiator adds to the monomer to the form an anion.

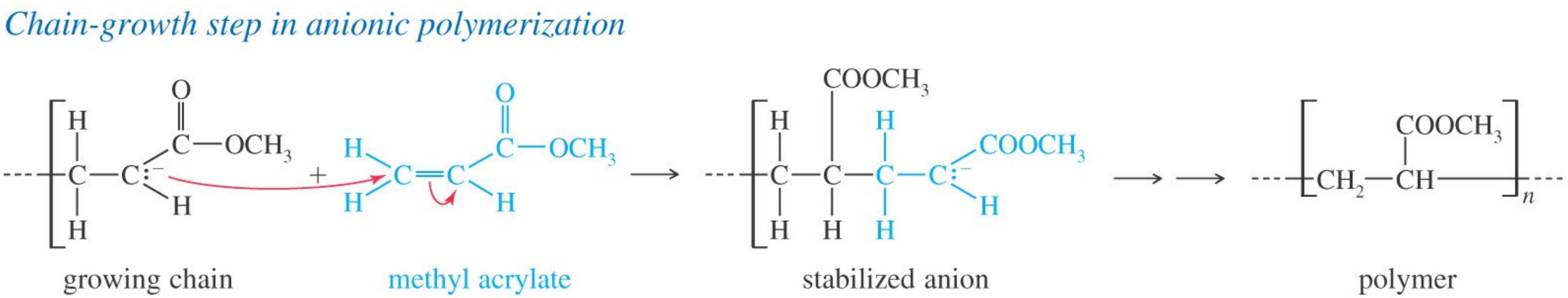


Propagation step: Another molecule of monomer adds to the chain.



- Alkene must have an electron-withdrawing group like C=O, C N, or NO_2.
- The reaction is initiated by a Grignard or organolithium reagent.

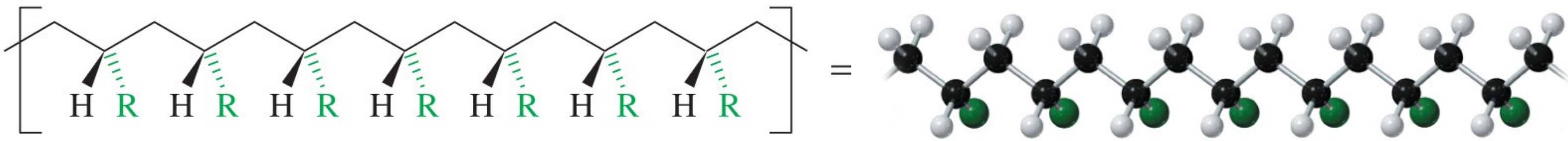
Chain-Growth Step in Anionic Polymerization



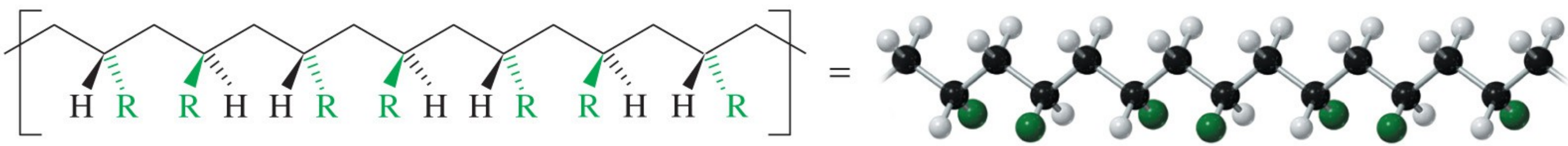
- Effective anionic polymerization requires a monomer that gives a stabilized carbanion when it reacts with the anionic end of the growing chain.

Stereochemistry of Polymers

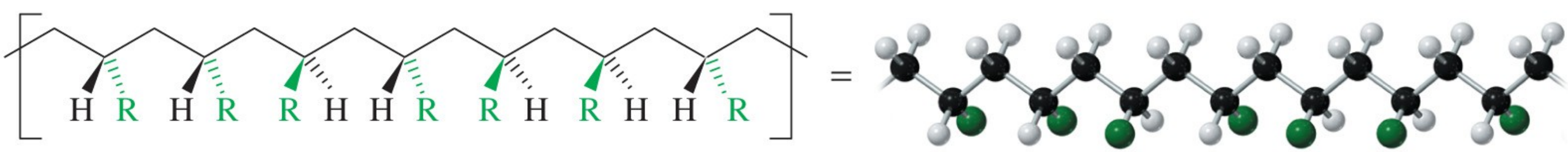
An isotactic polymer (side groups on the same side of the backbone)



A syndiotactic polymer (side groups on alternating sides of the backbone)



An atactic polymer (side groups on random sides of the backbone)



Properties of Polymers

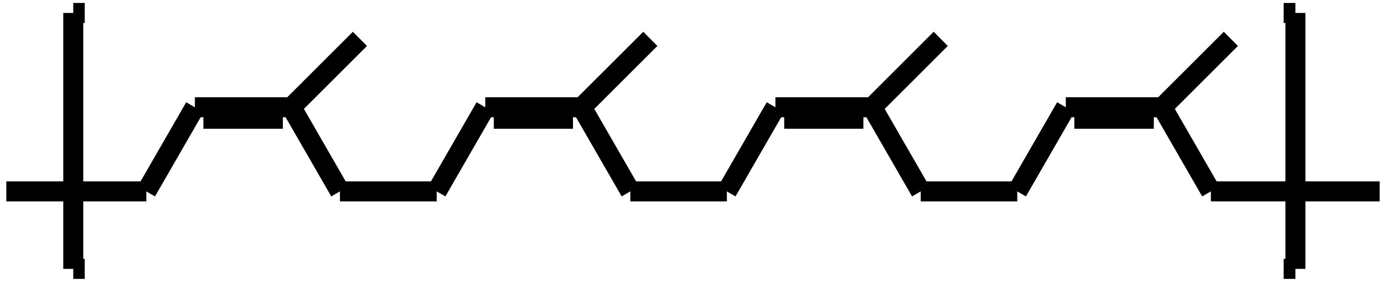
- Isotactic and syndiotactic polymers are stronger and stiffer due to their regular packing arrangement.
- Anionic intermediate usually gives isotactic or syndiotactic polymers.
- Free-radical polymerization is nearly random, giving branched atactic polymers.

Ziegler–Natta Catalyst

- Polymerization is completely stereospecific.
- Either isotactic or syndiotactic, depending on catalyst.
- Polymer is linear, not branched.
- Example of catalyst: Solution of $TiCl_4$ mixed with solution of $(CH_3CH_2)_3Al$ and heated for an hour.

Natural Rubber

- Soft and sticky, obtained from rubber tree.
- Long chains can be stretched, but then return to original structure.
- Chains slide past each other and can be pulled apart easily.



Structure is *cis*-1,4-polyisoprene

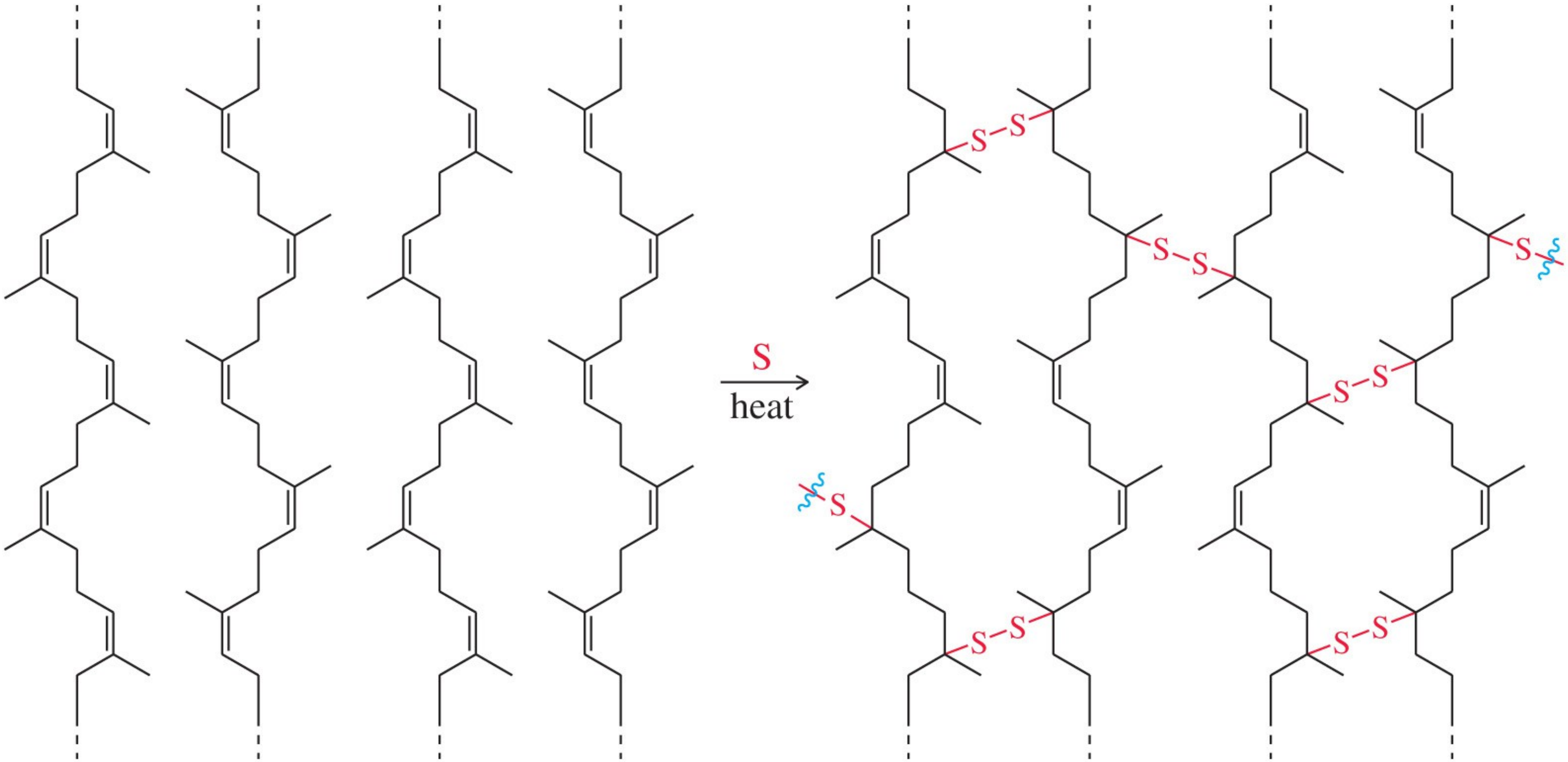
Latex

- White latex drips out of cuts in the bark of a rubber tree in a Malaysian rubber plantation.

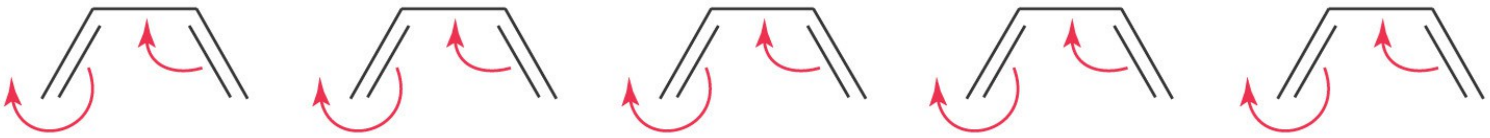
Vulcanization

- Process was discovered accidentally by Goodyear when he dropped rubber and sulfur on a hot stove.
- Sulfur produces cross-linking that strengthens the rubber.
- Hardness can be controlled by varying the amount of sulfur.

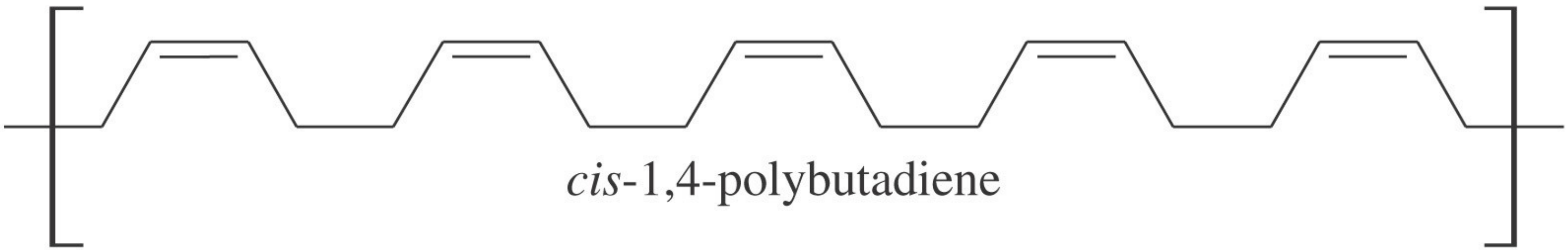
Vulcanization: Cross-Linking of Rubber



Synthetic Rubber



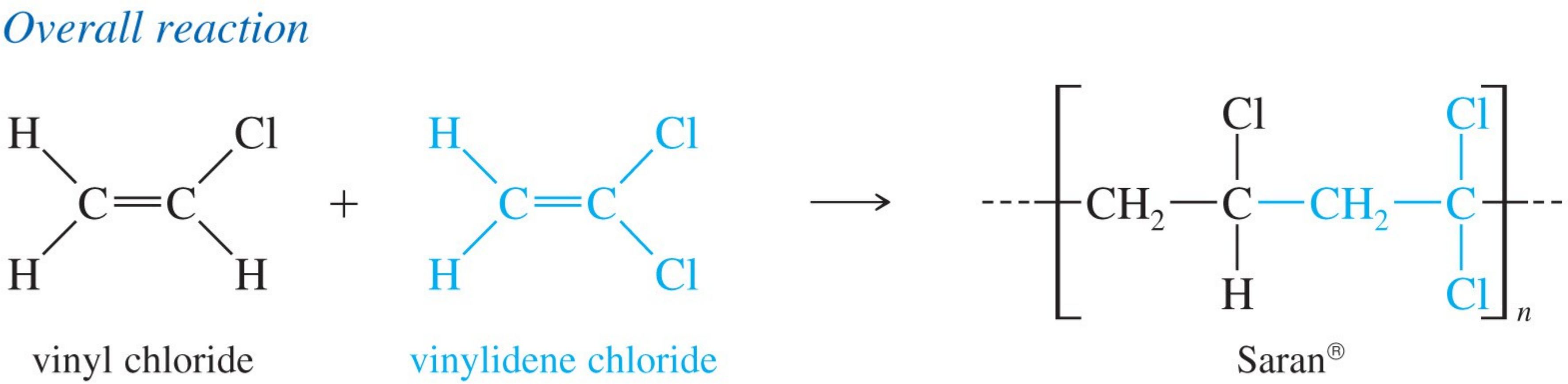
1,4-polymerization of 1,3-butadiene



cis-1,4-polybutadiene

- With a Ziegler–Natta catalyst, a polymer of 1,3-butadiene can be produced, in which all the additions are 1,4 and the remaining double bonds are all cis.
- It may also be vulcanized.

Copolymers of Two or More Monomers

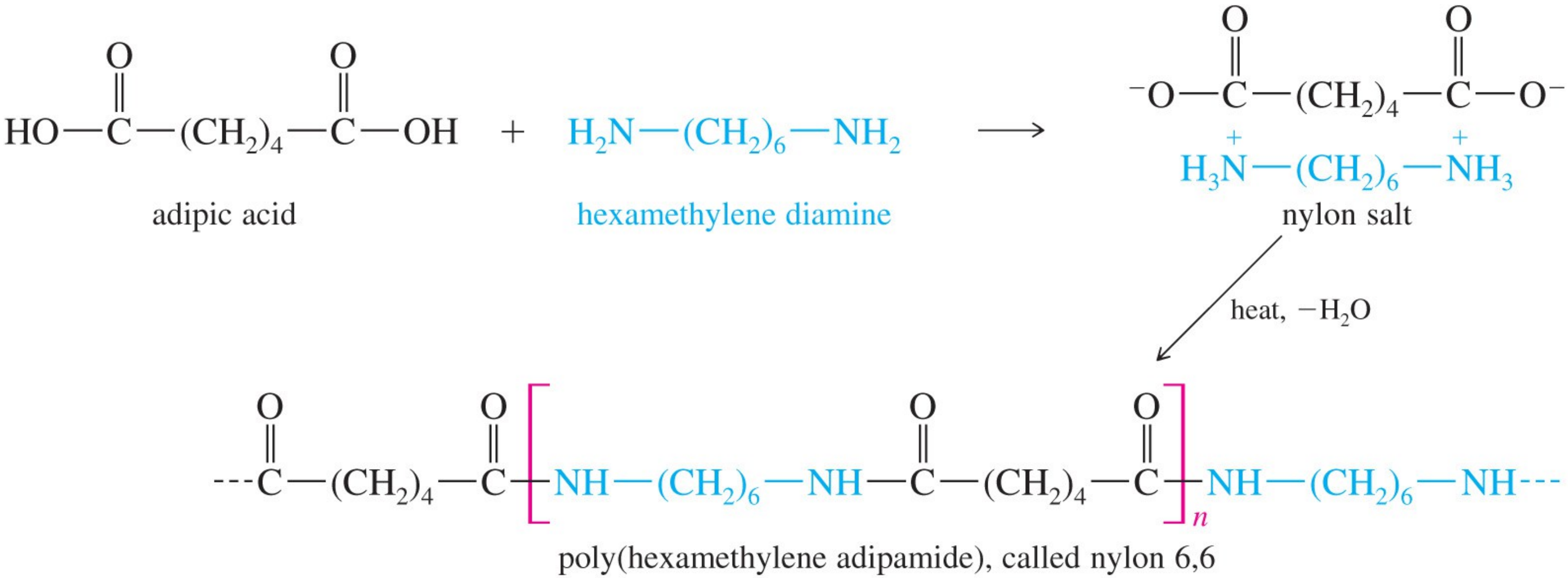


- Two or more different monomers.
- Saran®: Alternating molecules of vinyl choride and 1,1-dichloroethylene.
- ABS plastic: Acrylonitrile, butadiene, and styrene.

Condensation Polymers

- Polymer formed by ester or amide linkages between difunctional molecules.
- ***Step growth***: Monomers do not have to add one at a time. Small chains may condense into larger chains.
- Common types:
  - Polyamides
  - Polyesters
  - Polycarbonates
  - Polyurethanes

Synthesis of Nylon 6,6

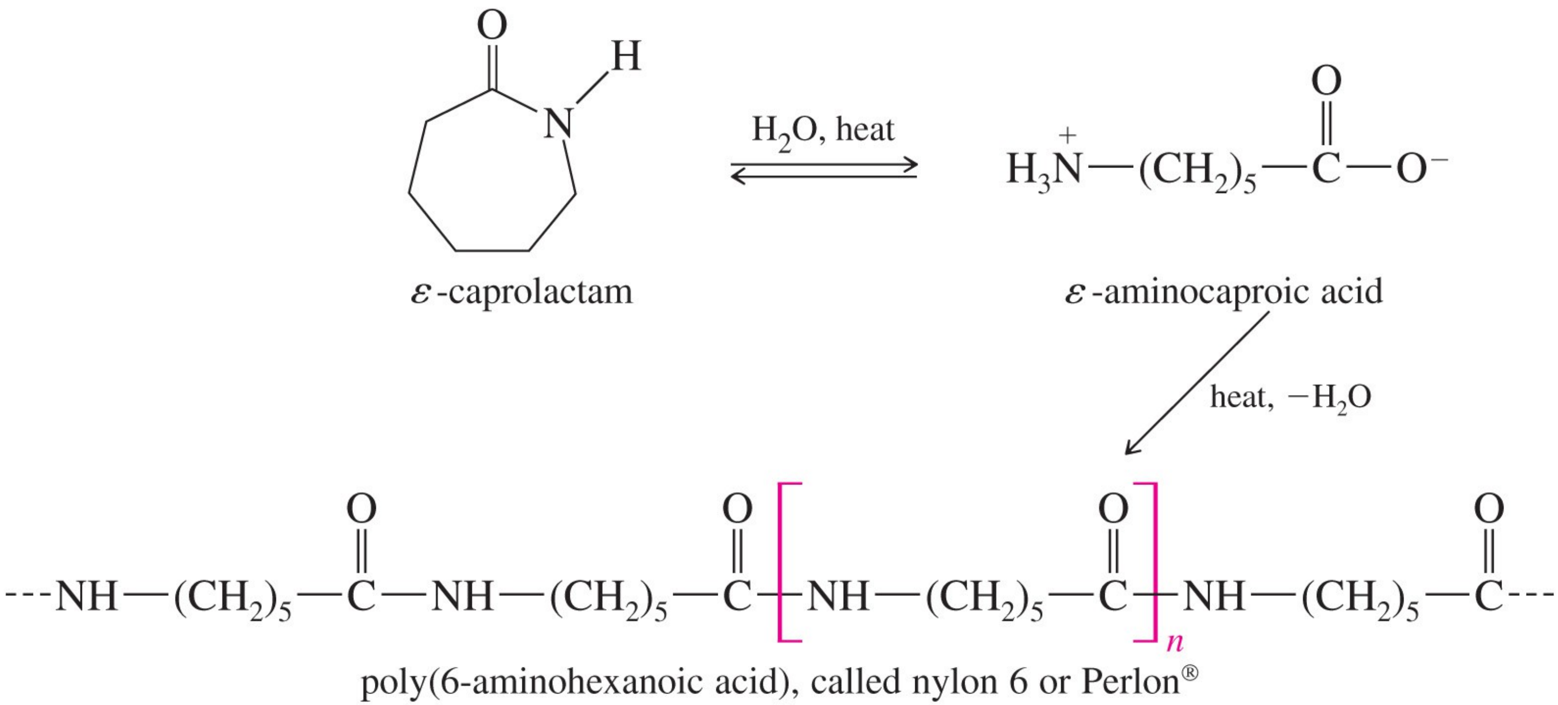


- Usually made from reaction of diacids with diamines, but may also be made from a single monomer with an amino group at one end and acid group at the other.

Nylon Stocking

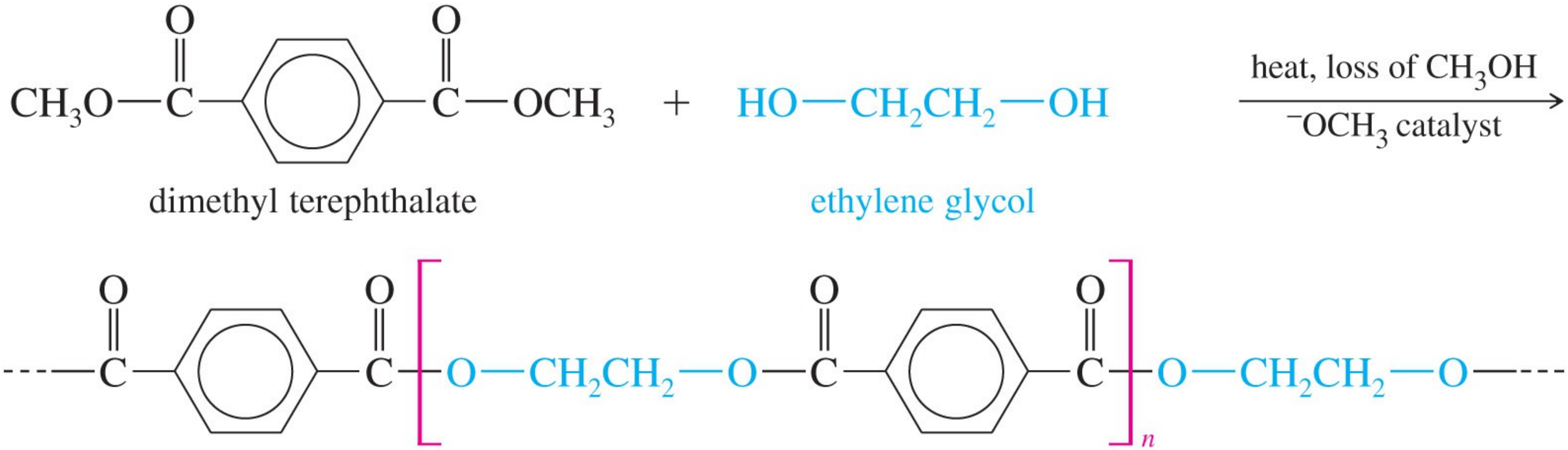
- Scanning electron micrograph of the material in a nylon stocking.
- Sheer stockings require long, continuous fibers of small diameter and enormous strength.

Nylon 6



- Nylon can also be made from a single monomer having an amino group at one end and an acid at the other.
- The reaction is similar to the polymerization of -amino acids to give proteins.

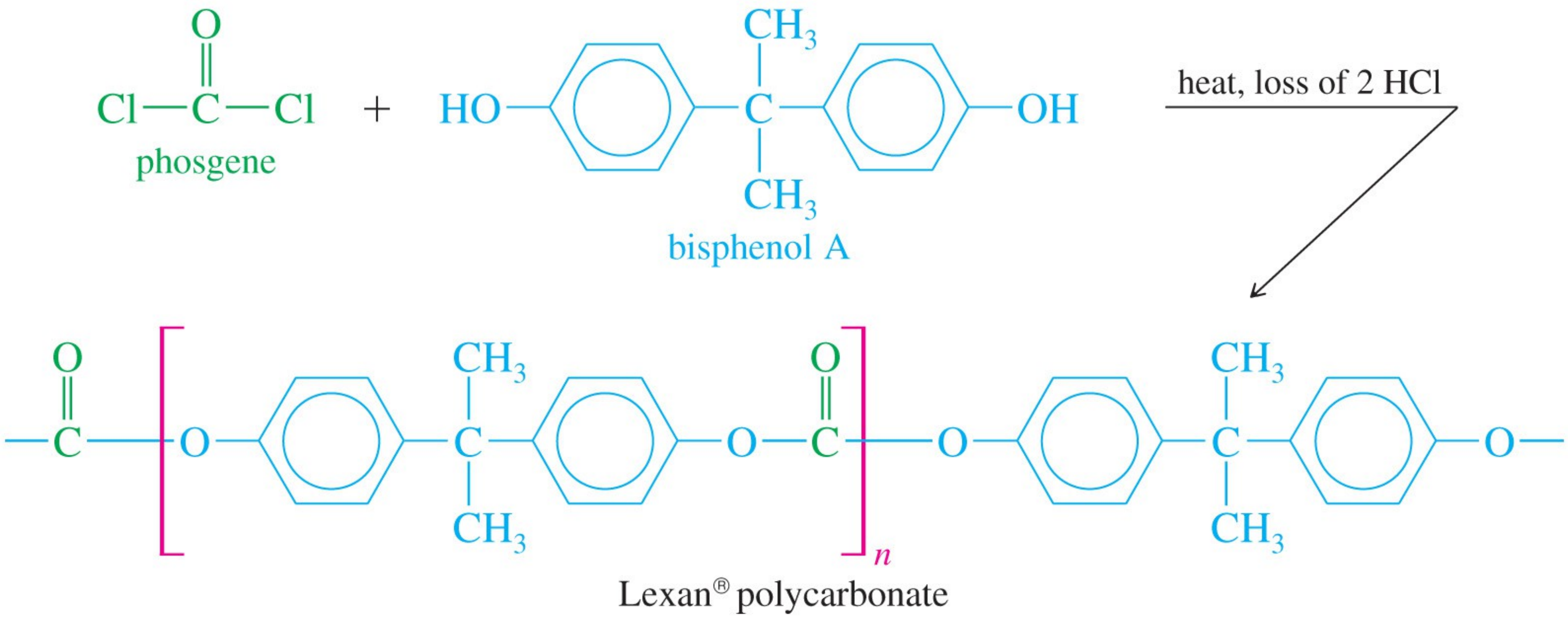
Polyesters



poly(ethylene terephthalate) or PET, also called Dacron® polyester or Mylar® film

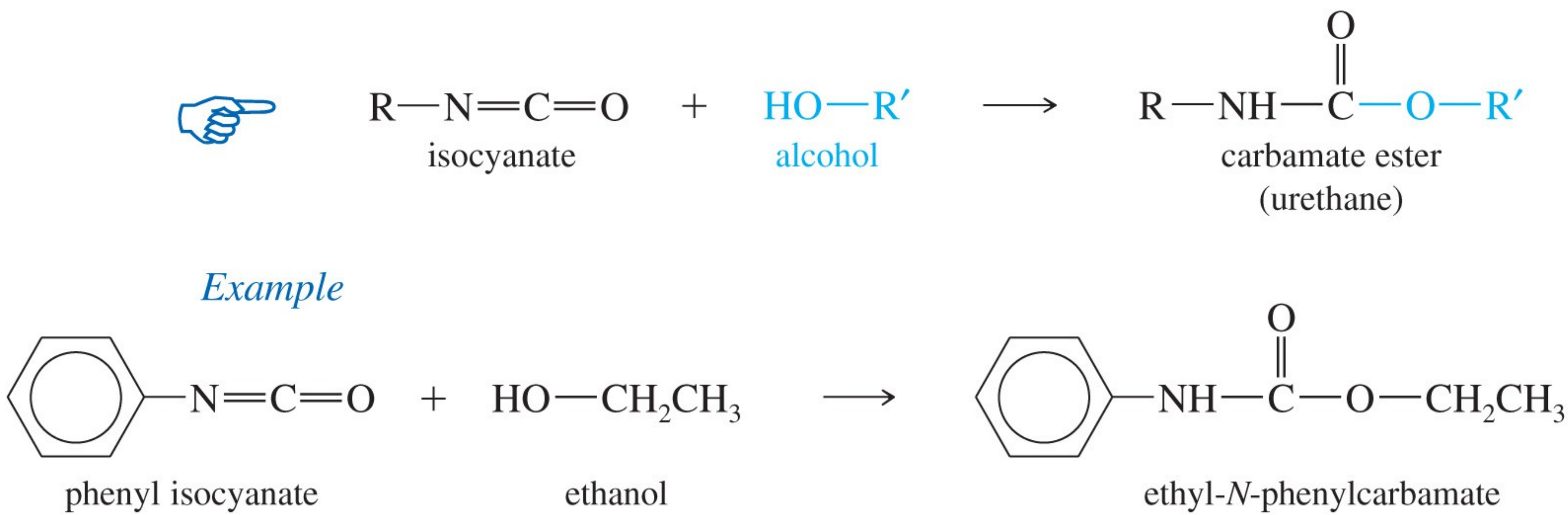
- Dacron® and Mylar®: Polymers of terephthalic acid and ethylene glycol.
- Made by the transesterification of the methyl ester.

Polycarbonates



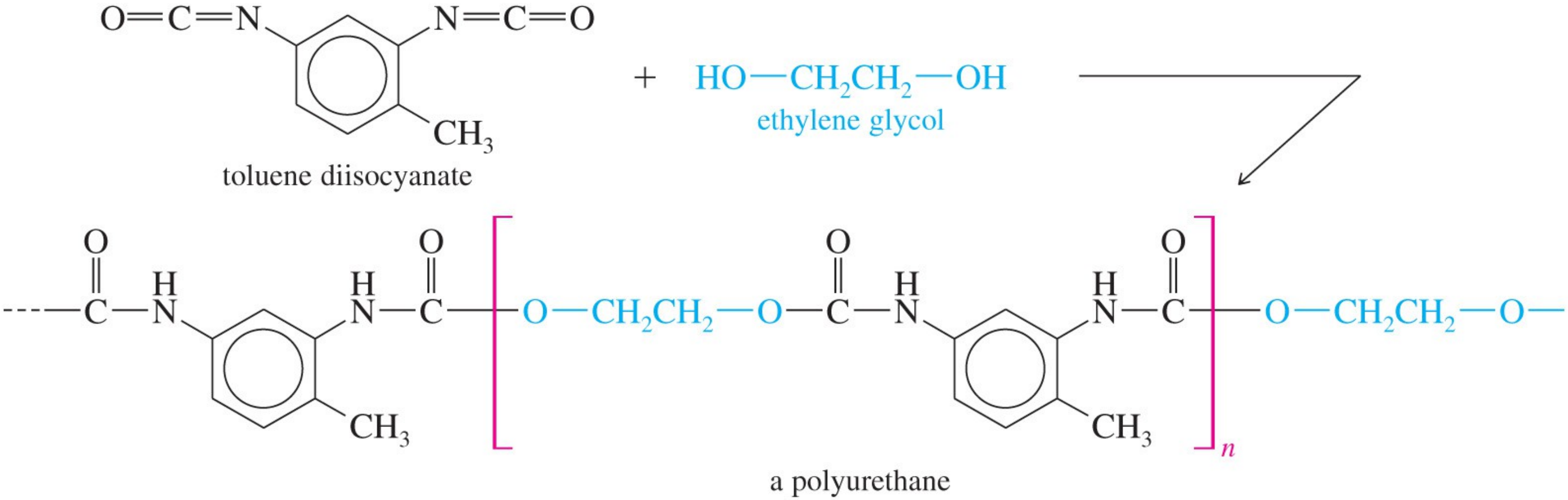
- Esters of carbonic acid.
- Carbonic acid is in equilibrium with CO_2 and water, but esters are stable.
- React phosgene with bisphenol A to obtain Lexan® for bulletproof windows.

Urethanes



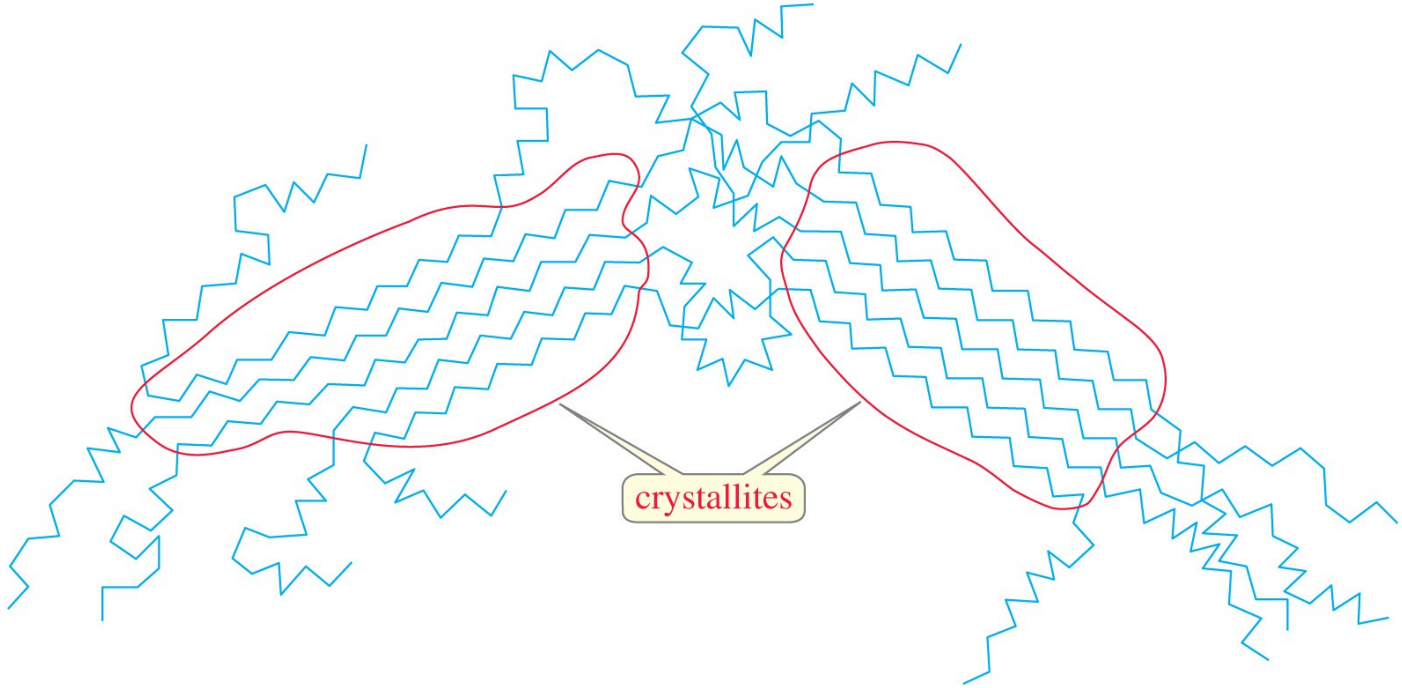
- Urethanes are most commonly made by treating an isocyanate with an alcohol or a phenol.
- The reaction is highly exothermic, and it gives a quantitative yield of a carbamate ester.

Polyurethanes



- Esters of carbamic acid, R—NH—COOH.
- Urethanes are prepared by reacting an alcohol with isocyanate.
- Polyurethanes are prepared by reacting a diol with a diisocyanate.

Polymer Crystallinity



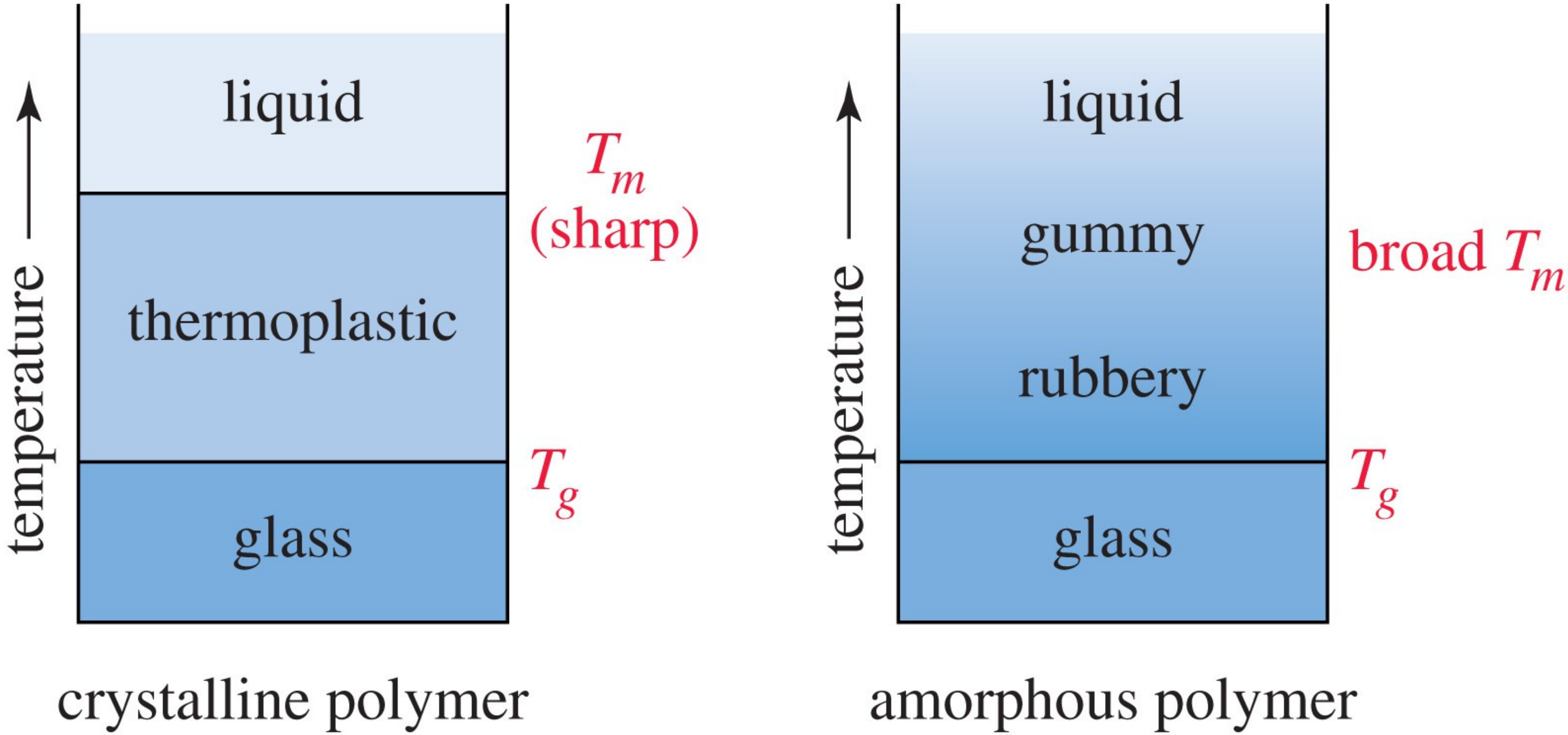
- Microscopic crystalline regions.
- A linear polymer will have a high degree of crystallinity and will be stronger, more dense, and more rigid.

Thermal Properties

- Glasses at low temperature, fracture on impact.
- At the glass transition temperature, T_g, crystalline polymers become flexible.
- At the crystalline melting temperature, T_m, crystalline polymers become a viscous liquid and can be extruded to form fibers.

Crystalline vs. Amorphous

Phase transitions for long-chain polymers.



Plasticizers

- Polymers can be too brittle for use even if their other properties are desirable.
- Addition of a plasticizer can make the polymer more flexible.
- A plasticizer lowers the attraction between chains and makes the polymer more flexible.
- The plasticizer evaporates slowly, so “vinyl” becomes hard and inflexible over time.