

Chap. 1. Basic Principles

1.1 Introduction & Historical Development

Stone age  Bronze age  Iron age

 Steel age [Industrial Revolution]

 Silicon age and silica age [telecom revolution])

 **Polymer age**

	Human	Nature
Machine	Computer	Brain
Material	Semiconductor	Macromolecules
Method	Electricity	Spirit
Regeneration	Waste, Regeneration	Reproduction

Polymer Science and Engineering

SCIENCE of **LARGE MOLECULES**

SYNTHESIS: linking of atoms

CHARACTERIZATION: physical property

POLYMER PHYSICS AND PHYSICAL CHEMISTRY:
law of nature (thermodynamics)

ENGINEERING: form of material

What are Polymers and Why Polymers are Important?

Long Chain Molecules

Extraordinary Range of Physical Properties

Many (Not All) are **Cheap**

What is a Polymer ?



Many **repeating units**

POLYMER

A **large molecule** made up of small **building blocks (monomers)**

MONOMERS

Building blocks

HOMOPOLYMER

What you get if the building blocks are all **the same**

COPOLYMER

A polymer made up of **different monomers**

BLEND

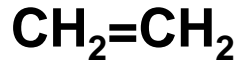
A mixture of **different polymers**

Classification by Origin

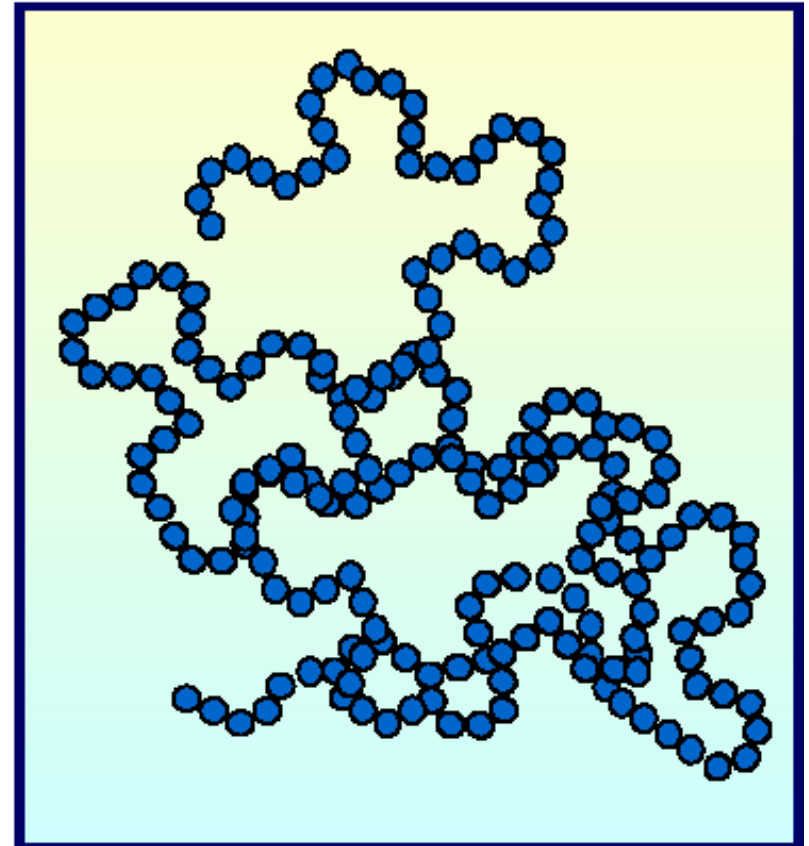
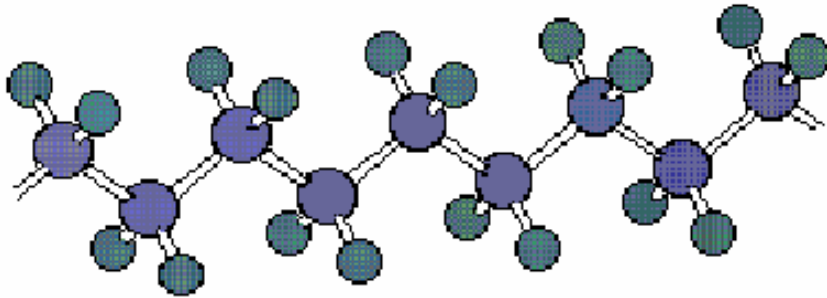
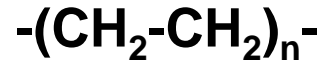
- **Synthetic** organic polymers
- **Biopolymers**
(proteins, polypeptides, polynucleotides, polysaccharides, natural rubber)
- **Semi-synthetic polymers**
(chemically modified biopolymers)
- **Inorganic polymers**
(siloxanes, silanes, phosphazenes)

How Big are Polymers ?

Ethylene



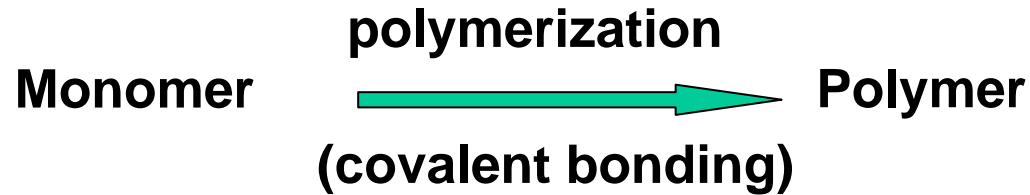
Polyethylene



Then because there are only 200 ethylene units in this chain (ie it is a **200-mer**), its molecular weight is only 5,600 (=28 x 200).

1.2 Definitions of Common Polymer Terms

A) Molecular Size/Weight



Greek

mono + mer
single part

poly + mer
many part

Monomer \Rightarrow Oligomer \Rightarrow Polymer

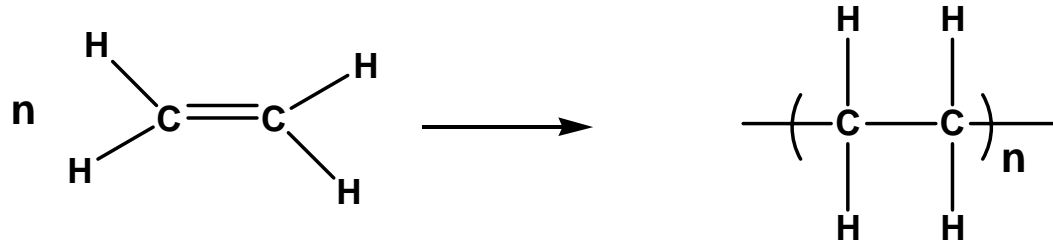
oligos + mer
few part

B) Polymer Structure

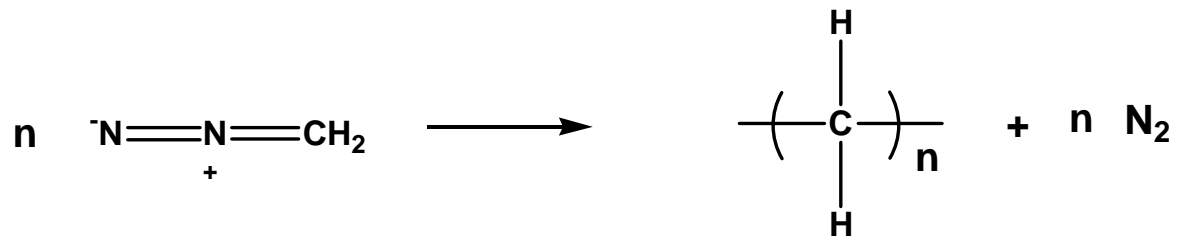
1) Repeating Unit

a) Conventional **Repeating unit** depends on **monomer** used in synthesis, e.g.

i) Polyethylene from Ethylene

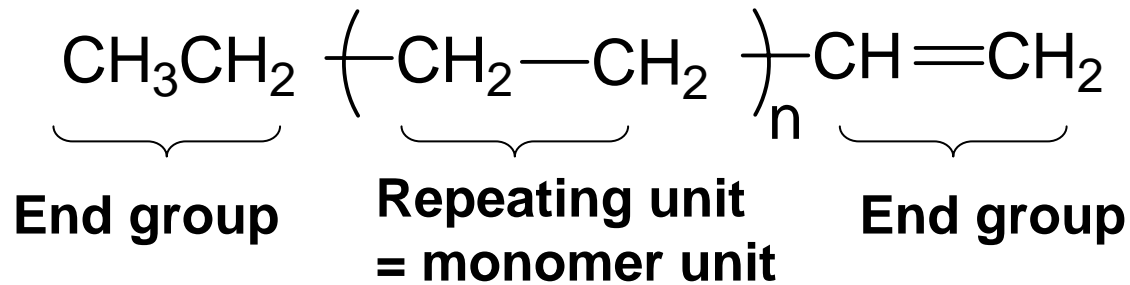


ii) Polymethylene from Diazomethane



b) The **Base Unit** is independent to synthetic route and is **smallest possible Repeating Unit**

2) End groups: structural units that terminate polymer chains



3) Living Polymers

a) Telechelic Polymers (reactive end groups)

tele + chele = far + claw



b) Reactive Oligomers

Oligomers containing reactive end groups capable of undergoing **polymerization**, usually by heating, to form **network** polymers

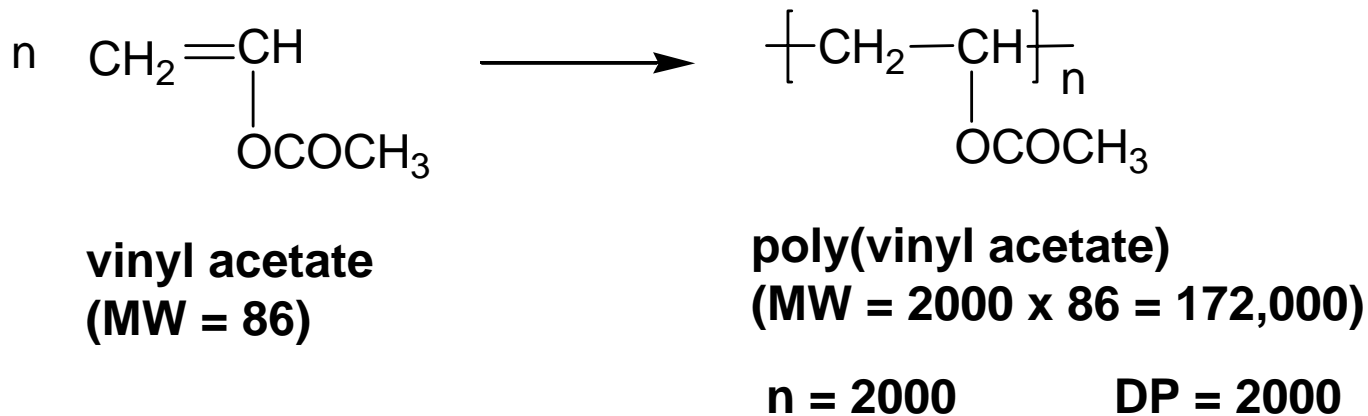
C) Average Degree of Polymerization = \overline{DP}

1) $DP = \# \text{ of repeating units in chain} + \# \text{ of end groups}$

2) $\overline{DP} = \text{Average Degree of Polymerization}$

3) $MW = DP \times (\text{MW of Repeating Unit})$

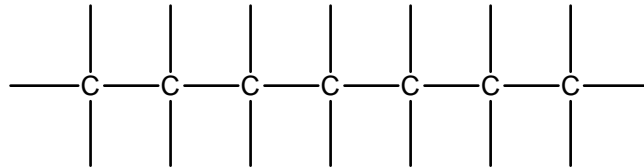
4) $\text{CH}_3-(\text{CH}_2)_{2000}-\text{CH}_3$ has a $DP = 2002$



D) Types of Atoms in Polymer Backbone

1) Homochain polymer

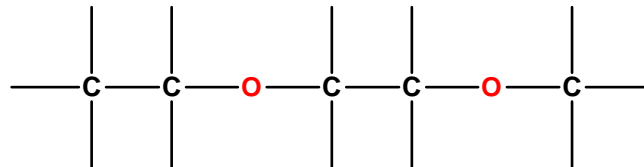
polymer chain (or backbone) consists of a single atom type



e.g., vinyl polymers, polyacetylene, polysulfur, poly(dimethyl silane)

2) Heterochain polymer

contain more than one atom type in the backbone



e.g., polyesters, polyethers, polyamides

E) Order of repeating units in backbone

1) Homopolymer (cf. Homochain Polymer)

**made from a single monomer
(or pair of monomers in cases like polyesters, etc.)**

2) Copolymer

a) Synthesis

- i) made from more than one type of monomer**
- ii) occasionally from more than one type of polymer**

b) Types of Copolymers

- i) Random Copolymer**
- ii) Block Copolymer**
- iii) Alternating Copolymer**
- iv) Graft Copolymer**

E) Order of repeating units in backbone

1) Homopolymer and Copolymer

-A-A-A-A-A-A-A-A-

Homopolymer

-A-B-B-A-B-A-A-B-

Random copolymer

-A-B-A-B-A-B-A-B-

Alternating copolymer

-A-A-A-A-B-B-B-B-

Block copolymer

-A-A-A-A-A-A-A-A-
 |
 B-B-B-B-B-B-

Graft copolymer

FIGURE 1.1. Representations of homopolymer and copolymers.

F) Conventional Polymer Structure Types

1) Linear

No branching other than the pendant groups associated with the monomer

2) Branched

may have only a few side chains or
may be every few repeating units

3) Network (Crosslinked)

a) Crosslink density related to “hardness”

b) an average of **more than two crosslinks per chain**
⇒ infinite network

F) Conventional Polymer Structure Types

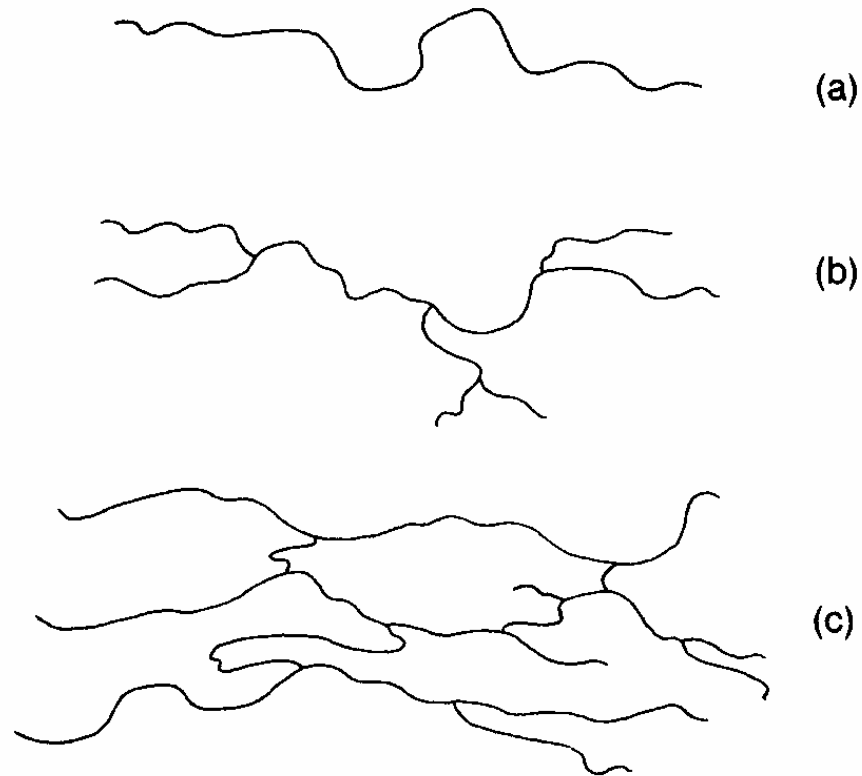


FIGURE 1.2. Representation of polymer types: (a) linear, (b) branched, and (c) network.

Network Formation

How would you make chains that branch and then perhaps interconnect to form **networks**?

- A. Use a mixture of bifunctional and monofunctional units
- B. Get a tube of **Molecular Super Glue** and stick a bunch of chains together
- C. Use **multifunctional ($f > 2$) monomers**

G) Unconventional Polymer Structures

1) Branched

a) Star

i) has a **central core** from which **3 or more arms branch**

ii) uses: **viscosity modifiers** in high performance engine oils

b) Dendrimer (also known as **Starburst** or **Cascade Polymers**)

i) generation numbers up to 5-7

ii) near spherical shapes

iii) steric crowding gradient

iv) uses: microencapsulation and drug delivery

c) Comb

i) from **Macromonomers** such as $1\text{-C}_{20}\text{H}_{40}$

ii) very high number of side chains, all of similar length



2) Network

a) Ladder cf. DNA (see next page)

b) Semiladder (Stepladder)

3) Supramolecular

a) molecular superstructures held together by non-covalent bonds

b) examples

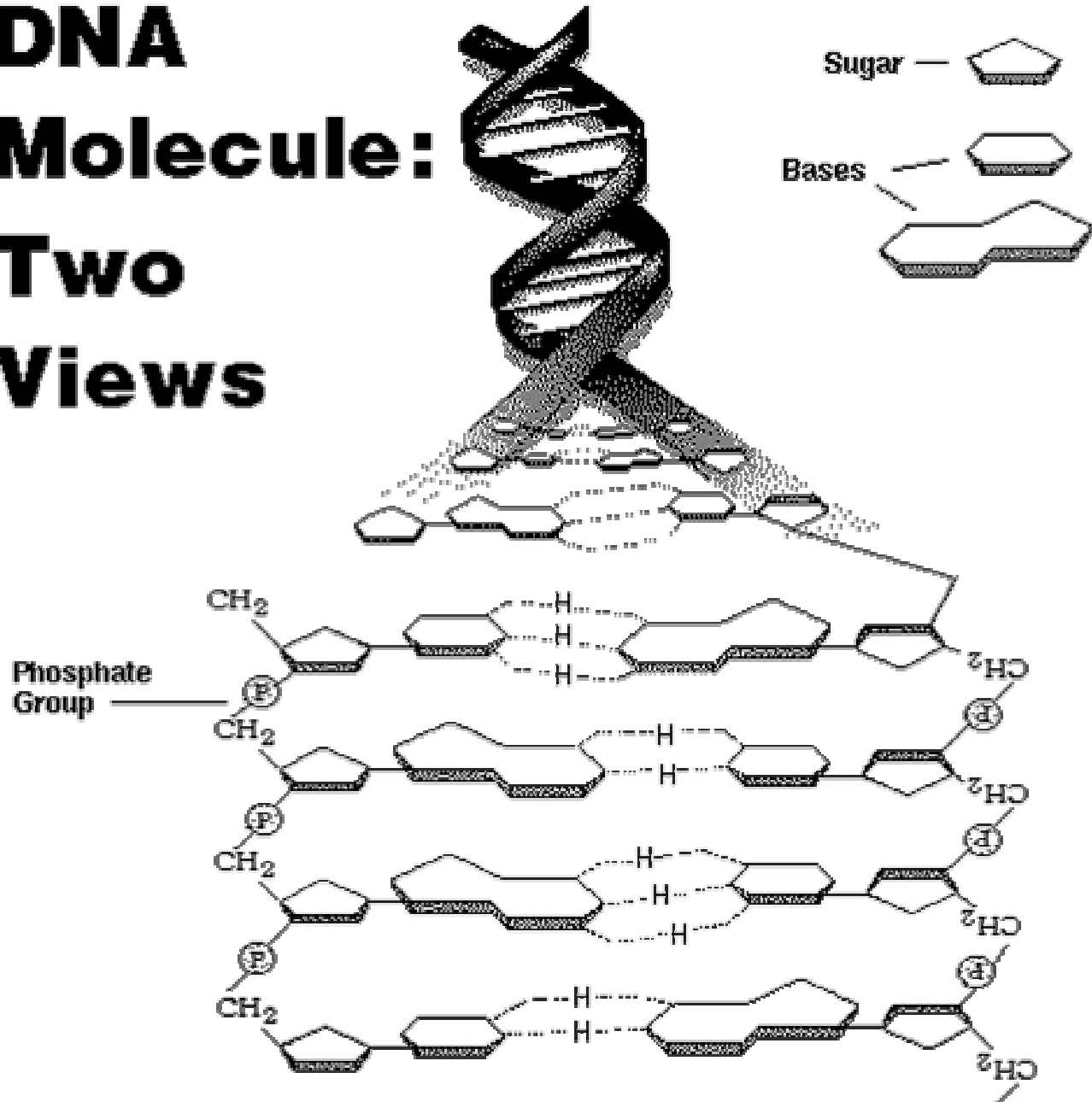
i) Polyrotaxane

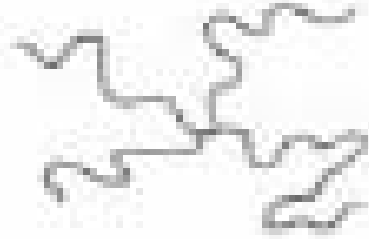
washers on a wire

ii) Polycatenane

chain links

DNA Molecule: Two Views





Star polymer



Comb polymer



Ladder polymer



**Semiladder polymer
(or Stepladder polymer)**



Polyrotaxane



Polycatenane



Dendrimer

Figure 1.3 (p9)

H) Crosslinking

- 1) Degree of Crosslinking directly correlated with:
 - a) hardness, elasticity, solvent induced swelling, etc.
 - b) degree of swelling indicates degree of solvent-polymer compatibility and the degree of crosslinking
- 2) First “designed” crosslinking process is
Vulcanization of rubber (Polyisoprene)
- 3) Can be via covalent bonds, ionic interactions, or
Van der Waals interactions

I) Thermoset Polymers

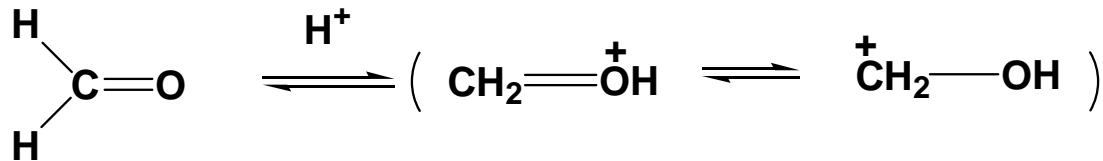
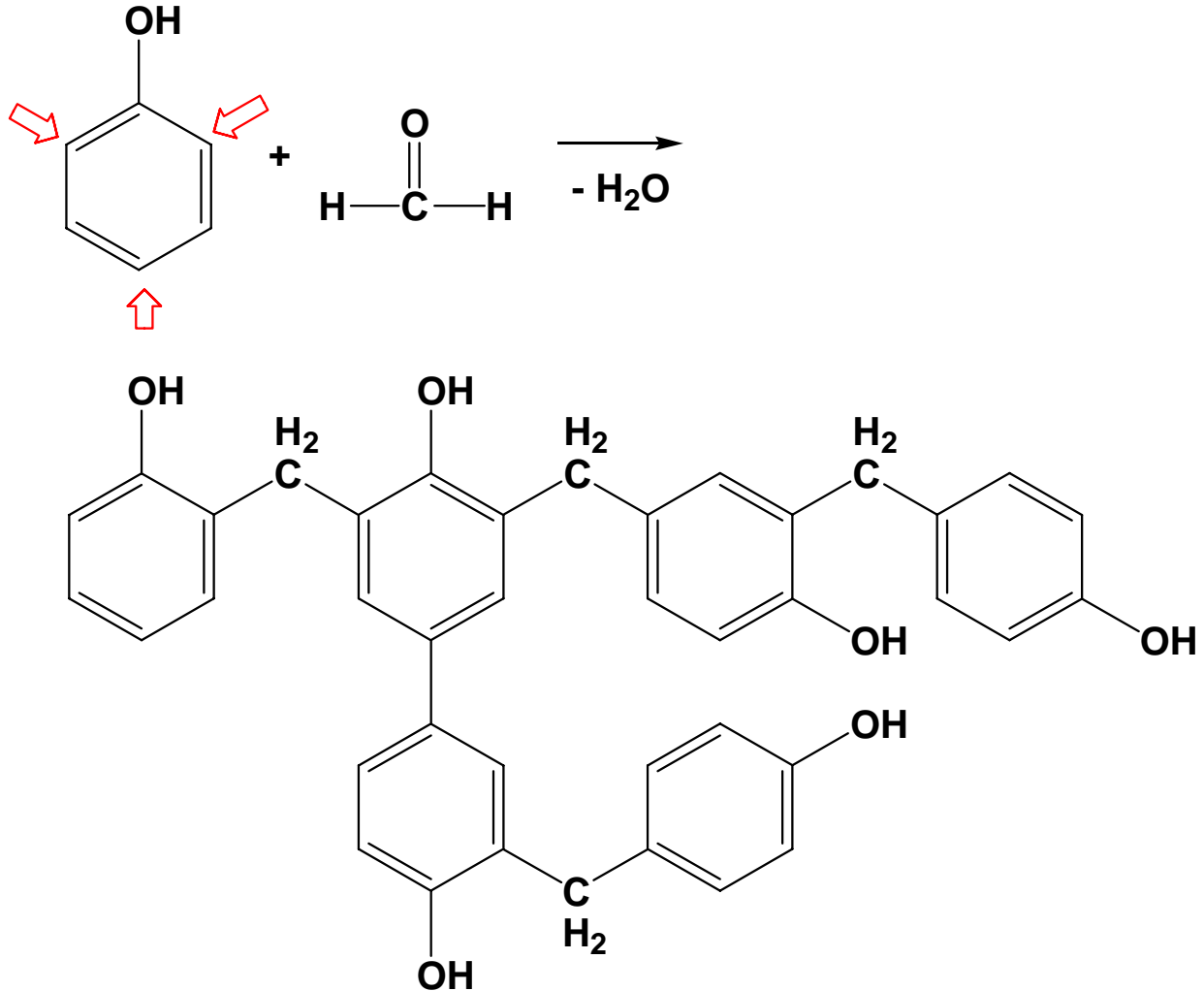
Example: Phenol-Formaldehyde resin (see next page)

- a) Crosslinked network**
- b) One gigantic molecule**
- c) Insoluble**
- d) Non-melting**
- e) Only swell in a solvent**

Thermoplastic Polymer (e.g., PE)

- a) Linear, branched**
- b) Melt or flow**

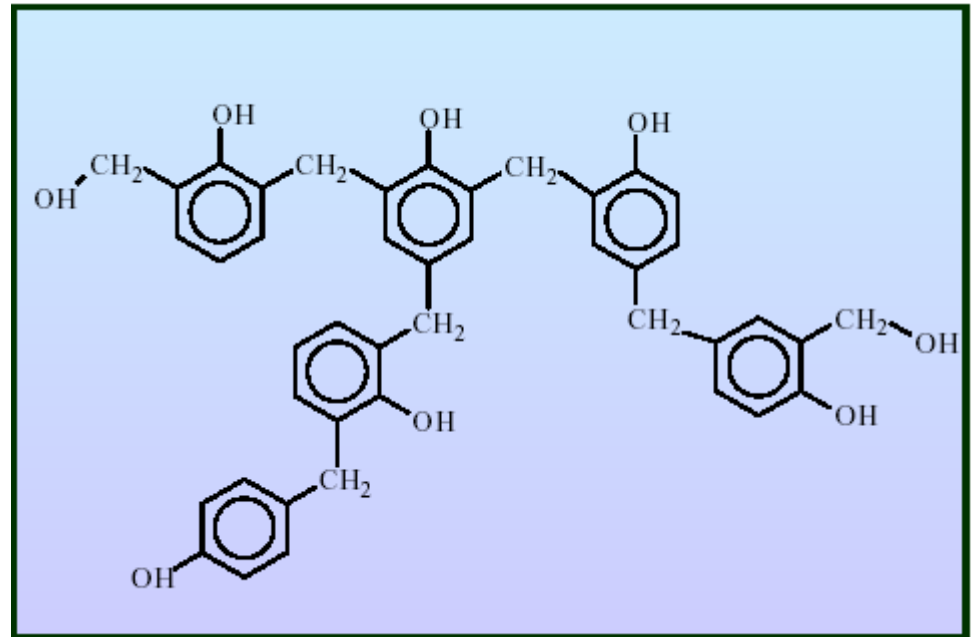
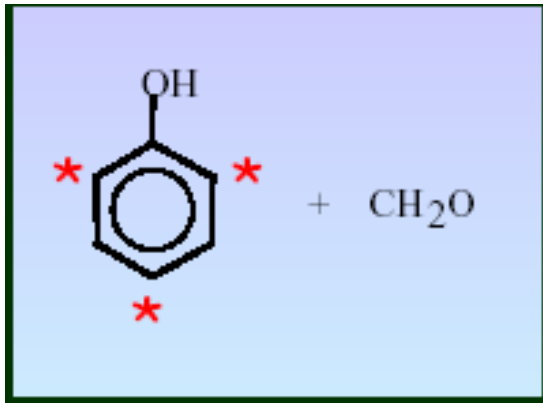
Phenol-formaldehyde resin



Bakelite

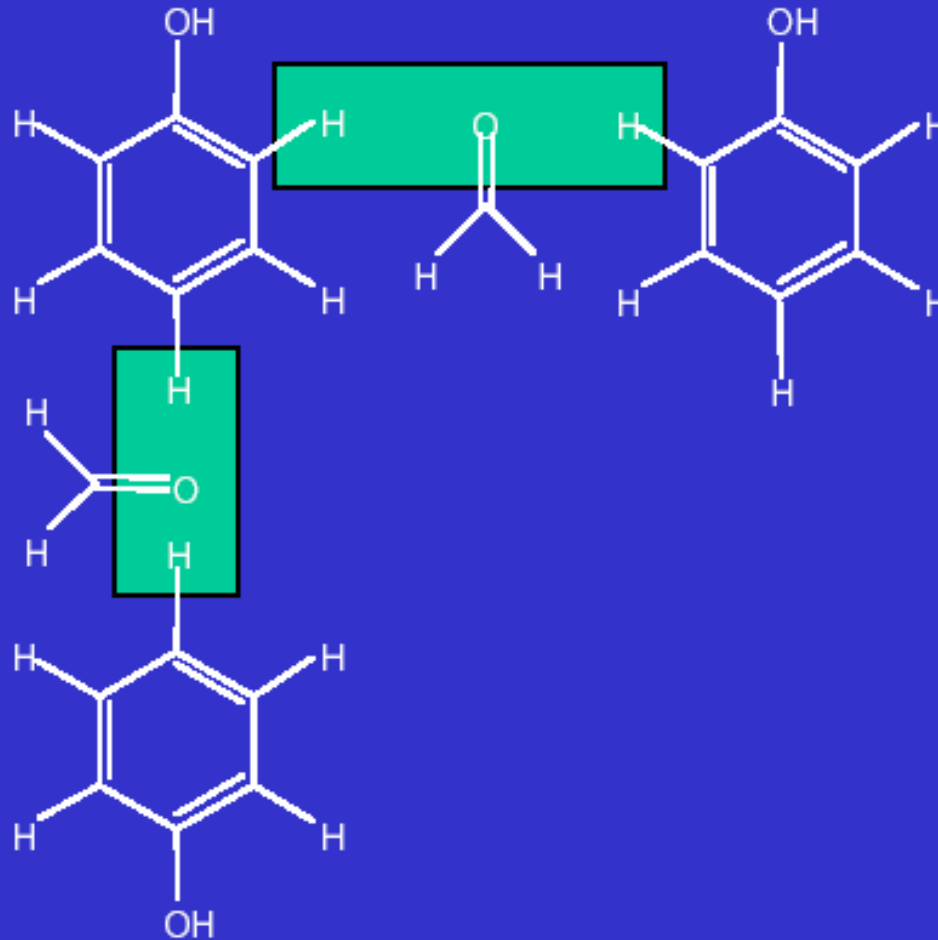
The first true synthetic plastic

The hydrogens in the ortho and para positions to the OH group, which by convention are not usually shown but here are indicated by a *, can react with **fomaldehede** to form (initially) oligomers.



Network Formation

Condensation Reaction!!



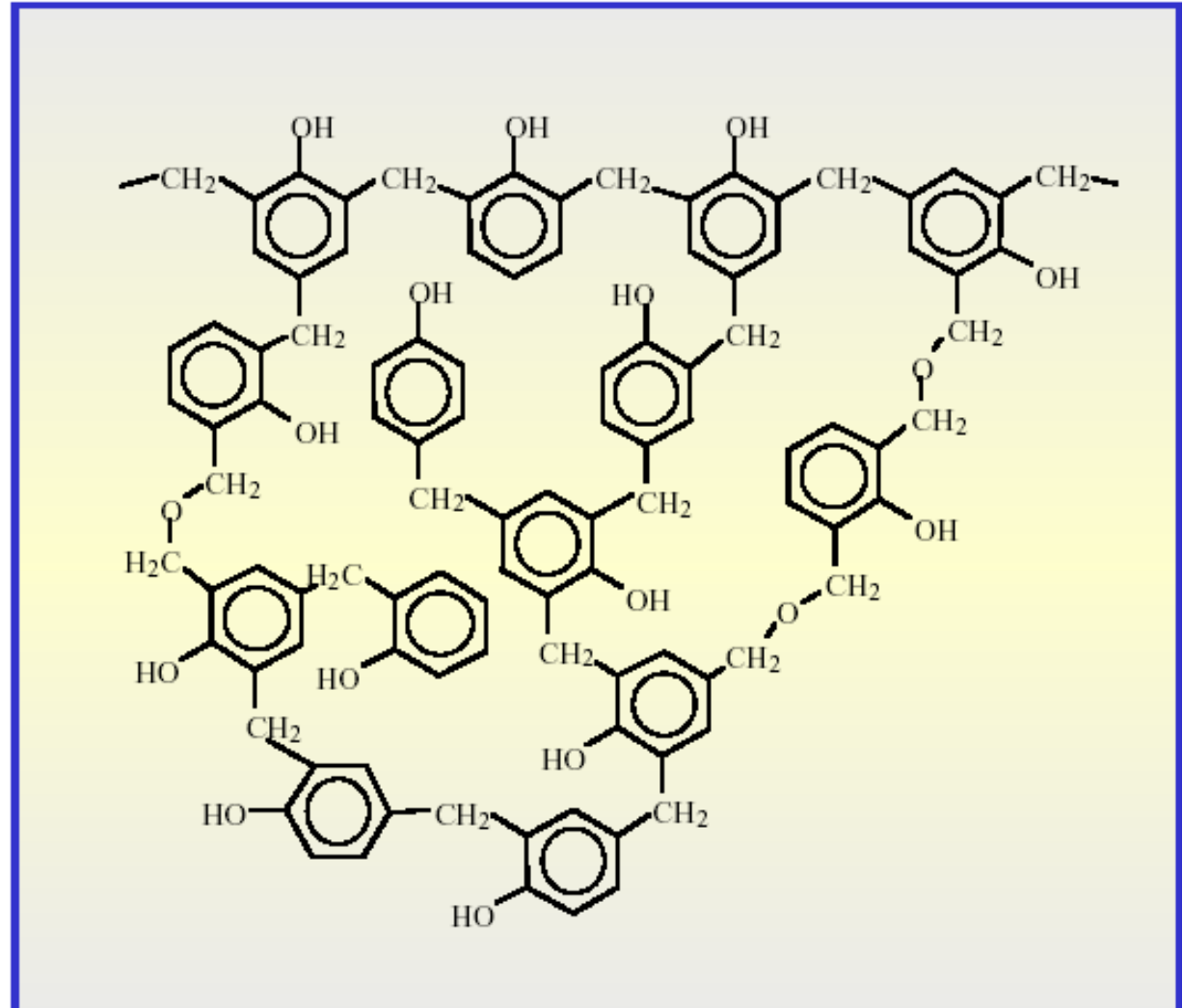
Network Formation

Continued reaction builds up a densely **cross-linked network**.

This is **Bakelite**, a thermosetting polymer.

Once the reaction is complete, the material **cannot be reheated and reformed**.

So, what do you think the definition of a thermoplastic is?



J) Classification by Use

- 1) Plastics
- 2) Fibers
- 3) Rubbers (Elastomers)
- 4) Coatings
- 5) Adhesives

Information Technology Applications

- **Photoresists** for **semiconductor** fabrication
- **Interlayer dielectrics** for **semiconductor** fabrication
- **Alignment layers** for liquid crystal **displays**
- **Lubricants** for computer **hard disks**

1.3. Polymerization Processes

Classification of Polymer Reactions

1) Reaction **Stoichiometric** Classification

a) **Condensation** vs. **Addition** Polymerization

b) Determined by **loss of weight** (or not) on polymerization

Condensation: Formation of **byproduct**, **weight loss**

Addition: No byproduct, No loss of weight

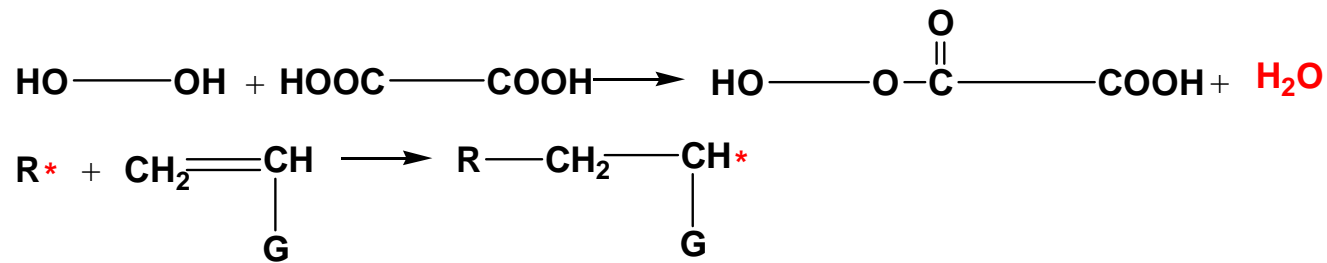
2) **Mechanistic** Classification

a) **Step-Growth** (Step-Reaction) vs. **Chain-Growth** (Chain-Reaction)

b) Determined by reactive species

Step-Growth: **All species** grow **step by step**

Chain-Growth: Successive linking of **monomers** to the **end of a growing chain**

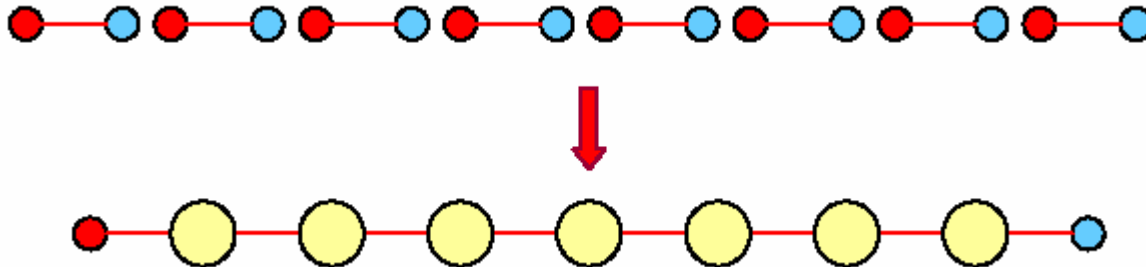


Making a Polymer

The molecules are **monofunctional**;



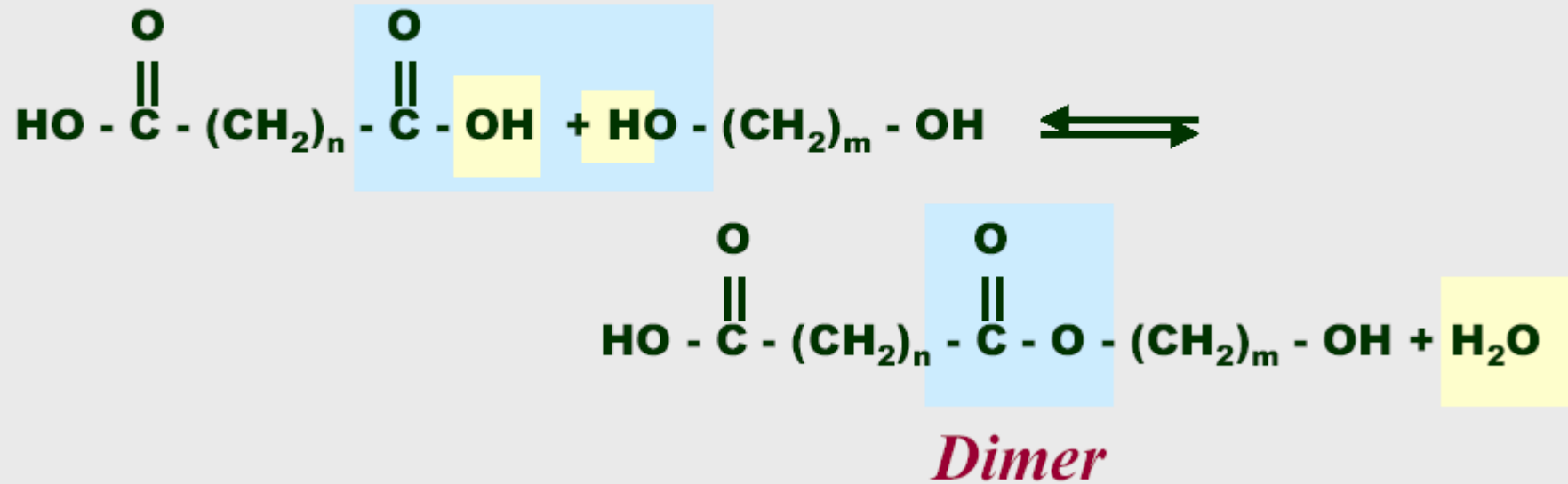
To make **linear chains** we need **bifunctional** molecules;



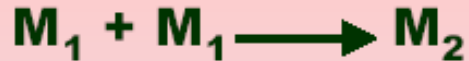
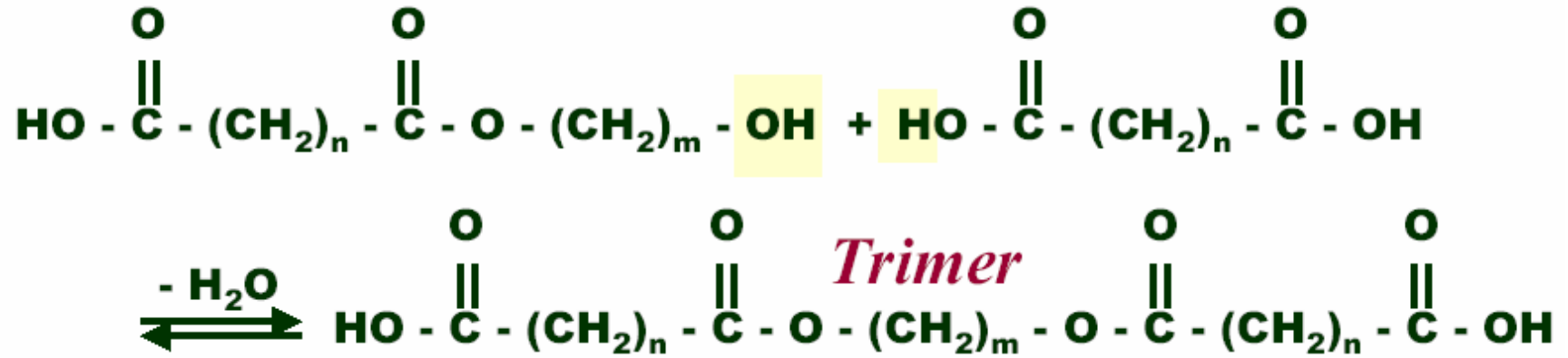
Except the reaction doesn't happen all in one go, like this, but in a **step-growth** fashion.

Making a Polyester

Monomers



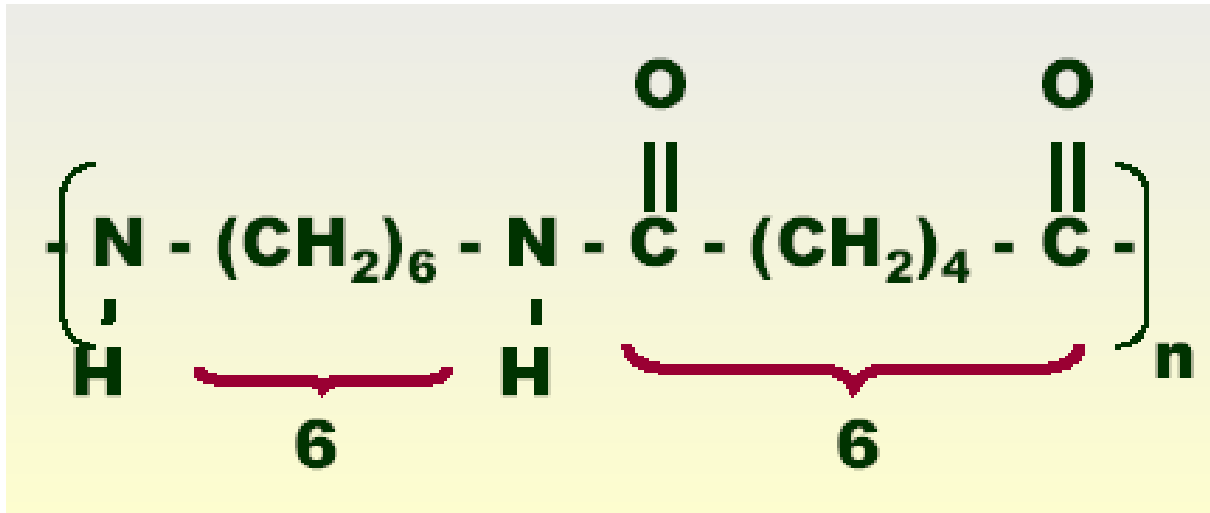
Making a Polyester



Etc.

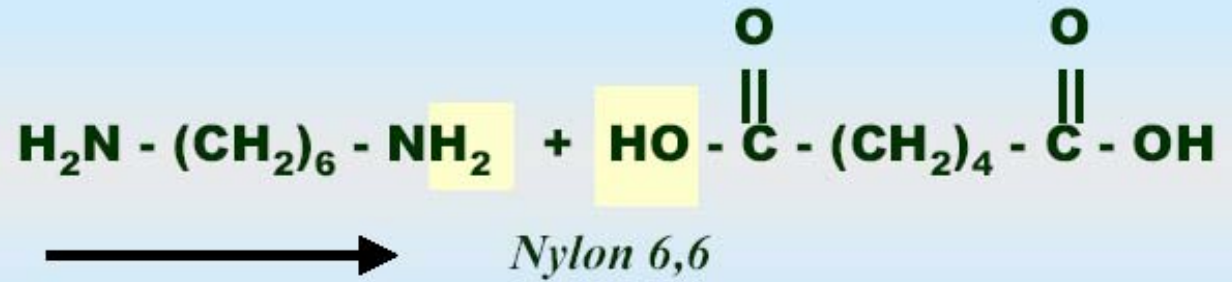
Note, reacting a diacid and a dialcohol will give you a polyester!

Nylon 6,6

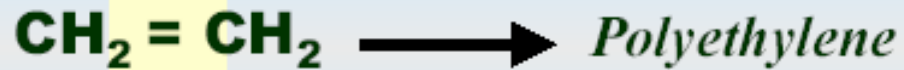


Types of Reactions

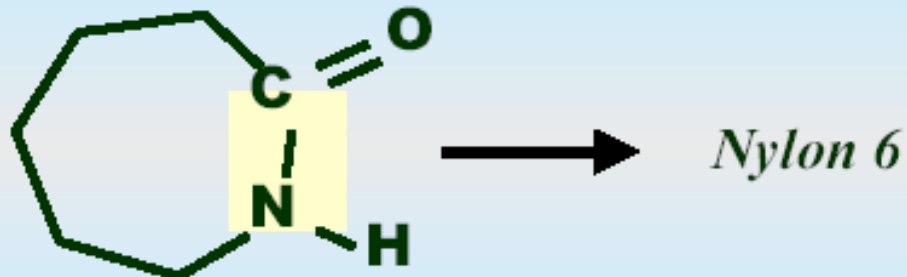
Condensation



Addition



Ring opening

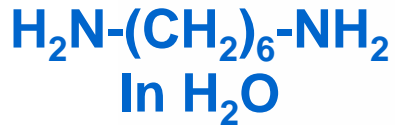


Nylon Rope Trick

Nylon "skin"
carefully drawn off
to form fiber or rope



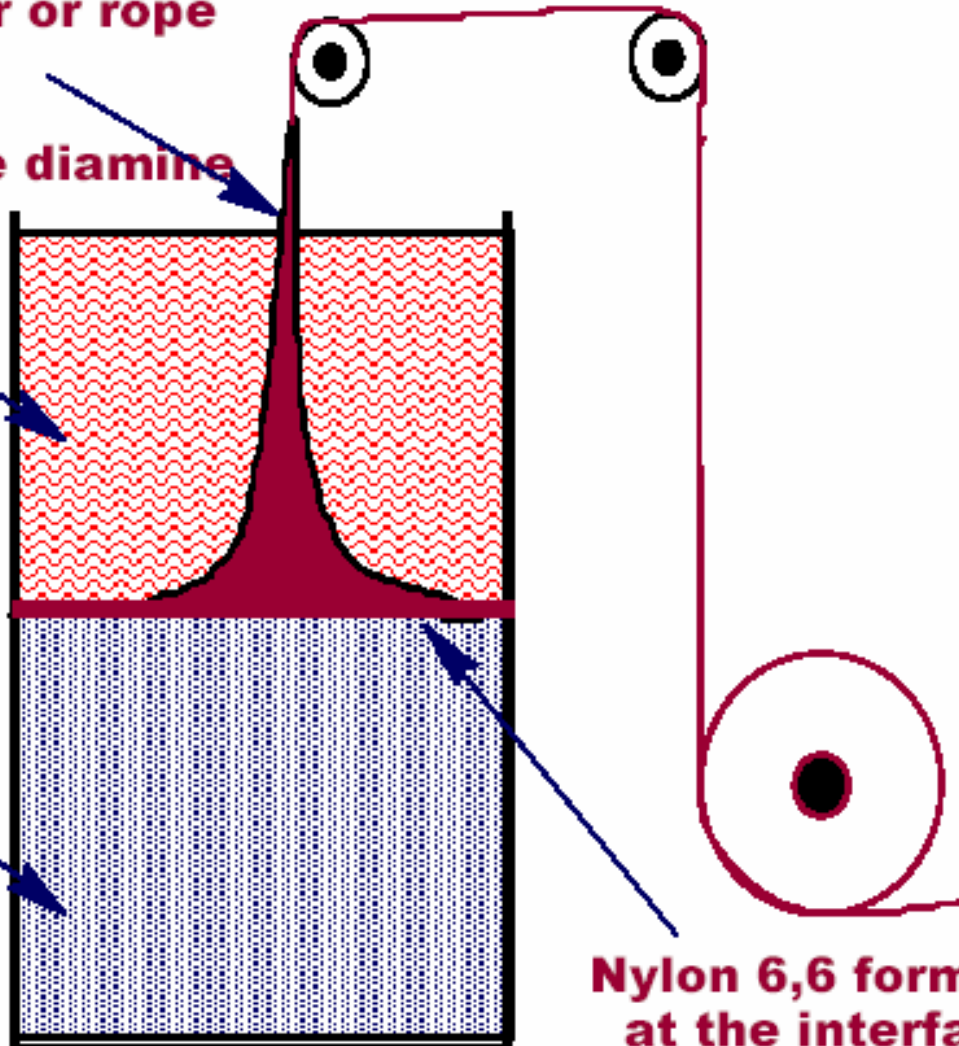
**Hexamethylene diamine
in water**



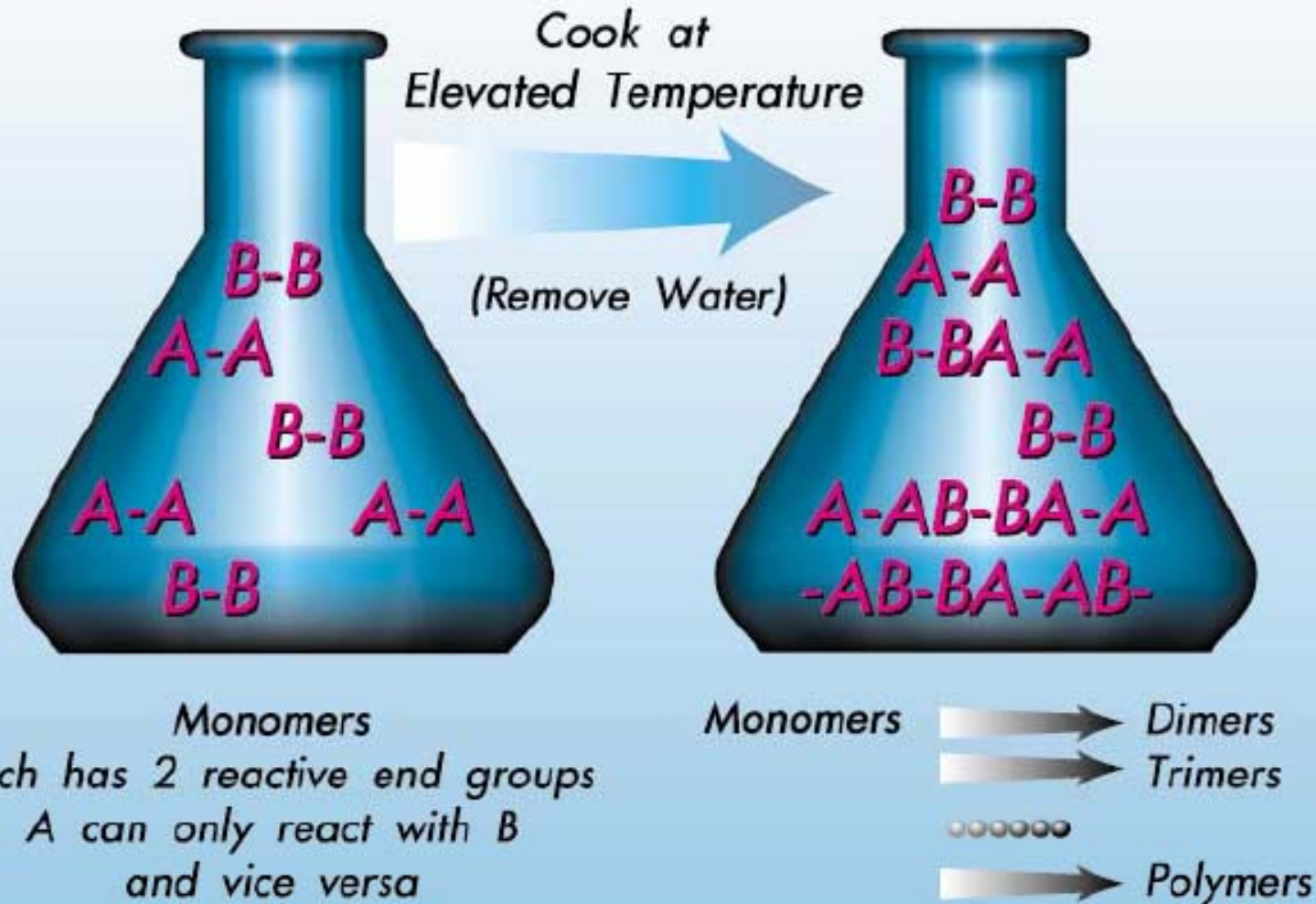
**Adipoyl chloride
in chloroform**



**Nylon 6,6 formed
at the interface**



Step-Growth Polymerization ; Summary



Schematic representation of step-growth polymerization

1.4 Step-Reaction Polymerization

- 1) Most commonly found with **condensation** reactions but there are **exceptions**
 - a) Bonds formed **one at a time**
 - b) Most **monomer used up quickly** but get **high MW only near end**
 - c) **Wide MW distributions** typical
- 2) Work out the \overline{DP} & \overline{MW} for the following
 - a) $\overline{DP} \approx$ Number of **repeating units** in chain

$$\overline{MW} = \overline{DP} \times (\text{Repeating Unit MW})$$
 - b) $\overline{DP} =$ Average Number of repeating units in chain
(plus the number of end groups)

$$\overline{MW} = \overline{DP} \times (\text{Repeating Unit MW})$$

$$\overline{DP} = \overline{MW} / \text{Repeating Unit MW}$$

$$= \text{Average Number of Repeating Units in Chain}$$

c) p = reaction conversion = **extent of reaction**

$$\text{i) } p = \frac{N_o - N}{N_o} \quad \text{or } N = N_o(1 - p)$$

where

p = fraction of the original **functional groups** consumed
 N_o = number of molecules **initially**
 N = number of molecules **finally**

$$\text{ii) } \overline{DP} = \frac{N_o}{N} = \frac{1}{1 - p}$$

$p = 0$ **at start** when no polymerization

$p \approx 1$ when polymerization **complete** (the numerical value of p gets closer to 1 at higher final MW)

for **98%** reaction conversion (i.e., $p = 0.98$) $\overline{DP} = 50$

iii) To get **high MW** you need

- excellent **reaction conversions**
(i.e., clean reactions that go to completion)
- very **pure reagents** (no monofunctional species)
- very **precise reaction stoichiometries**

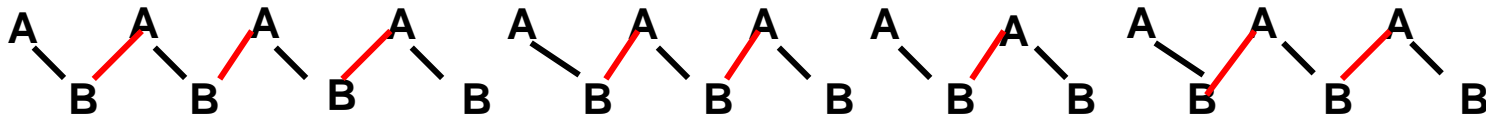
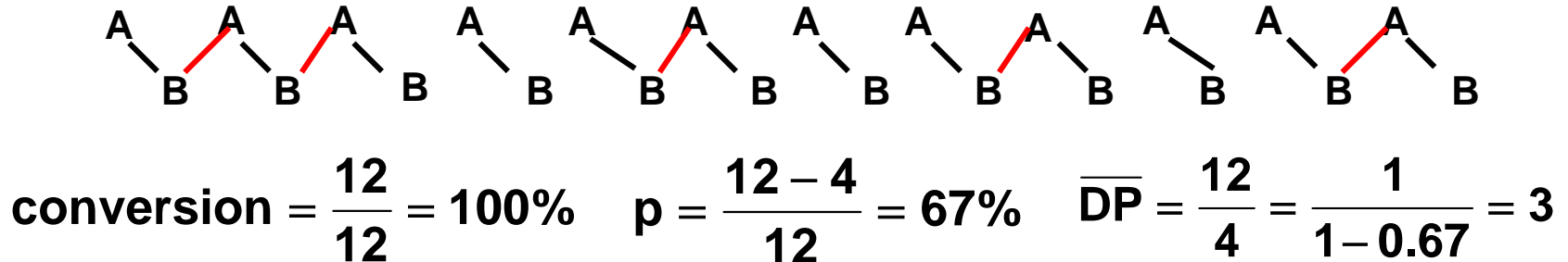
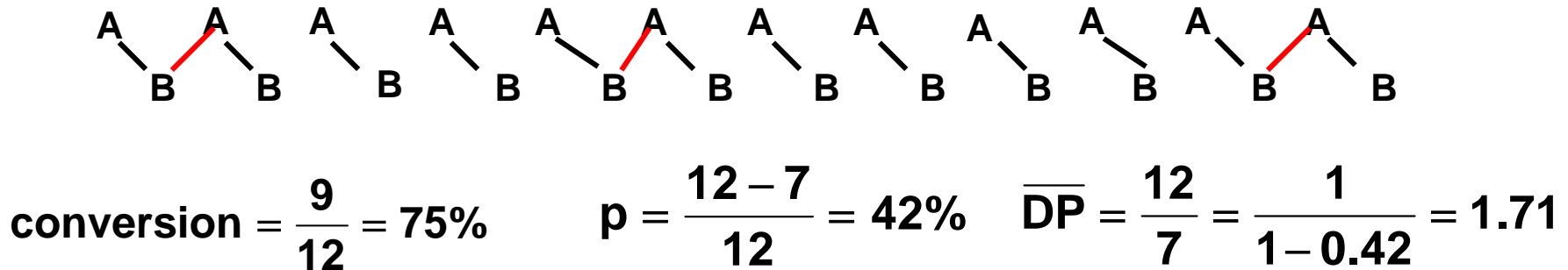
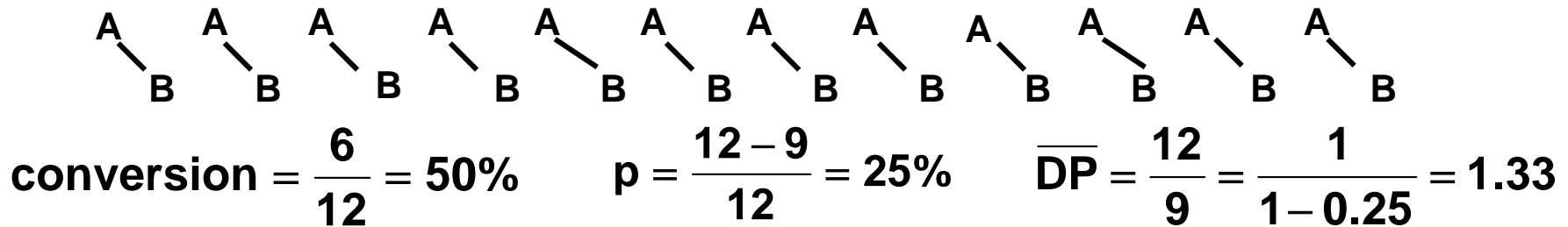
Figure 1.4

- i) Step Reaction Polymerization of monomer A-B
- ii) Show how polymerization effects array of A-B monomers
- iii) Shows how even as **p approaches 1**, the **average chain length stays low**
- iv) Only **at very end** when **almost no low MW species** present **long chains form**

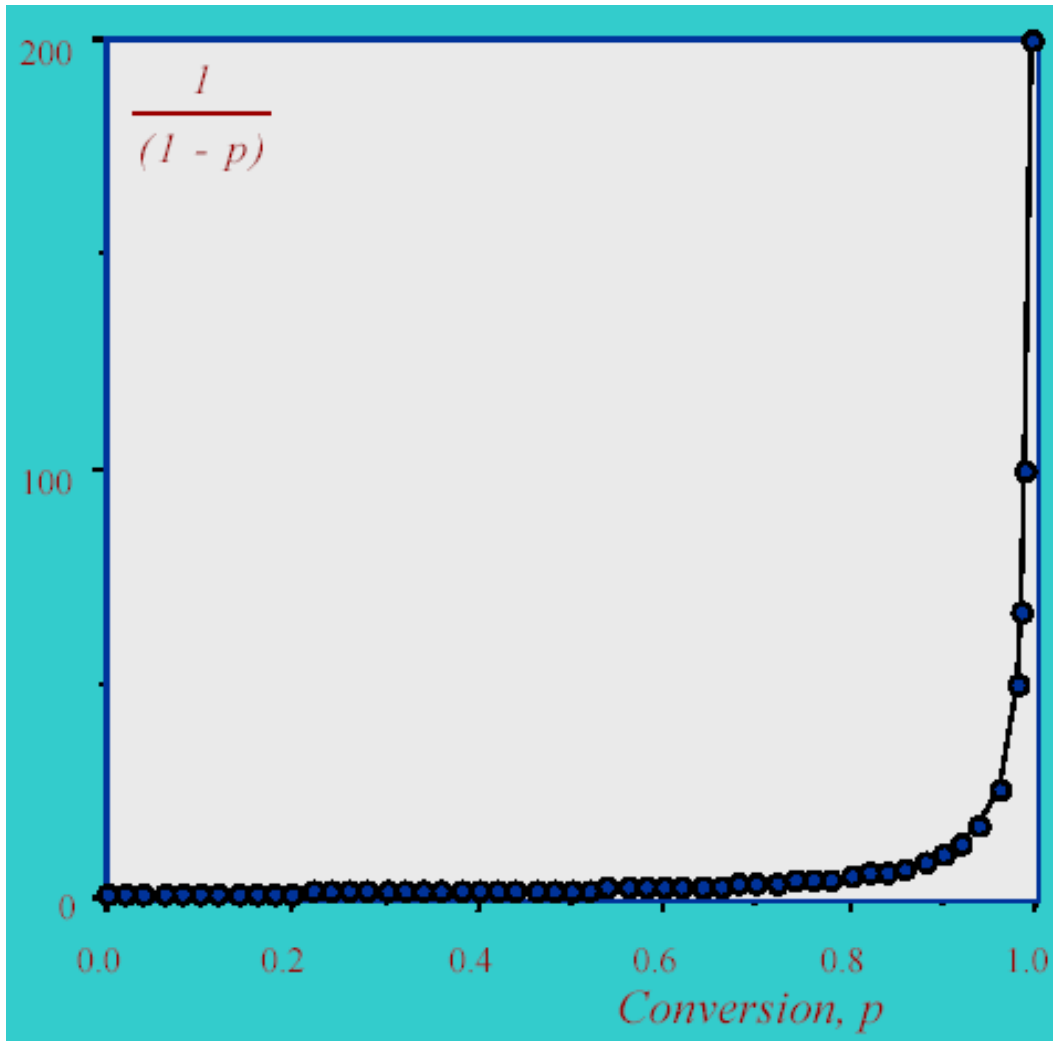
Figure 1.4 Step-reaction polymerization

Unreacted monomer

Conversion : monomer to polymer



Conversion and Molecular Weight in Step-Growth Polymerizations



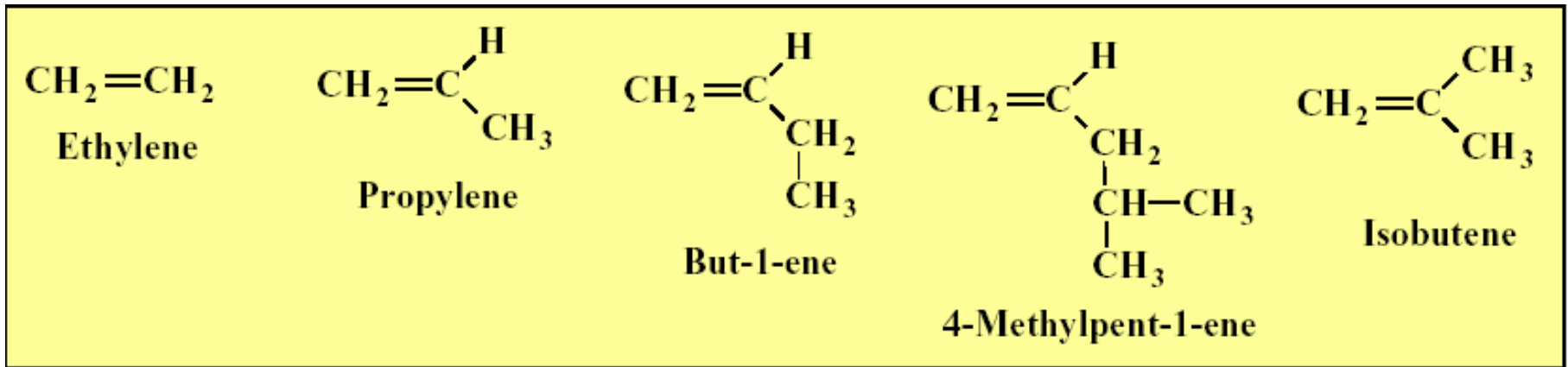
$$\bar{X}_n = \frac{1}{(1-p)}$$

\bar{X}_n = DP
= degree of polymerization
= number of repeating unit

Note;
you only get
**high molecular
weight polymer
at high degrees
of conversion.**

What Are Polyolefins?

The term polyolefin embraces all polymers that are derived from simple **unsaturated aliphatic hydrocarbons** that contain **one double bond per monomer**. Examples include:



The most important **polyolefins** in terms of production volume are polyethylene (**PE**), polypropylene (**PP**) and the **ethylene/p**ropylene copolymers (**EP**).

Other significant polyolefins include, **polybut-1-ene**, **poly-4-methylpent-1-ene** and **polyisobutene (PIB)**.

1.5 Chain-reaction Polymerization

1) Most commonly found with **addition reactions** but there are **exceptions** (e.g., the **Chain/Condensation** polymerization of diazomethane)

2) Generic Mechanisms

a) **Chain Initiation** Step(s)

Generation of **highly reactive species**, e.g.

- **Free radical** intermediate
- **Carbocation** or **carbanion**
- **Transition metal** species

b) **Chain Propagation** Step(s)

Increase MW by **adding monomers** to **end of growing chain**

c) **Chain Termination** Step(s)

Consume the **active species** by **recombination**, etc.

d) **Chain Transfer** Step(s)

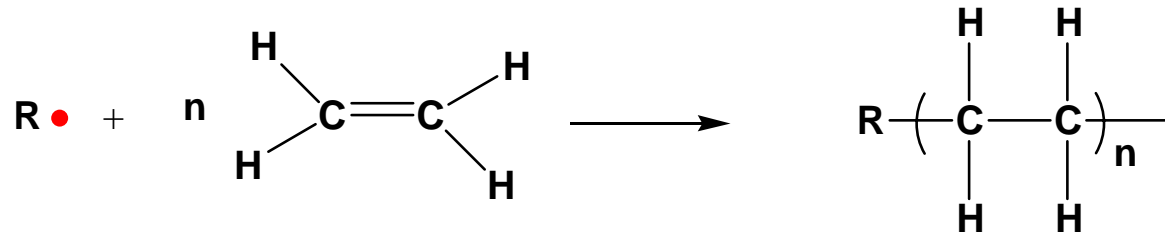
May be present and typically **modify** final polymer structure and **MW**

3) Commonly found when have **highly reactive intermediates**

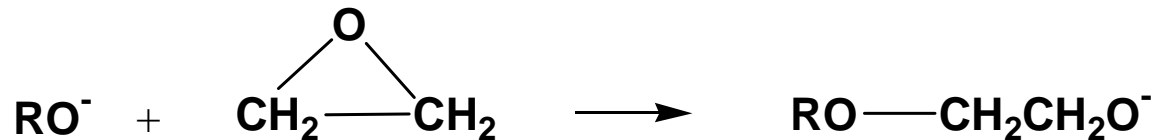
Free Radicals, Carbocations, Carbanions, etc.

4) Examples

a) FR Polymerization of Ethylene



b) Nucleophilic Polymerization of Ethylene Oxide (**Ring Opening**)

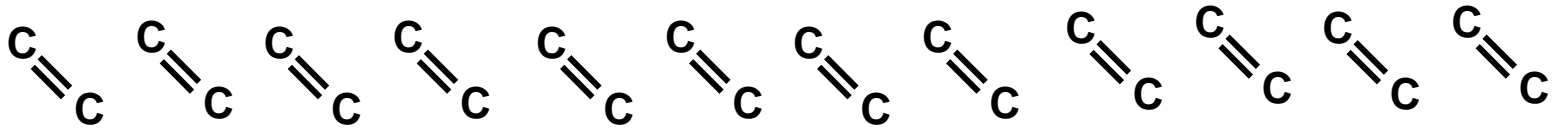


5) Figure 1.5

- a) **Chain-Reaction Polymerization** of monomer $C = C$
- b) Show how polymerization effects array of $C = C$ monomers
- c) Even **at low values of p** (reaction conversion),
some **high MW chains** are present

Figure 1.5 Chain-reaction polymerization

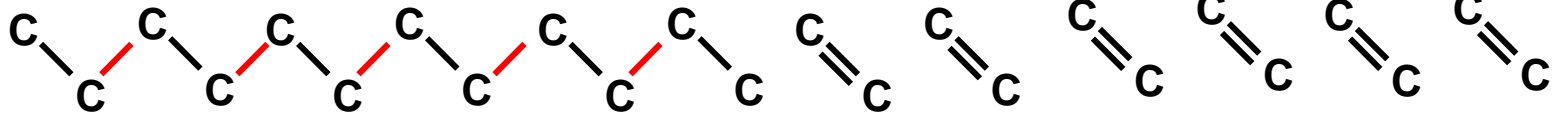
Unreacted monomer



$$\text{conversion} = \frac{6}{12} = 50\%$$

$$p = \frac{12-7}{12} = 42\%$$

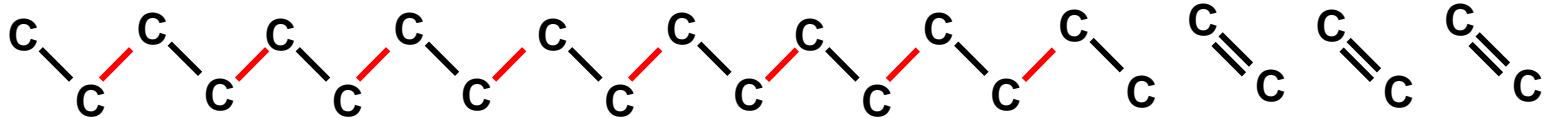
$$\overline{DP} = \frac{12}{7} = \frac{1}{1-0.42} = 1.71$$



$$\text{conversion} = \frac{9}{12} = 75\%$$

$$p = \frac{12-4}{12} = 67\%$$

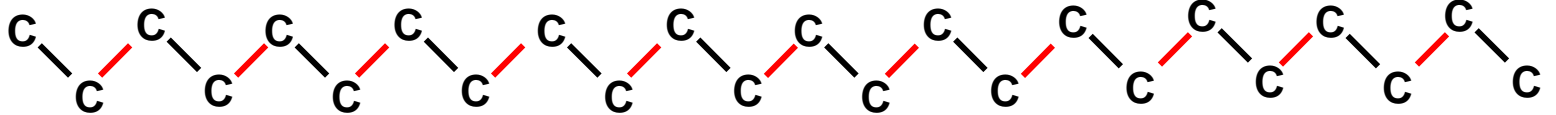
$$\overline{DP} = \frac{12}{4} = \frac{1}{1-0.67} = 3$$



$$\text{conversion} = \frac{12}{12} = 100\%$$

$$p = \frac{12-1}{12} = 92\%$$

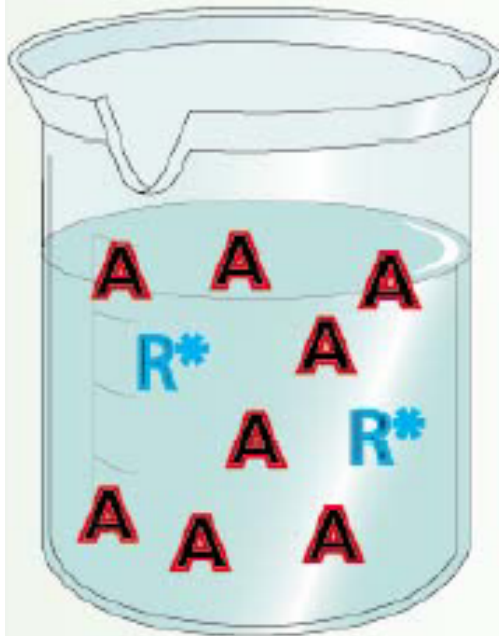
$$\overline{DP} = \frac{12}{1} = \frac{1}{1-0.92} = 12$$



Chain Polymerizations

Monomers

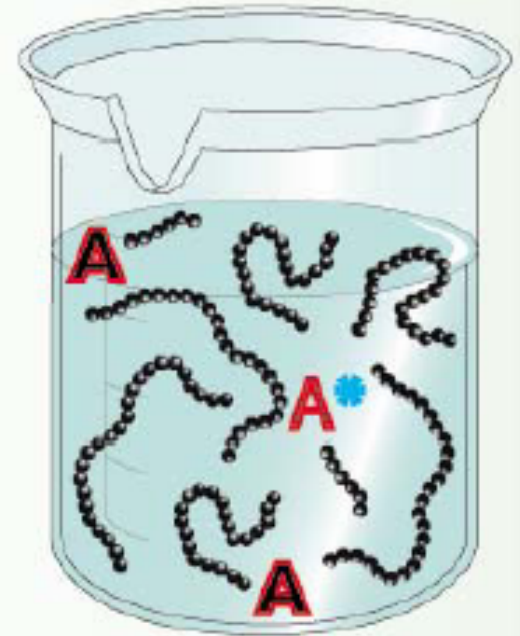
One type of reactive monomer $A + R^*$



FAST

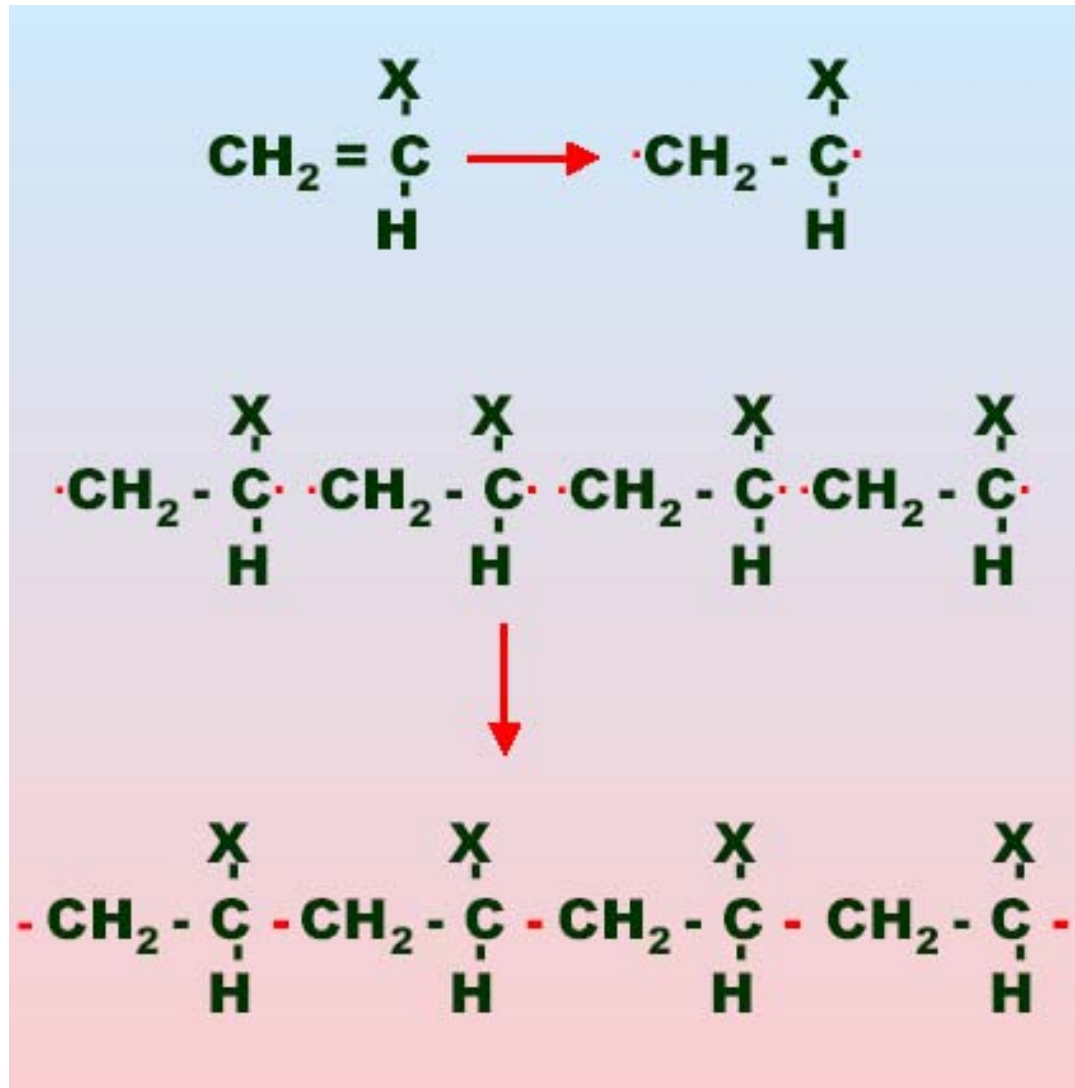
Polymer

Plus residual monomer A and very small amount of growing chains A^*



Chain Polymerizations

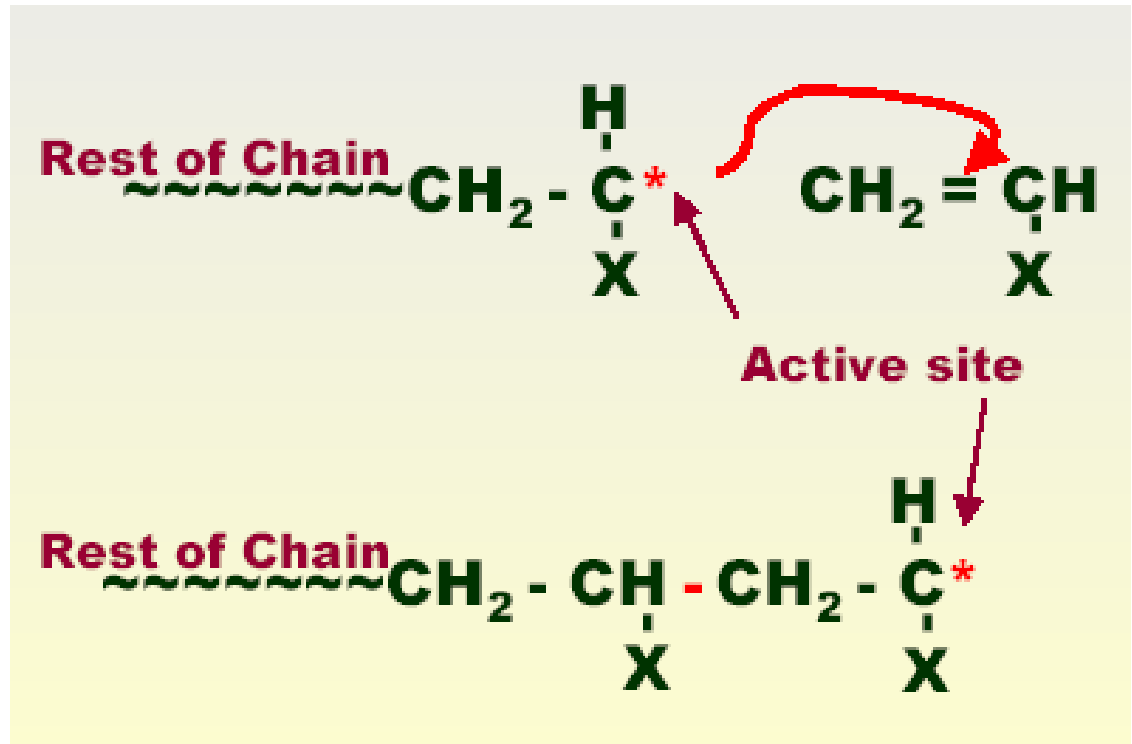
- a simplistic view



Characteristics of Chain Polymerizations

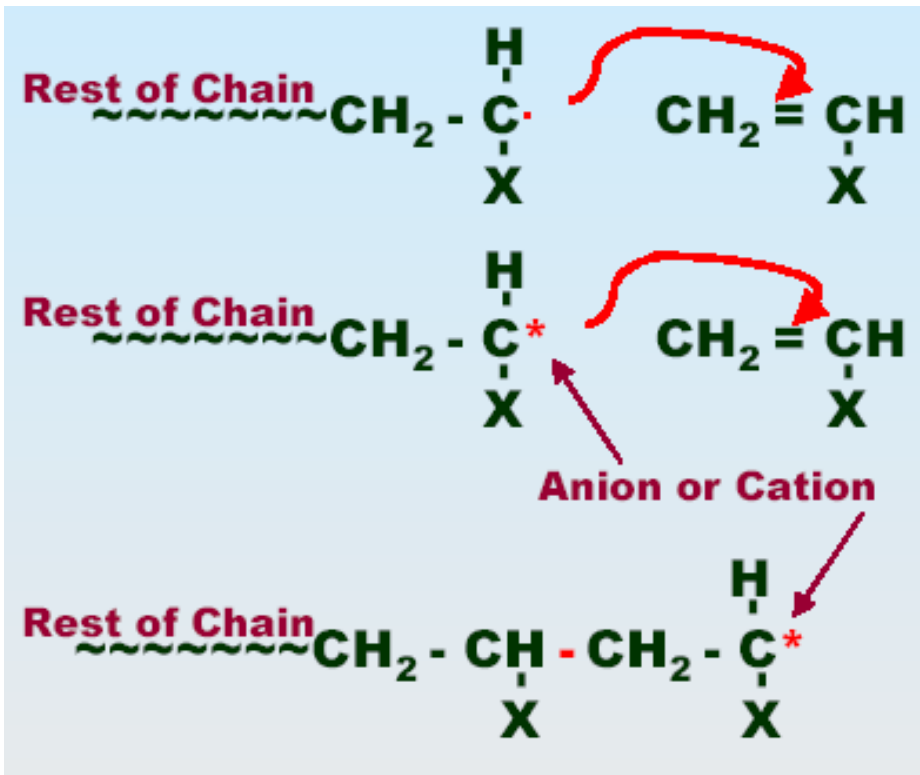
Need to consider;

1. Initiation
2. Propagation
3. Termination
4. Chain Transfer



Chain Polymerizations– Types

(nature of the **active site**)



Free Radical

Anionic

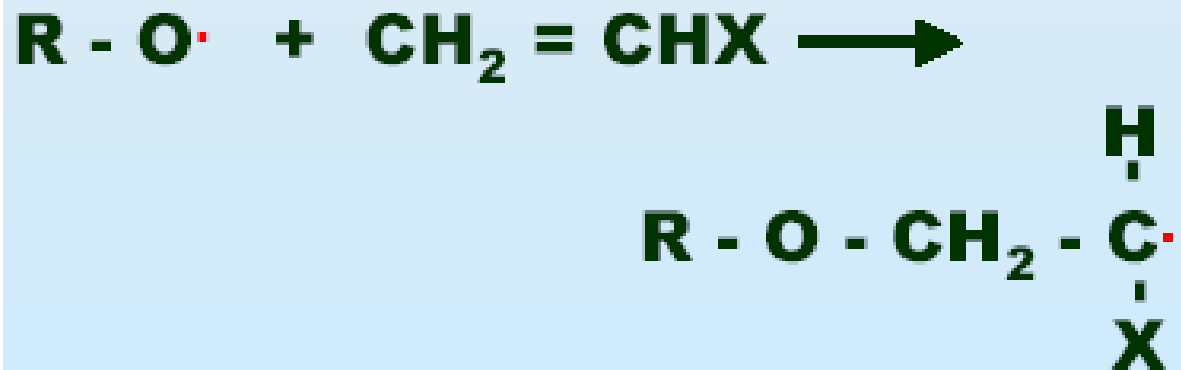
Cationic

Coordination (Catalyst)

Free Radical Polymerization

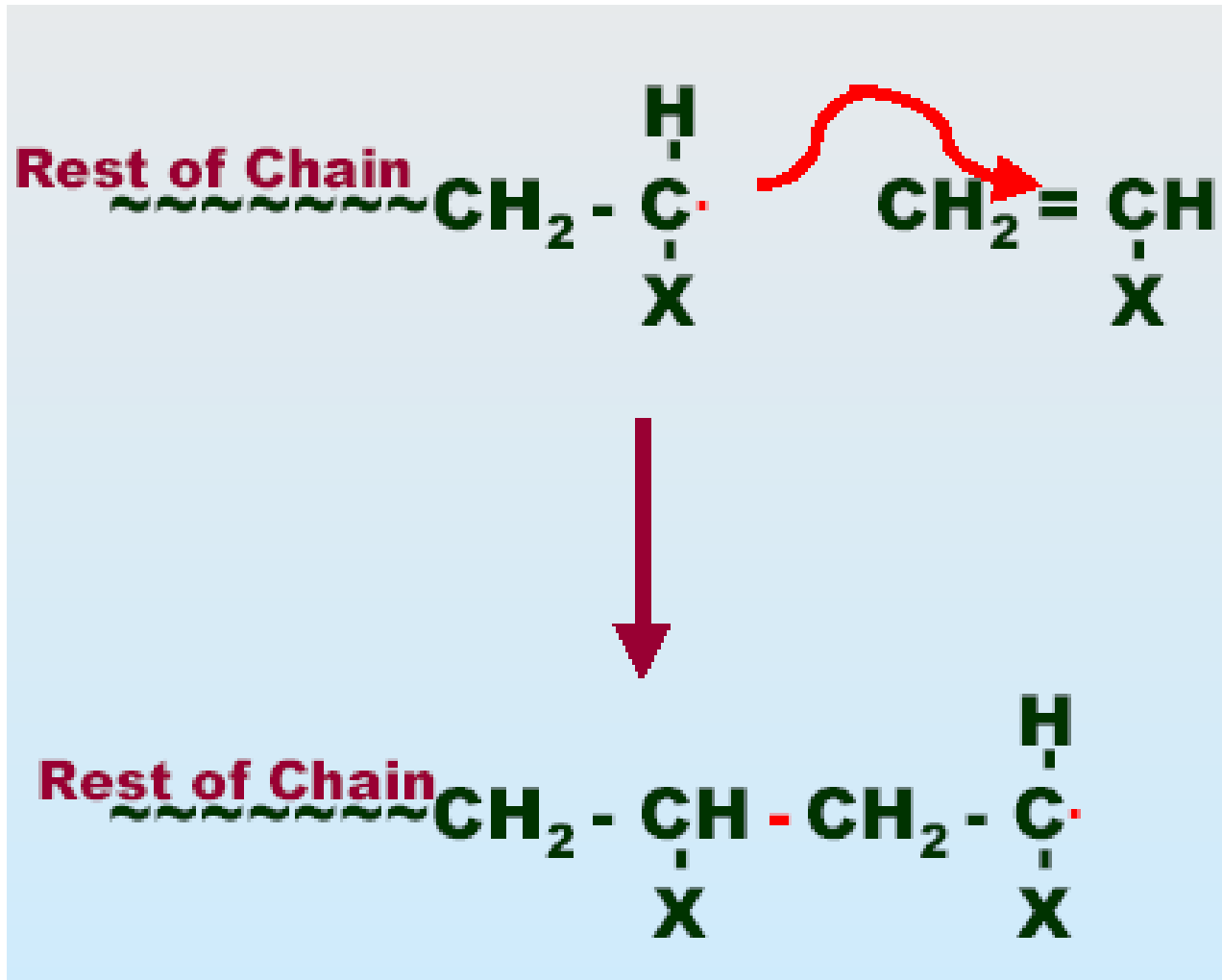
- Initiation

INITIATION



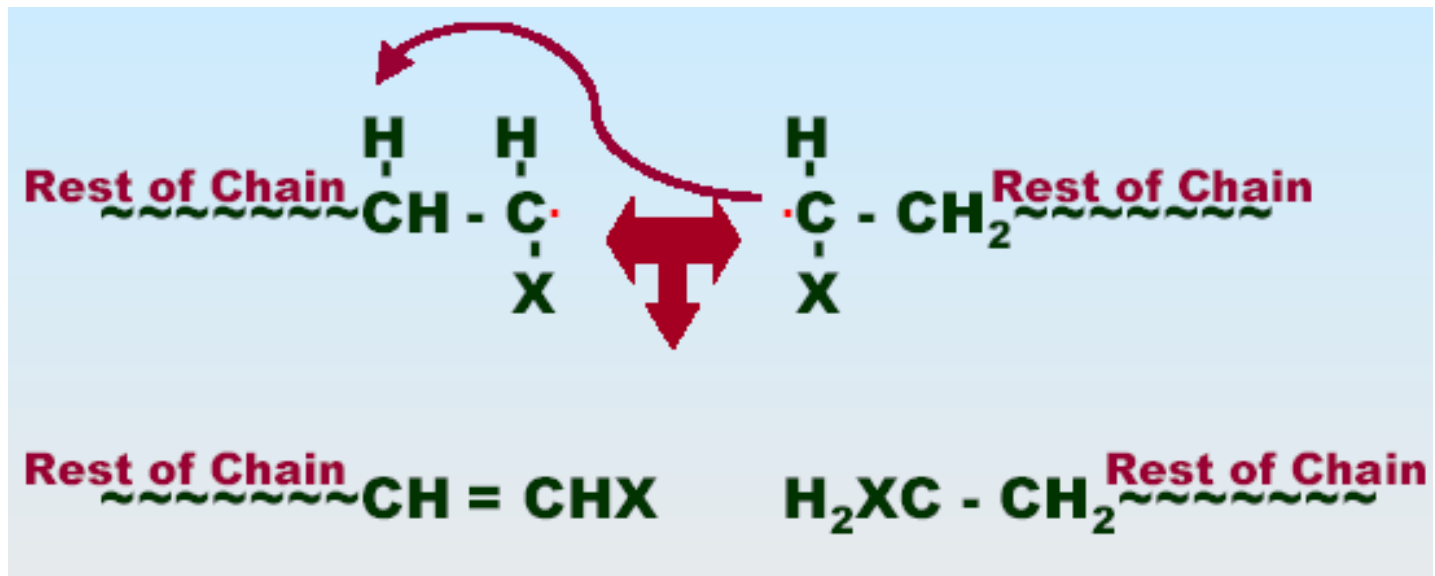
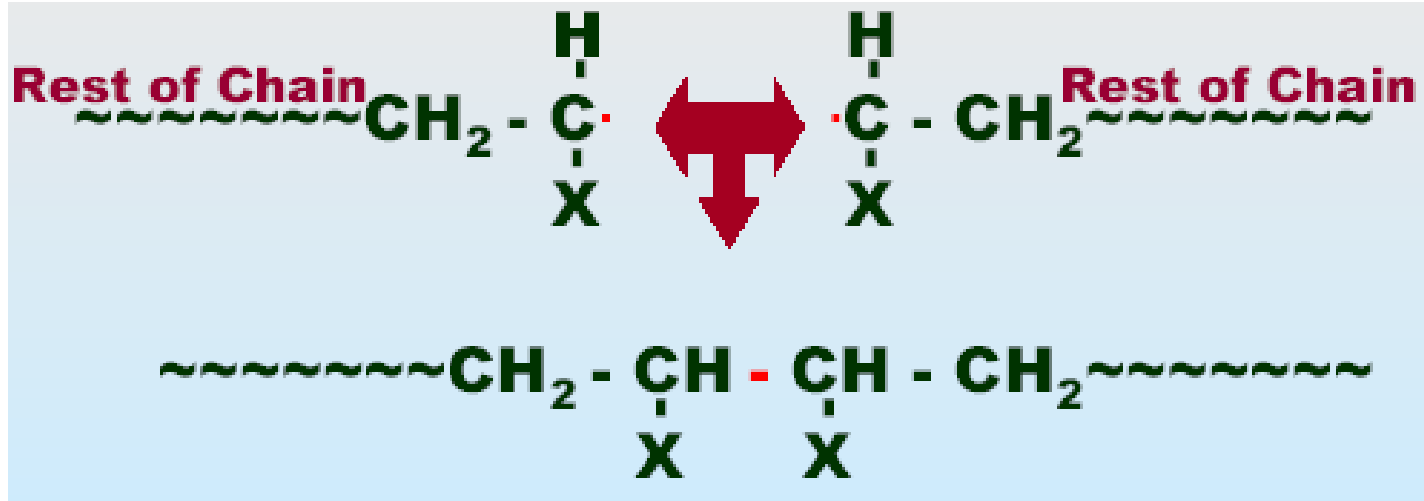
Free Radical Polymerization

- Propagation

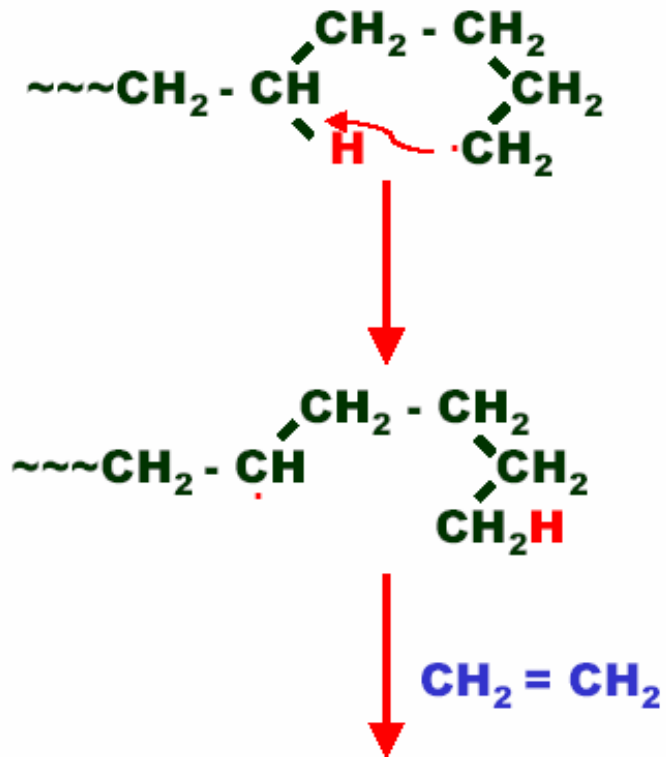


Free Radical Polymerization

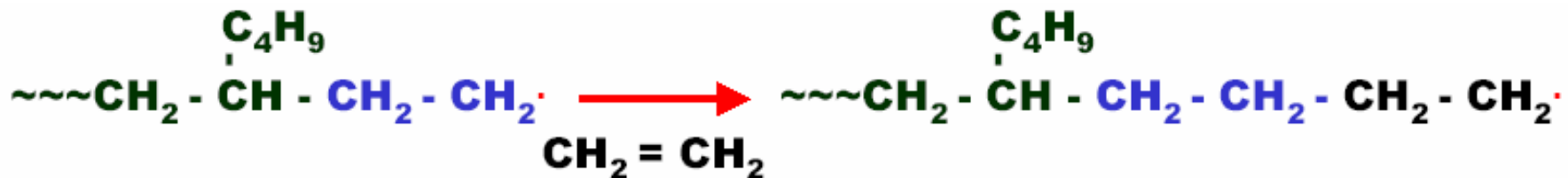
- Termination



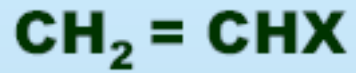
Short Chain Branching in Polyethylene



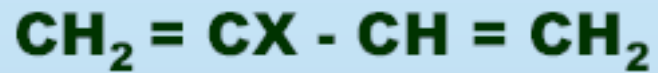
Formation of **short chain branches** in polyethylene



Chain Polymerizations



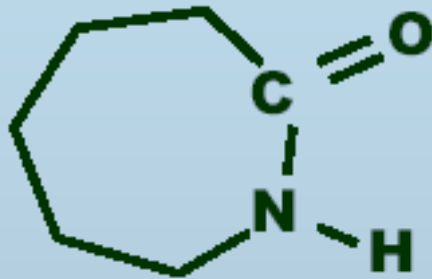
Various Olefins and Vinyl Monomers



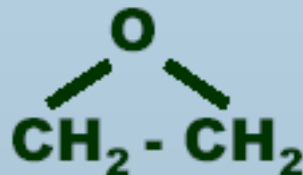
Various Dienes



Acetylene



Caprolactam



Ethylene Oxide

TABLE I.1. Comparison of Step-Reaction and Chain-Reaction Polymerization

<i>Step Reaction</i>	<i>Chain Reaction</i>
Growth occurs throughout matrix by reaction between <u>monomers, oligomers, and polymers</u>	Growth occurs by <u>successive addition of monomer units</u> to limited number of <u>growing chains</u>
<u>DP^a low to moderate</u>	<u>DP can be very high</u>
<u>Monomer consumed rapidly</u> while <u>molecular weight increases slowly</u>	<u>Monomer consumed relatively slowly</u> , but <u>molecular weight increases rapidly</u>
<u>No initiator needed; same reaction mechanism throughout</u>	<u>Initiation and propagation mechanisms different</u>
<u>No termination step; end groups still reactive</u>	Usually <u>chain-terminating step</u> involved
<u>Polymerization rate decreases steadily as functional groups consumed</u>	<u>Polymerization rate increases initially as initiator units generated</u> ; remains <u>relatively constant until monomer depleted</u>

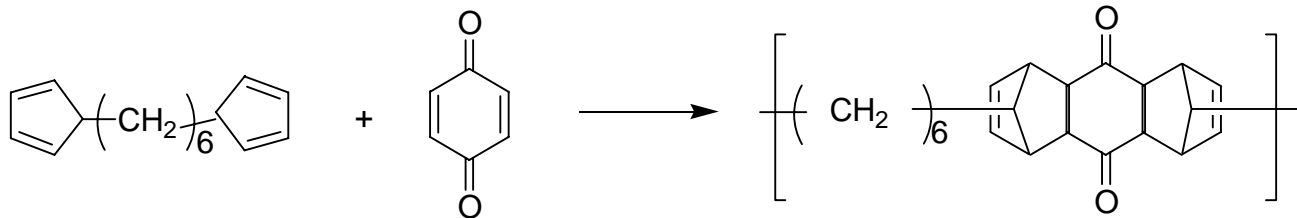
1.6 Step-Reaction Addition & Chain-Reaction Condensation

1) Step-Reaction Addition

a) diisocyanates (OCN~R~NCO) + diols (HO~R'~OH)
 → polyurethane -(CONH~R~NHCOO~R'~O)-

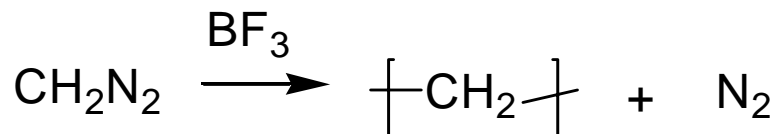
b) diisocyanates (OCN~R~NCO) + diamines (H₂N~R'~NH₂)
 → polyurea -(CONH~R~NHCONH~R'~NH)-

c) Diels-Alder reaction of 1,6-bis(cyclopentadienyl)hexanes with benzoquinone



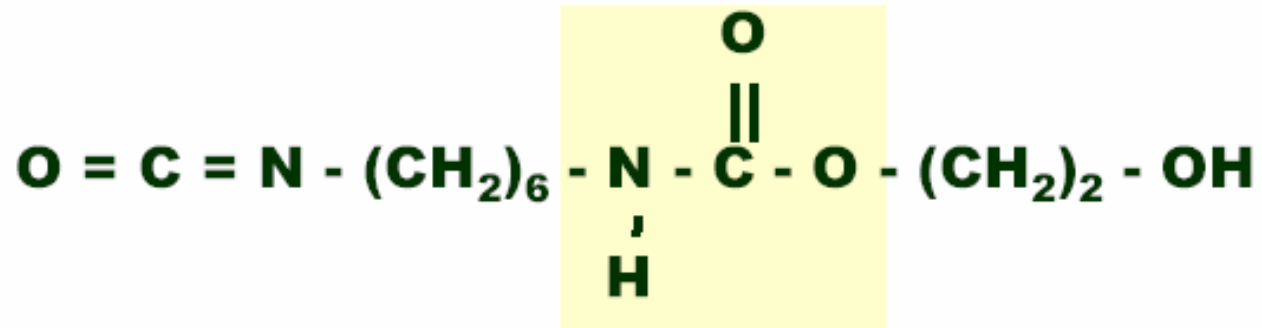
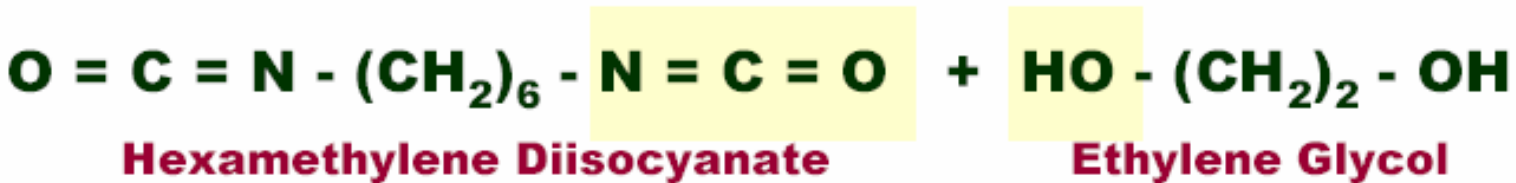
2) Chain-Reaction Condensation

Polymerization of CH₂N₂ initiated by BF₃



Polyurethanes

A reaction that does **not** involve the **splitting out** of a small molecule;



International Union of Pure and Applied Chemistry (IUPAC)

1) Polycondensation: condensation + step-reaction

Formation of low-mol-wt **byproduct**

Step-reaction polymerization

2) Polyaddition: addition + step-reaction

No byproducts

Step-reaction polymerization

3) Chain polymerization: addition + chain polymerization

No byproducts

Chain-reaction polymerization

4) Condensative chain polymerization: condensation + chain-reaction

Formation of low-mol-wt **byproduct**

Chain-reaction polymerization

1.7 Nomenclature

IUPAC name

- 1) The **smallest constitutional repeating unit (CRU)** is identified
- 2) **Substituent groups** are assigned the **lowest possible numbers**
- 3) The name is placed in **parenthesis**, and prefixed with **poly**

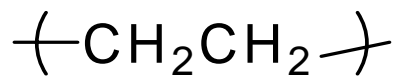
1.7.1 Vinyl polymers

poly + monomer name

Source name

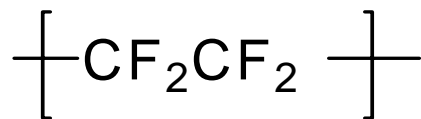
= common name

IUPAC name



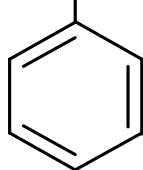
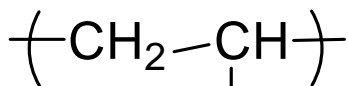
polyethylene

poly(methylene)



polytetrafluoroethylene

poly(difluoromethylene)



polystyrene

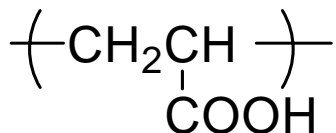
poly(1-phenylethylene)

poly + (monomer name)

more than one word or letter or number

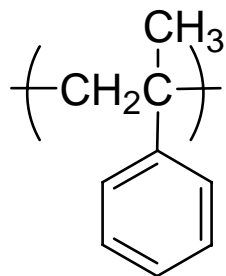
Source name
= common name

IUPAC name



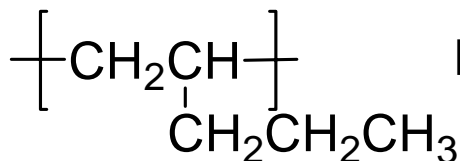
poly(acrylic acid)

poly(1-carboxylatoethylene)



poly(α -methylstyrene)

poly(1-methyl-1-phenylethylene)



poly(1-pentene)

poly[1-(1-propyl)ethylene]

	Source name = common name	IUPAC name
$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$	1,3-butadiene	
$\left(\text{---CH}_2\text{---}\underset{\text{CH}=\text{CH}_2}{\text{CH}_2}\text{---} \right)$	1,2-poly(1,3-butadiene)	Poly(1-vinylethylene)
1,2-addition		
$\left(\text{---CH}_2\text{CH}=\text{CHCH}_2\text{---} \right)$	1,4-poly(1,3-butadiene)	Poly(1-butene-1,4-diyl)
1,4--addtion		

TABLE 1.2 Nomenclature of Vinyl Polymers (p19)

1.7.2. Vinyl Copolymers

IUPAC recommends **source-based nomenclature** for copolymers.

Systematic

Concise

Poly[styrene-**co**-(methyl methacrylate)]

Copoly(styrene/methyl methacrylate)

Poly[styrene-**alt**-(methyl methacrylate)]

Alt-copoly(styrene/methyl methacrylate)

Polystyrene-**block**-poly(methyl methacrylate)

Block-copoly(styrene/methyl methacrylate)

Polystyrene-**graft**-poly(methyl methacrylate)

Graft-copoly(styrene/methyl methacrylate)

Poly(styrene-**co**-ethylene-**co**-propylene)

Copoly(styrene/ethylene/propylene)

1.7.3. Nonvinyl Polymers

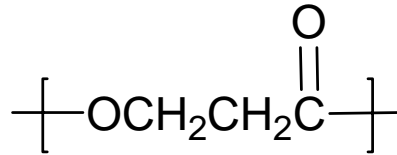
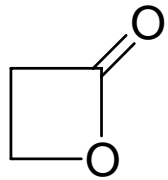
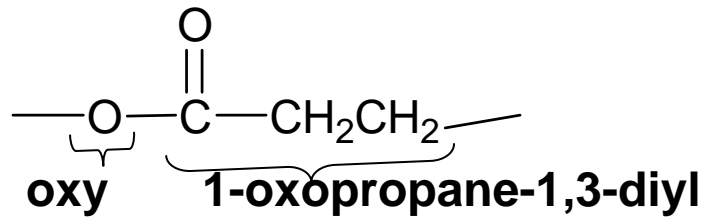
Polyethers, polyesters, polyamides

Heteroatoms Seniority: **O, S, N, P**

1) Polyethers

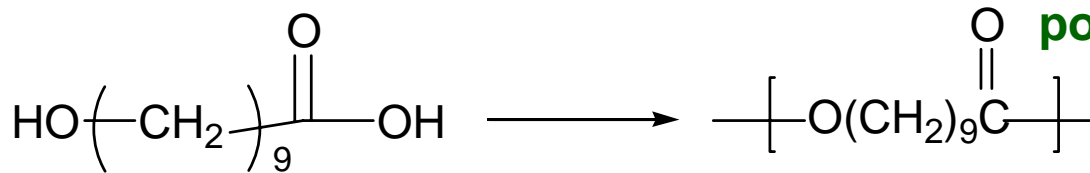
		Source name	IUPAC name	
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{H}_2\text{C} - \text{CH}_2 \end{array}$	\longrightarrow	$\left(\text{CH}_2\text{CH}_2\text{O} \right)$	Poly(ethylene oxide)	Poly(oxyethylene)
CH_2O	\longrightarrow	$\left(\text{CH}_2\text{O} \right)$	Polyformaldehyde	Poly(oxymethylene)
CH_3CHO	\longrightarrow	$\left(\begin{array}{c} \text{CHO} \\ \\ \text{CH}_3 \end{array} \right)$	Polyacetaldehyde	Poly(oxyethylidene)

2) Polyesters



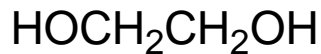
poly(β -propiolactone)
= poly(3-propionate)

poly[oxy(1-oxopropane-1,3-diyl)]

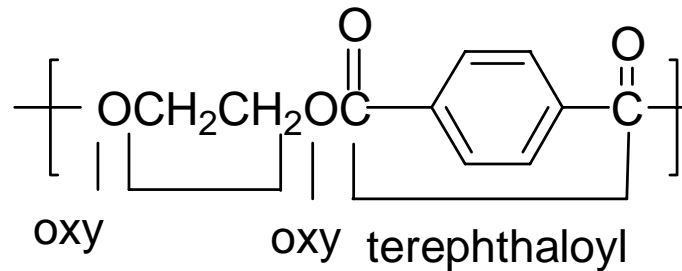
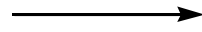


poly(10-decanoate)

poly[oxy(1-oxodecane-1,10-diyl)]



+

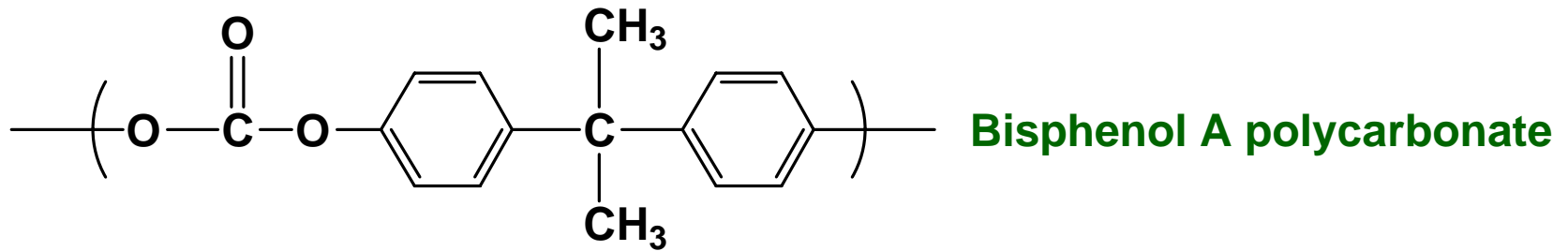


poly(ethylene terephthalate)

poly(oxyethyleneoxyterephthaloyl)

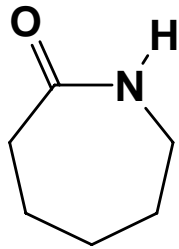
3) Polycarbonate

Heteroatoms Seniority: **O, S, N, P**

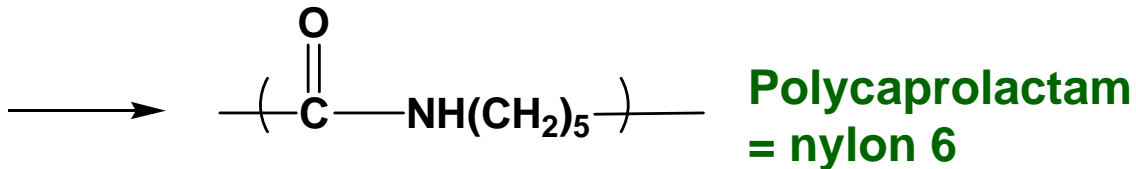


poly(oxycarbonyloxy-1,4-phenyleneisopropylene-1,4-phenylene)

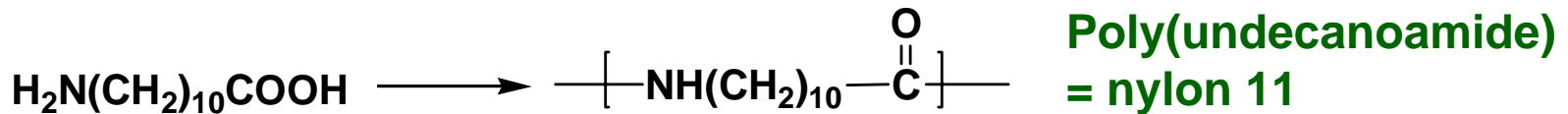
4) Polyamide



caprolactam



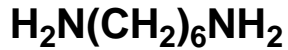
Poly[imino(1-oxohexane-1,6-diyl)]



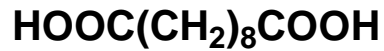
11-aminoundecanoic acid

Poly[imino(1-oxoundecane-1,11-diyl)]

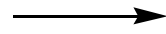
Hexamethylenediamine



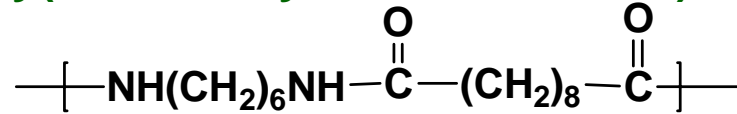
+



Sebacic acid

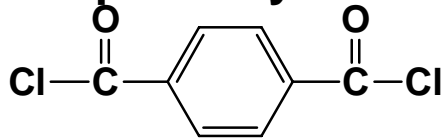


Poly(hexamethylenesebacamide) or nylon 610

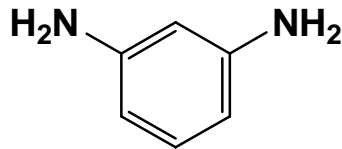


Poly(iminohexane-1,6-diyliminosebacoyl)

Terephthaloyl chloride



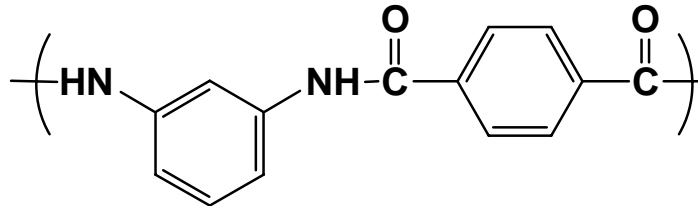
+



m-Phenylenediamine

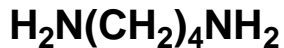


Poly(m-phenyleneterephthalate)

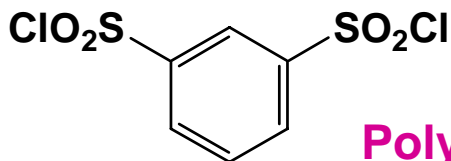


Poly(imino-1,3-phenyleneiminoterephthaloyl)

Tetramethylenediamine



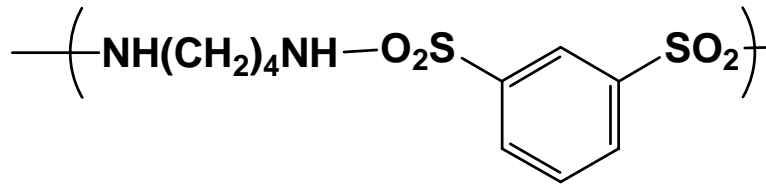
+



m-Benzenedisulfonyl chloride



Poly(tetramethylene-m-benzenesulfonamide)



Poly(sulfonyl-1,3-phenylenesulfonylimino-butane-1,4-diylimino)

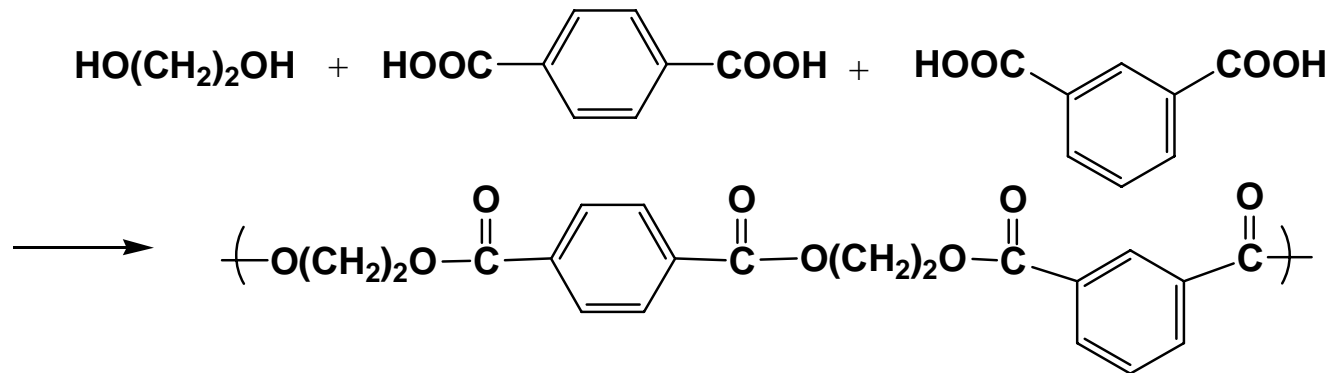
1.7.4 Nonvinyl copolymers

IUPAC **source-based nomenclature** for nonvinyl copolymers

2:1:1 –molar ratio of the monomers

ethylene glycol, terephthalic acid, and isophthalic acid

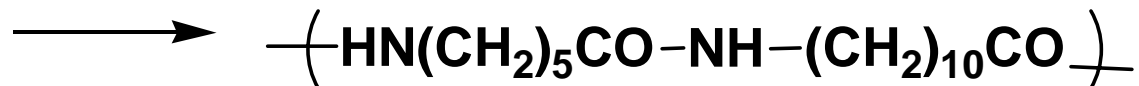
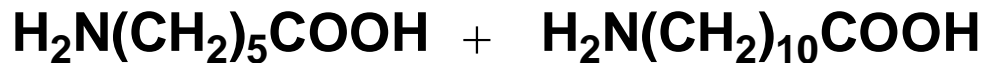
→ **poly(ethylene terephthalate-co-ethylene isophthalate)**



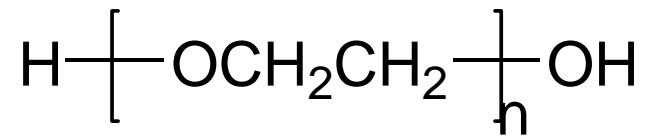
6-aminohexanoic acid + 11-aminoundecanoic acid

→ **poly[(6-aminohexanoic acid)-co-(11-aminoundecanoic acid)]**

poly[(6-hexanoamide)-co-(11-undecanoamide)]



1.7.5 End Groups



α -Hydro- ω -hydroxypoly(oxyethylene)

1.7.6 Abbreviations

Appendix A (p515)

1.8 Industrial Polymers

Plastics **weigh less** and are **more corrosion resistant** than metals

Lower energy process

Five major classifications of the polymer industry

Plastics

Fibers

Rubber (elastomers)

Adhesives

Coatings

1.8.1 Plastics

1) Commodity plastics

a) High volume and low cost

b) Materials properties limited by relatively low intermolecular forces (primarily Van der Waals, dipole - induced dipole, and dipole-dipole \therefore need relatively high MW to get desired strengths, etc.

2) Engineering plastics

a) Lower volume and higher cost

b) Superior mechanical properties and greater durability

c) Mostly Heterochain polymers

Hydrogen-Bonds hold even relatively short chains together very strongly

Most building blocks are quite highly aromatic in character

TABLE 1.4 Five Major Commodity Plastics p26

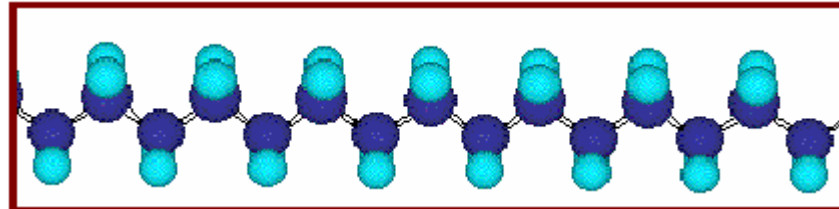
Type	Abbreviation	Major Use
Low-density polyethylene	LDPE	Packaging film, wire and cable insulation, toys, flexible bottle, housewares, coatings
High-density polyethylene	HDPE	Bottles, drums, pipe, conduit, sheet, film, wire and cable insulation
Polypropylene	PP	Automobile and appliance parts, furniture, cordage, webbing, carpeting, film packaging
Poly(vinyl chloride)	PVC	Construction, rigid pipe, flooring, wire and cable insulation, film and sheet
Polystyrene	PS	Packaging (foam and film), foam insulation, appliances, housewares, toys

Low-density: < 0.94 g/cm³, branched

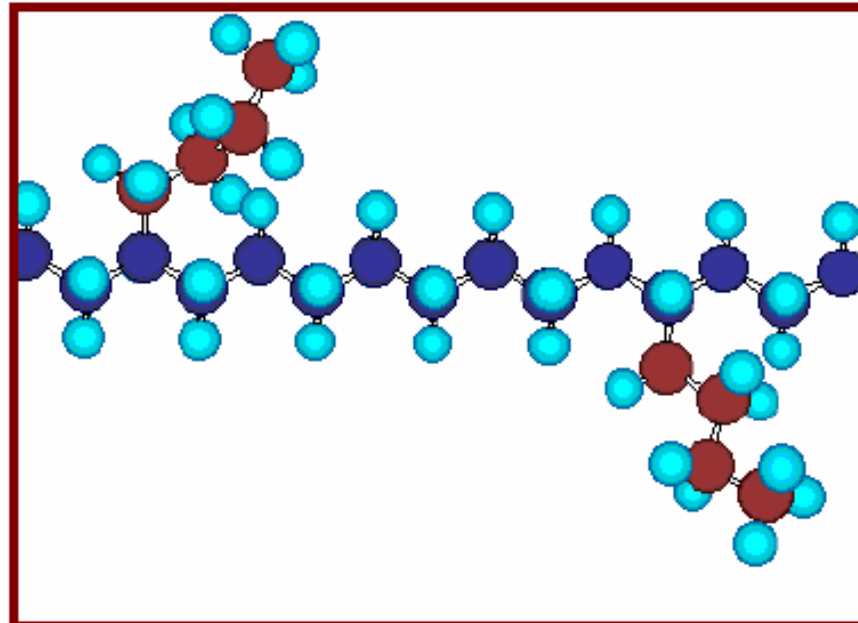
High-density: > 0.94 g/cm³, linear

Linear and Branched Polyethylenes

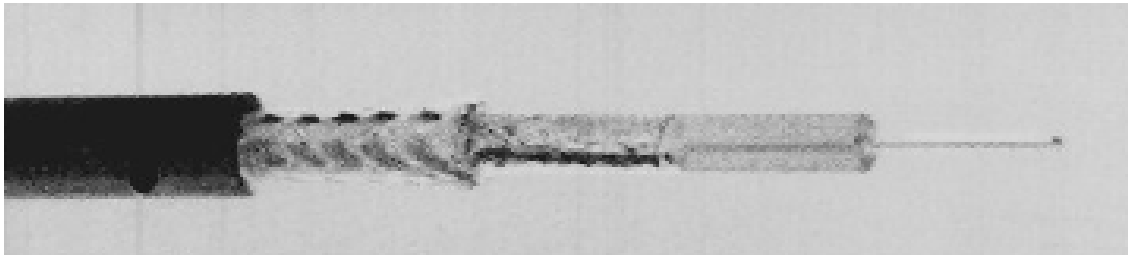
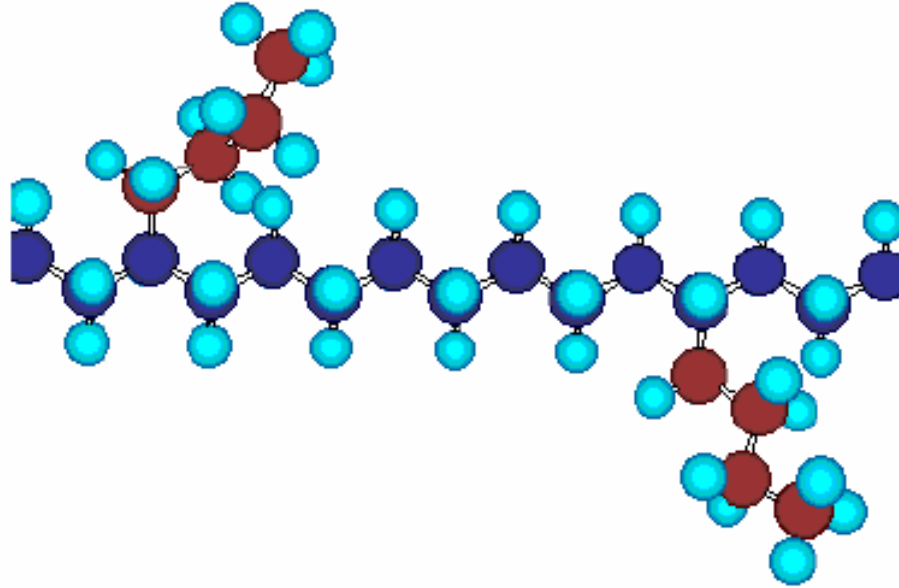
Linear



Branched

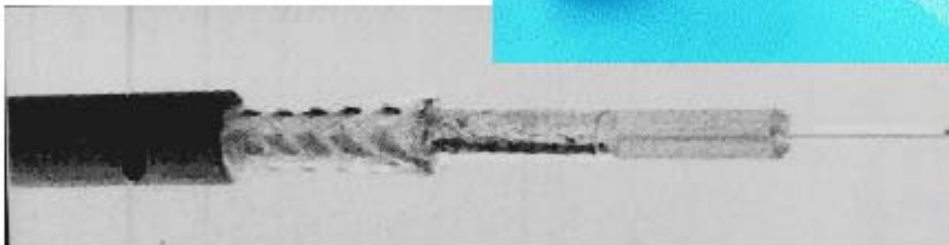


Low Density Polyethylene



A modern cable coating

Low Density Polyethylene





The Many Uses of Polypropylene



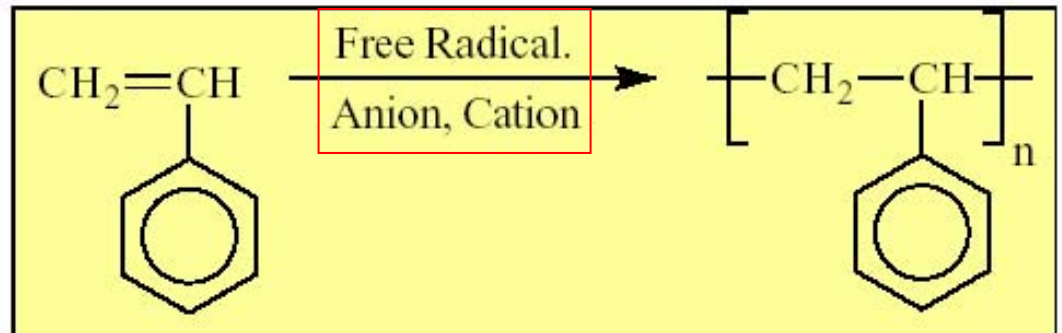
Polystyrene



Clear polystyrene articles



Foamed polystyrene articles



Getting Flexible – PVC



PVC siding



PVC door and frame



PVC pipe & fixtures



PVC roofing material



PVC window

Plasticized PVC



Cable sheathing.



PVC "leather".



Cling wrap.



PVC bottles.



PVC apparel.

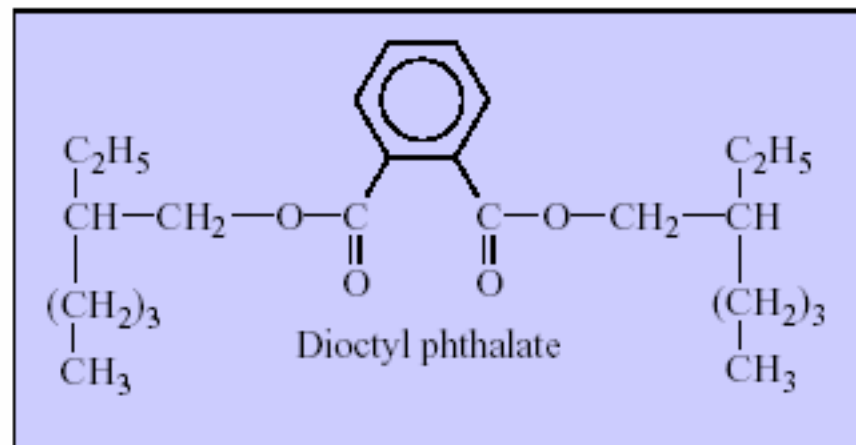


PVC apparel.

Plasticized PVC



Soft plasticized PVC toys



A water filled plasticized PVC teething ring.



2) Engineering Plastics

TABLE 1.5 Principal Engineering Plastics (p27)

a) Polyamide: nylon 6, nylon 66

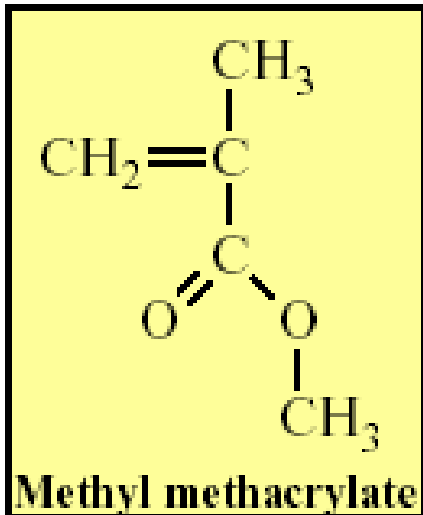
b) Polyester: poly(ethylene terephthalate (PET),
poly(butylene terephthalate (PBT)

c) Polycarbonate (PC)

d) Acetal: Polyoxymethylene (POM) = polyformaldehyde

e) Poly(phenylene oxide) (PPO)

Poly(methyl methacrylate) (PMMA)



An beautifully **clear glassy** material

'Plexiglas' or 'Perspex'

Cockpit **canopies** for military aircraft



A Hawker "Hurricane" with
Perspex canopy

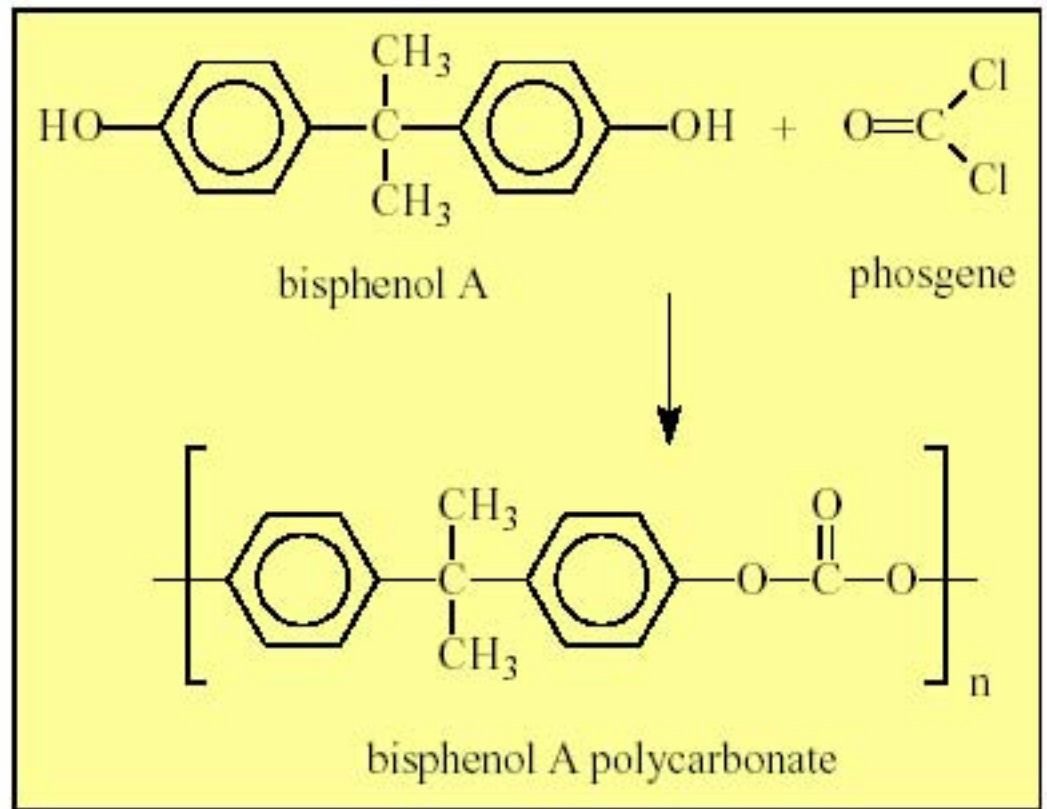
Poly(methyl methacrylate)



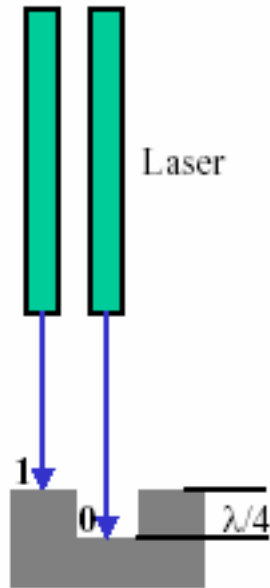
Polycarbonate



Tough Stuff!



Polycarbonate



Polycarbonate CD's.

*Schematic of
hole in disc*



*Good
definition*



*Poor
definition*



TABLE 1.6 Thermosetting Plastics

p28

Type	Abbreviation	Major Use
Phenol-formaldehyde	PF	Electrical and electronic equipment, automobile parts, utensil handles, plywood adhesives, particle board binder
Urea-formaldehyde	UF	Similar to PF polymers, treatment of textiles (crease-resistant), coatings
Melamine-formaldehyde	MF	Similar to UF polymers, decorative panels, counter and table tops, dinnerware
Unsaturated polyester	UP	Construction, automobile parts, boat hulls, marine accessories, corrosion-resistant ducting, pipe, tank, etc., Business equipment
Epoxy		Protective coatings, adhesives, electrical and electronics applications, industrial flooring, highway paving materials, composites

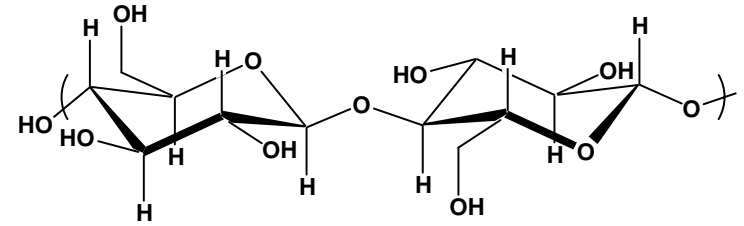
1.8.2 Fibers

High strength and modulus, good elongation (**stretchability**), good **thermal stability** (enough to withstand ironing), **spinnability** (the ability to be converted to filaments)

TABLE 1.7 Principal Synthetic Fibers

Cellulosic

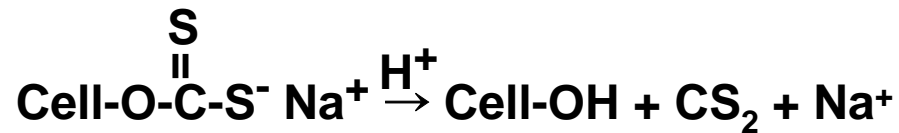
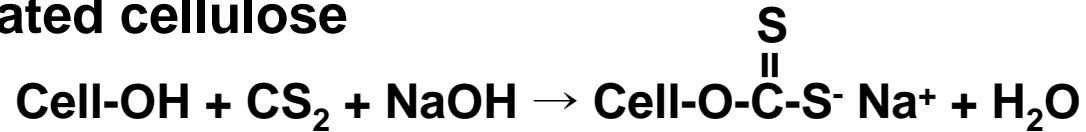
Acetate rayon Cellulose acetate



Cellulose



Viscose rayon Regenerated cellulose



Noncellulosic

Polyester ; PET

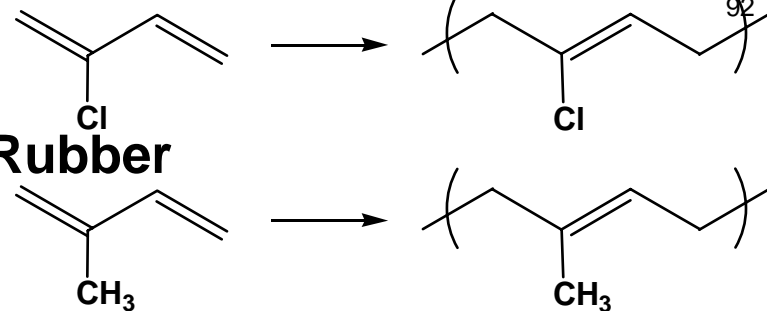
Nylon ; nylon 66, nylon 6, aromatic polyamide

Olefin ; PP

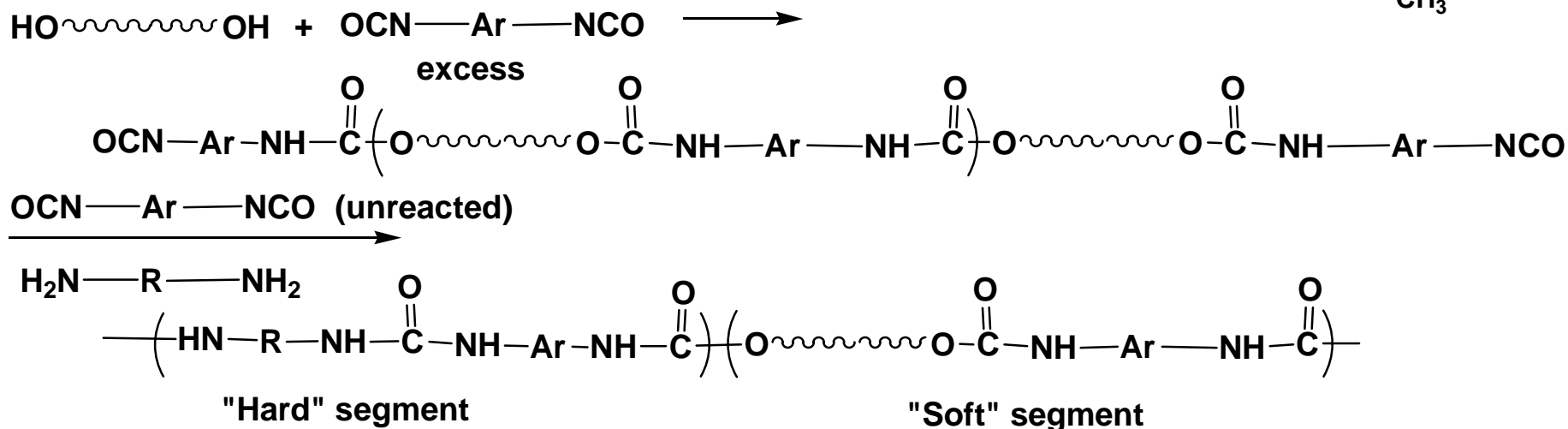
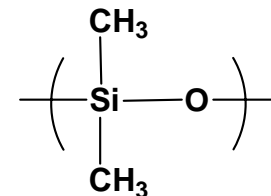
Acrylic ; polyacrylonitrile

1.8.3 Rubber (Elastomers)

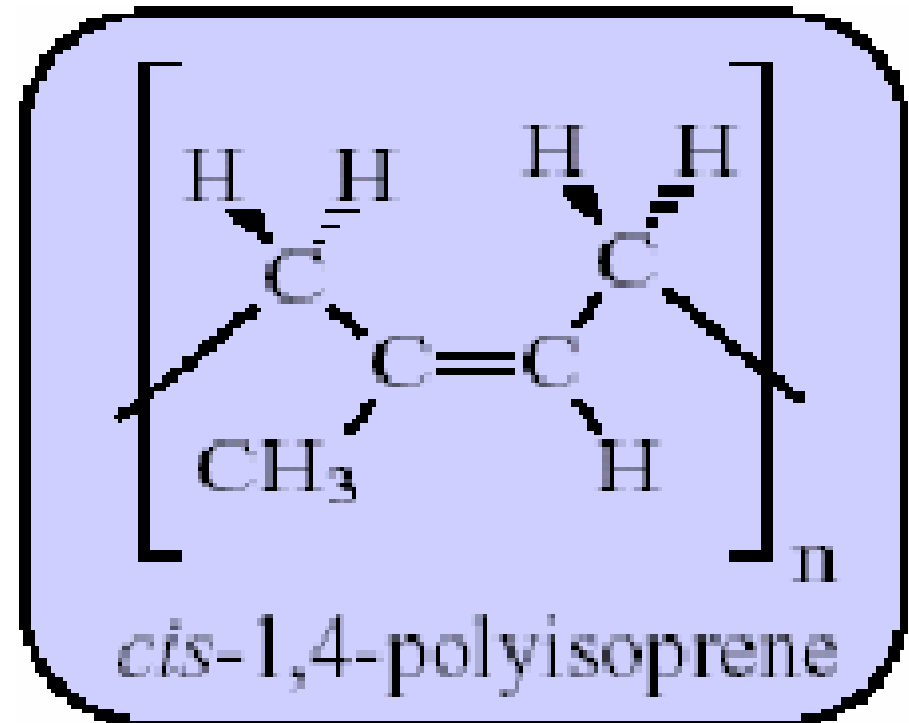
TABLE 1.8 Principal Types of Synthetic Rubber



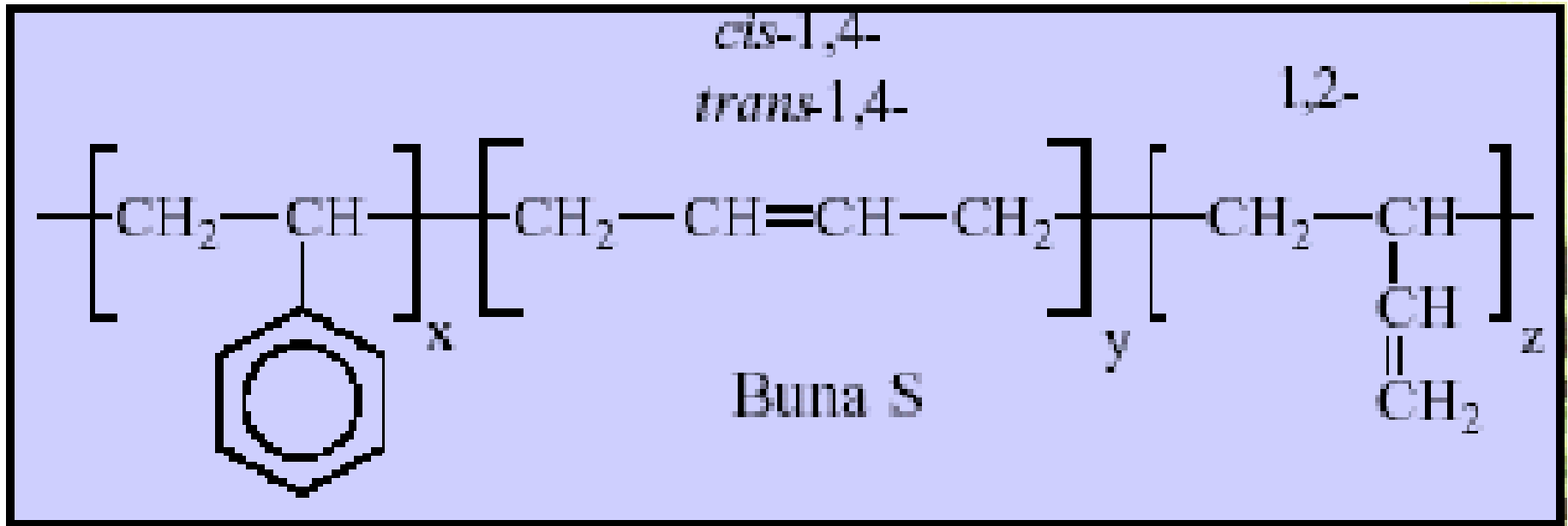
Type	Description
Styrene-butadiene	Styrene-butadiene rubber (SBR)
Polybutadiene	cis-1,4 polymer
Ethylene-propylene	EPDM for ethylene-propylene-diene monomer
Polychloroprene	Trans-1,4 polymer, known as neoprene rubber
Polyisoprene	Cis-1,4 polymer, " synthetic natural rubber "
Nitrile	Copolymer of acrylonitrile and butadiene
Butyl	Copolymer of isobutylene and isoprene
Silicone	Polysiloxane
Urethane	Linking polyethers through urethane groups



Natural Rubber



Buna S Rubber



Styrene-butadiene rubber (SBR)

1.8.4 Coatings and Adhesives

Coatings

Polyester (alkyd):	varnishes, paints
Styrene-butadiene copolymer:	interior latex wall paints
Poly(vinyl acetate) and poly(acrylate esters):	exterior latex paints

Adhesives

Phenol-formaldehyde and urea-formaldehyde:	wood industries (plywood, particle board)
Epoxides	
Cyanoacrylate	

Efforts to reduce **VOC** (volatile organic carbon)

1.9 Polymer Recycling

- Solutions of polymer waste
 - Degradable polymer: **landfill**
 - Combustible polymer: **energy recovery**
 - Recycling
 - Innovative uses: **Automobile tires**; ground and blended into molded **rubber products** or **asphalt paving materials**, construct **barrier reefs**



TABLE 1.9 Plastics Recycling Code

Number	Letters	Plastic
1	PETE	Poly(ethylene terephthalate)
2	HDPE	High-density polyethylene
3	V or PVC	Poly(vinyl chloride)
4	LDPE	Low-density polyethylene
5	PP	Polypropylene
6	PS	Polystyrene
7	Other	Others or mixed plastics