Course:Polymer Synthesis and Formulation

(Synthèse et formulation des polymères)

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First part (Partie 01)

- **Part 1: Synthesis : (En)**
- **1- Definitions, classification, nomenclature, importance of the discipline.**
- **2- Polycondensations: definitions, kinetic study, three-dimensional structures,molecular distributions.**
- **3- Polyadditions: definitions, kinetic study, three-dimensional structures, molecularmolecular distributions.**
- **4- Radical copolymerisations.**
- **5- Dispersed-state polymerisations.**
- Partie 1 : Synthèse (Fr)
- 1- Définitions, classification, nomenclature, importance de la discipline.
- 2- Polycondensations : définitions, étude cinétique, structures tridimensionnelles,
- distributions moléculaires.
- 3- Polyadditions : définitions, étude cinétique, structures tridimensionnelles, distributions
- moléculaires.
- 4- Copolymérisations radicalaires.
- 5- Polymérisations à l'état dispersé.

Second part (Partie 2): Formulation :

- 1- Study of systems formulated from emulsions (normal and inverse).
- 2- Study of surfactants (structure, classification, choice of the right surfactant for theapplication, properties at interfaces, organisation in solution).
- 3- Nature, stability and characterisation of emulsions.
- 4- Study of encapsulation (micro, nano) based on the three main families of processes(physical, physico-chemical, chemical).

- 1- Etude des systèmes formulés à partir des émulsions (normales et inverses).
- 2- Etude des tensioactifs (structure, classement, choix du tensioactif approprié à
- l'application, propriétés aux interfaces, organisation en solution).
- 3- Nature, stabilité et caractérisation des émulsions.
- 4- étude de l'encapsulation (micro, nano) à partir des trois grandes familles de procédés
- (physiques, physico-chimiques, chimiques).

Evaluation method

- ✓Written exam: 67%.
- ✓Continuous assessment: 33%.

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PART Ⅰ POLYMER STRUCTURE AND PROPERTIES

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PART Ⅱ VINYL POLYMERS

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PART Ⅲ NONVINYL POLYMERS

Chapter 1. Basic principles

- 1.1 Introduction and Historical Development
- 1.2 Definitions
- 1.3 Polymerization Processes
- 1.4 Step-reaction Polymerization
- 1.5 Chain-reaction Polymerization
- 1.6 Step-reaction Addition and Chain-reaction Condensation
- 1.7 Nomenclature
- 1.8 Industrial Polymers
- 1.9 Polymer Recycling

1.1 Introduction and Historical Development

A. Development of civilization

Stone age → Bronze age → Iron age → Polymer age

B. Application of polymeric materials

- PE milk bottles
- Polyamide bulletproof vests
- Polyurethane artificial heart
- Fluorinated phosphazene elastomer for arctic environments

C. The purpose of this book

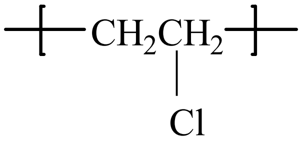
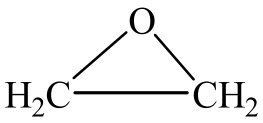
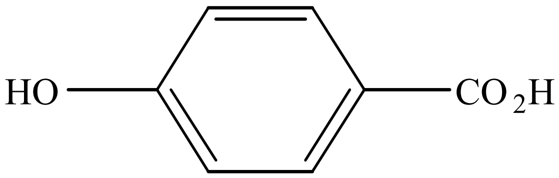
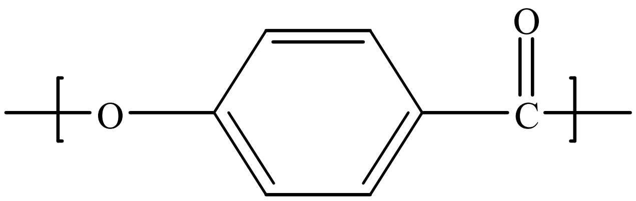
1. Property difference between polymer and low molecular weight compound
2. Chemistry of polymer synthesis
3. Chemistry of polymer modification

D. Development of polymer chemistry

- 1833s : Berzelius, the first use of terminology, polymer
- 1839s : Synthesis of polystyrene
- 1860s : Poly(ethylene glycol), Poly(ethylene succinate)
- 1900s : Leo Baekeland, synthesis of phenol formaldehyde resin
- 1920s : Hermann staudinger

  Structure of polymer(long-chain molecules), Novel Prize(1953s)
- 1939s : W.H. Carothers, Nylon synthesis (Du Pont)
- 1963s : Ziegler-Natta, stereoregular polymerization
- 1974s : Paul Flory, polymer solution property
- 1984s : Bruce Merrifield, solid-phase protein process

E. Examples of monomers and polymers

Monomer	**Polymer**
$CH_2{=}CH_2$	$-\!\!\left[CH_2CH_2\right]\!\!-$
$CH_2{=}CHCl$	 $-\!\!\left[CH_2\underset{\displaystyle Cl}{\underset{\vert}{CH_2}}\right]\!\!-$
	$-\!\!\left[CH_2CH_2O\right]\!\!-$
$HOCH_2CH_2OH$	$-\!\!\left[CH_2CH_2O\right]\!\!-$
	

1.2 Definitions

A. Acoording to the amount of repeating units

- **monomer** : one unit
- **oligomer** : few
- **polymer** : many (poly – many, mer – part)
- **telechelic polymer** : polymer containing reactive end group

  (tele = far, chele = claw)
- **telechelic oligomer** : oligomer containing reactive end group
- **macromer(=macro monomer)** : monomer containing long chain

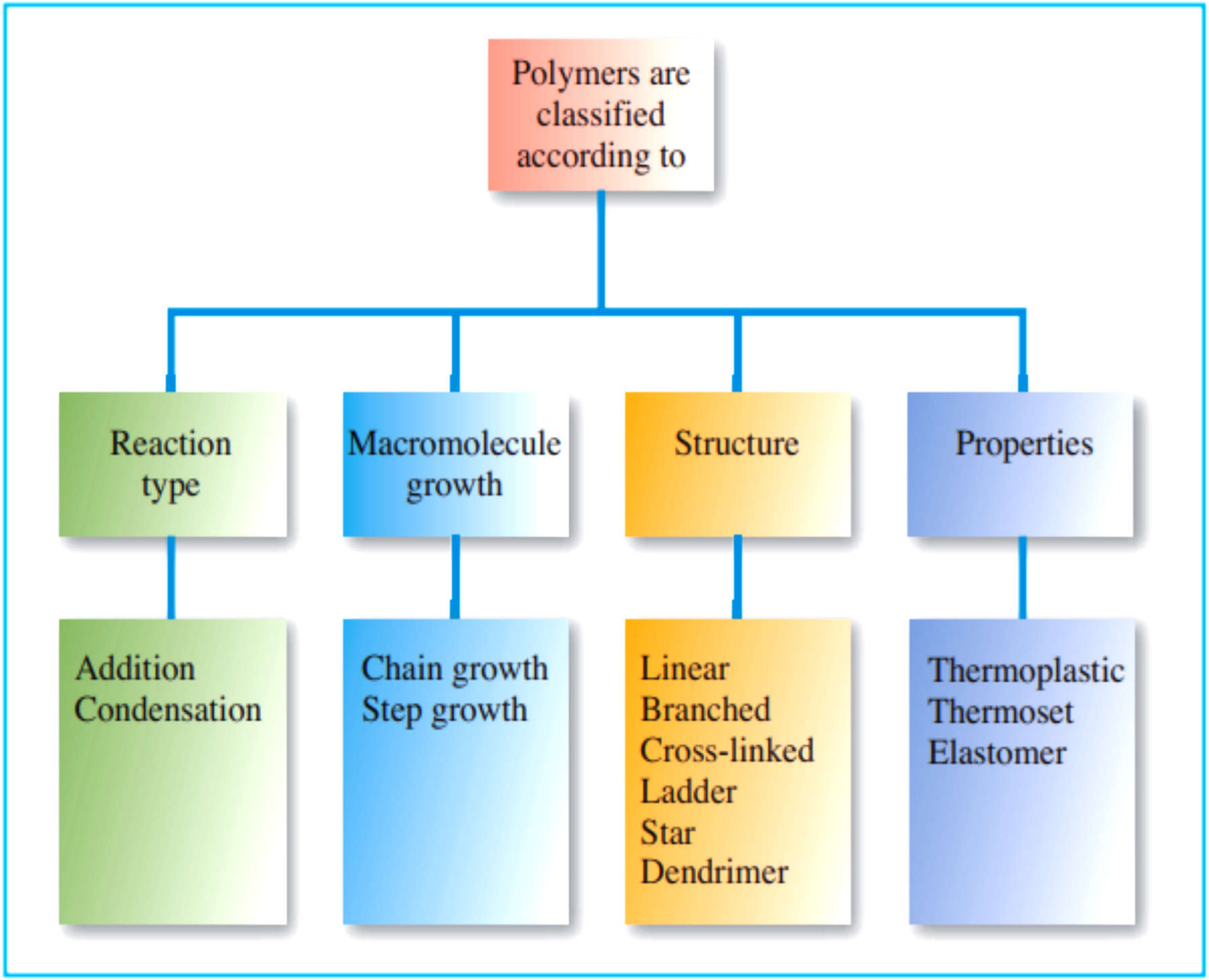
1.2 Definitions

B. DP : Degree of polymerization

The total number of repeating units contained terminal group

C. The kinds of applied monomers

- One kind : Homopolymer
- Two kinds : Copolymer
- Three kinds : Terpolymer



Polymers are classified according to

- Reaction type
  - Addition
  - Condensation
- Macromolecule growth
  - Chain growth
  - Step growth
- Structure
  - Linear
  - Branched
  - Cross-linked
  - Ladder
  - Star
  - Dendrimer
- Properties
  - Thermoplastic
  - Thermoset
  - Elastomer

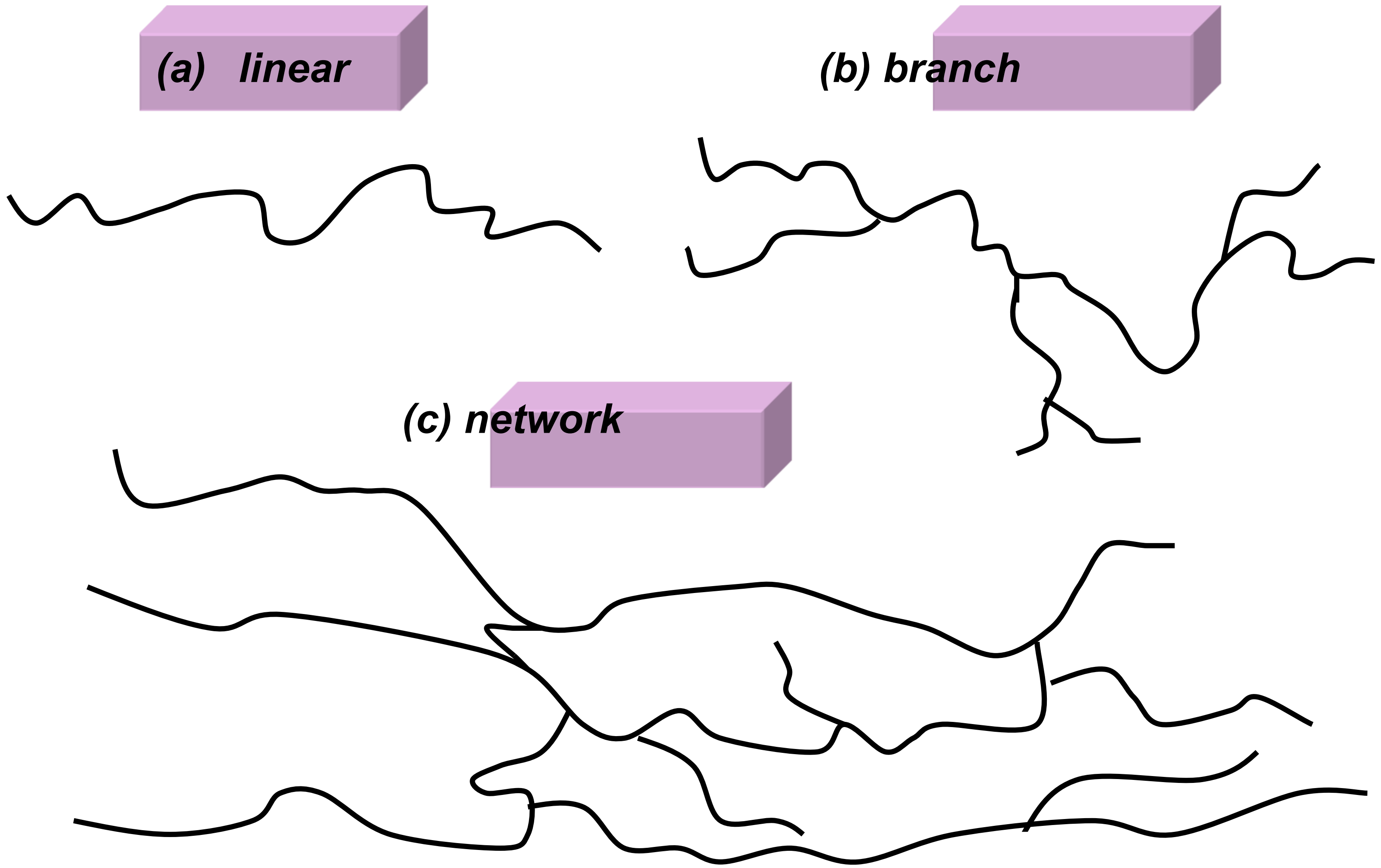
D. Types of copolymer

- Homopolymer : -A-A-A-A-A-A-A-A-
- Random copolymer : -A-B-B-A-B-A-A-B-
- Alternating copolymer : -A-B-A-B-A-B-A-B-
- Block copolymer : -A-A-A-A-B-B-B-B-
- Graft copolymer : -A-A-A-A-A-A-A-A-

|

B-B-B-B-B-

E. Representation of polymer types

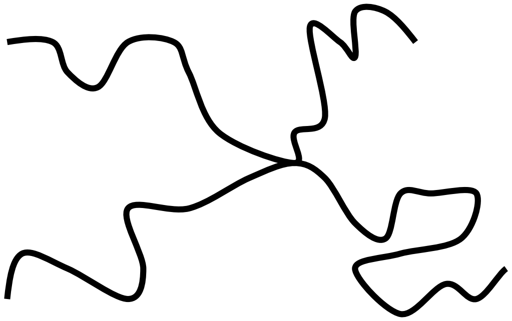


(a) linear

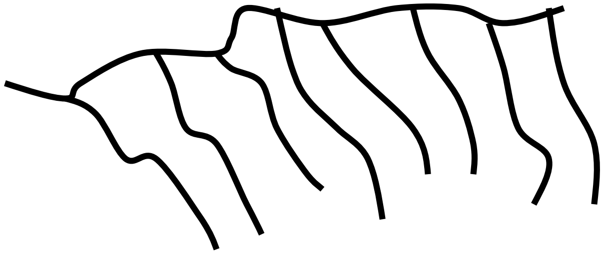
(b) branch

(c) network

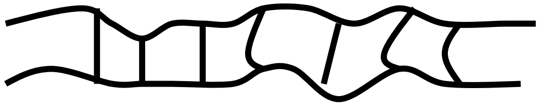
F. Representation of polymer architectures



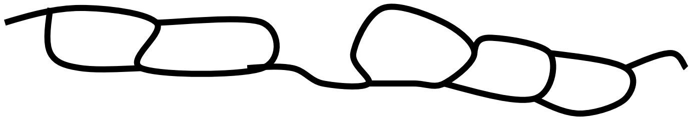
(a) star polymer



(b) comb polymer

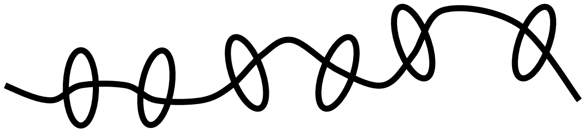


(c)ladder polymer



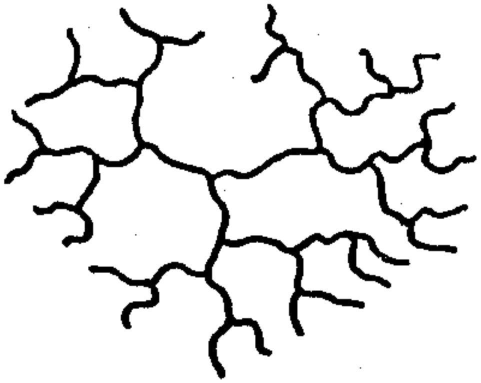
(d) semi- ladder
(or stepladder) polymer

F. Representation of polymer architectures



(e) polyrotaxane

(f) polycatenane



(g) dendrimer

G. Thermoplastic and thermoset (reaction to temperature)

- **Thermoplastic** : Linear or branched polymer
- **Thermoset** : Network polymer

1.3 Polymerization Processes

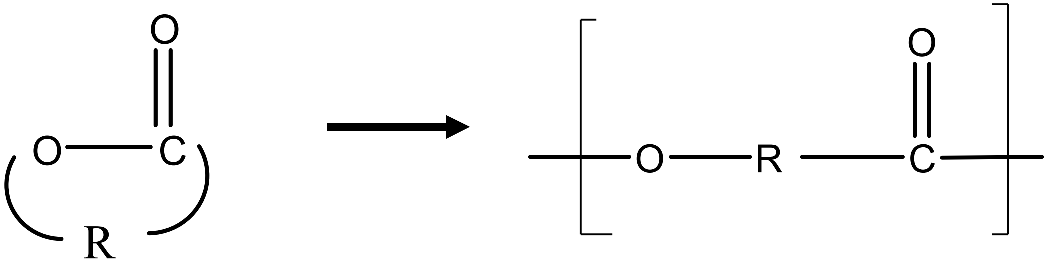
A. Classification of polymers to be suggested by Carothers

- **Addition polymers : repeating units and monomers are same**
- **Condensation polymers : repeating units and monomers are not equal, to be split out small molecule**

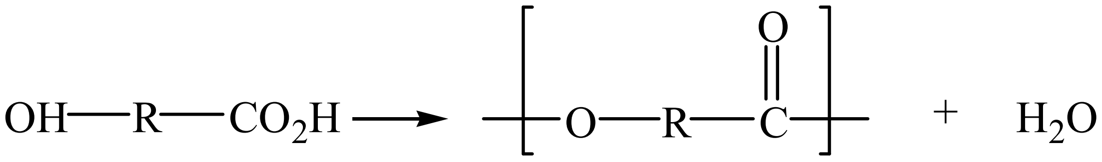
Other examples

1. **Polyester from lactone (1.7) &**

   from ω-hydroxycarboxylic acid (1.8)



(1.7)

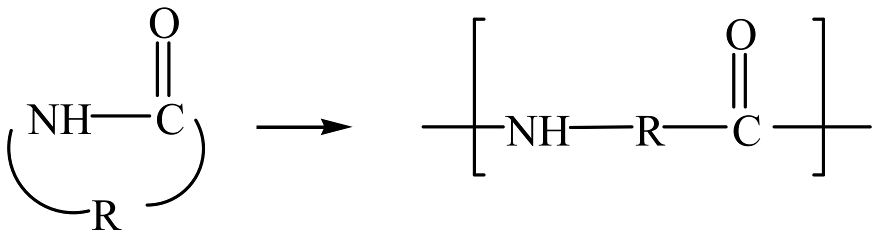


$$HO{-}R{-}CO_2H \longrightarrow \left[O{-}R{-}\overset{O}{\overset{\|}{C}} \right] + H_2O$$

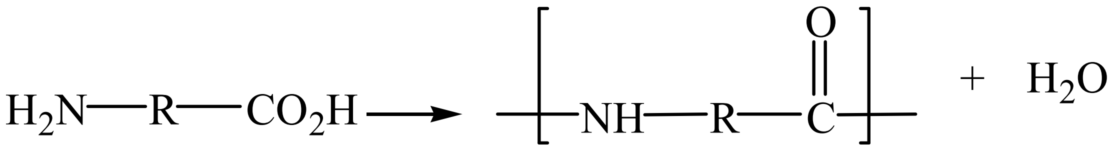
(1.8)

Other examples

2. Polyamide from lactam (1.9), and from ω-aminocarboxylic acid (1.10)



(1.9)

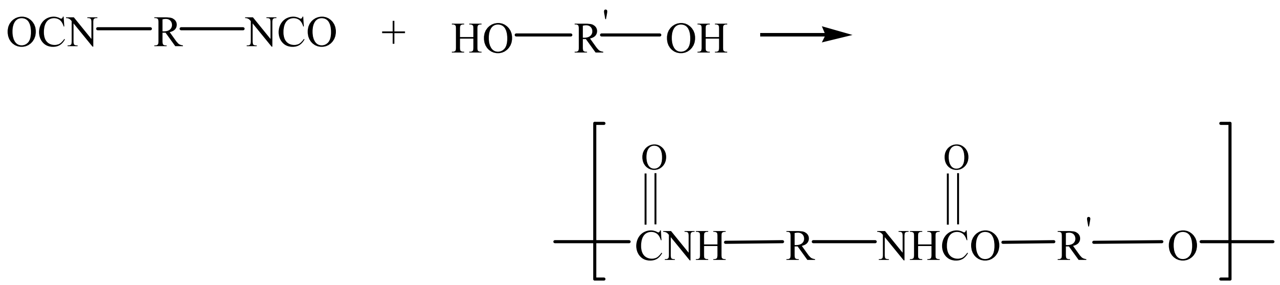


$$H_2N{-}R{-}CO_2H \longrightarrow \left[NH{-}R{-}\overset{\overset{\displaystyle O}{\|}}{C} \right] + H_2O$$

(1.10)

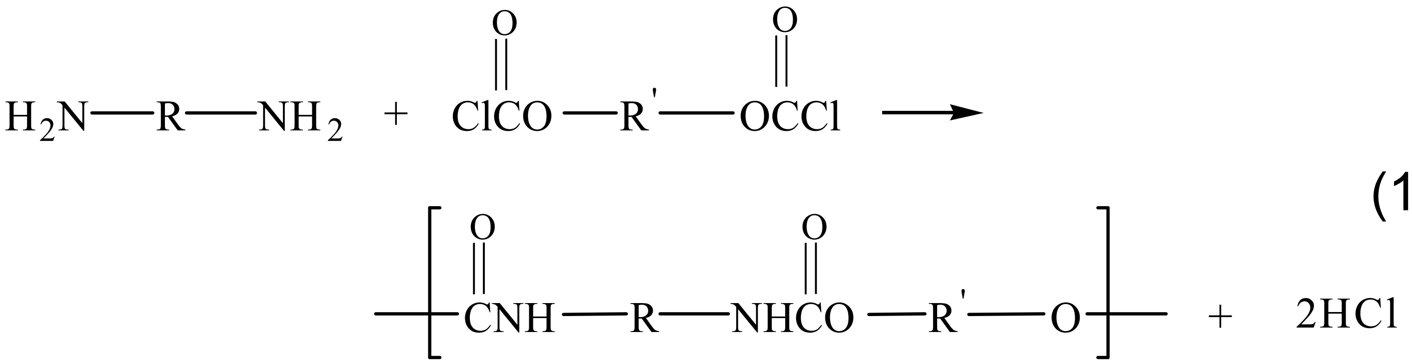
Other examples

3. Polyurethane from diisocyanate and dialcohol(1.11) and from diamine and bischloroformate(1.12):



$$OCN{-}R{-}NCO + HO{-}R'{-}OH \longrightarrow \left[\overset{O}{\overset{\|}{C}}NH{-}R{-}NH\overset{O}{\overset{\|}{C}}O{-}R'{-}O \right]$$

(1.11)



$$H_2N{-}R{-}NH_2 + Cl\overset{O}{\overset{\|}{C}}O{-}R'{-}O\overset{O}{\overset{\|}{C}}Cl \longrightarrow \left[\overset{O}{\overset{\|}{C}}NH{-}R{-}NH\overset{O}{\overset{\|}{C}}O{-}R'{-}O \right] + 2HCl$$

(1.12)

Other examples

4. Hydrocarbon polymer from ethylene (1.13), and from α,ω-dibromide (1.14)

$$CH_2{=}CH_2 \xrightarrow{\text{initiator}} -\!\!\left[\,CH_2CH_2\,\right]\!\!- \qquad (1.13)$$

$$BrCH_2(CH_2)_8CH_2Br \xrightarrow{2Na} -\!\!\left[\,CH_2CH_2\,\right]_5\!\!- \;+\; 2NaBr \qquad (1.14)$$

1.3 Polymerization Processes

B. Modern classification of polymerization according to polymerization mechanism

Step growth polymerization : Polymers build up stepwise

Chain growth polymerization : Addition polymerization
molecular weights increase successively,
one by one monomer

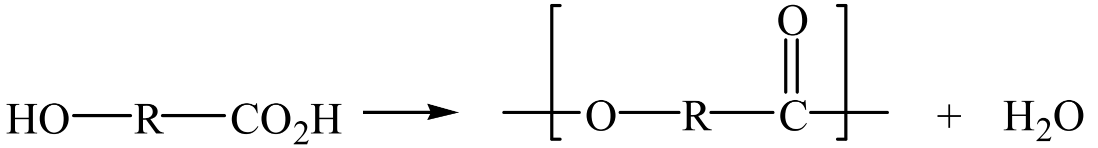
Ring-opening polymerization may be either step
or chain reaction

1.4 Step-reaction Polymerization

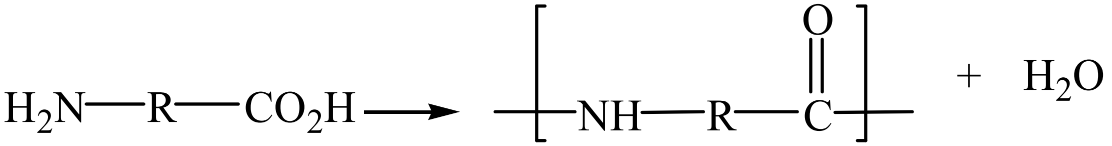
A. Monomer to have difunctional group

1. One having both reactive functional groups in one molecule

$$\mathrm{A{-}R{-}B} \longrightarrow \mathrm{{-}\!\!\left[R{-}X\right]\!\!{-}}$$



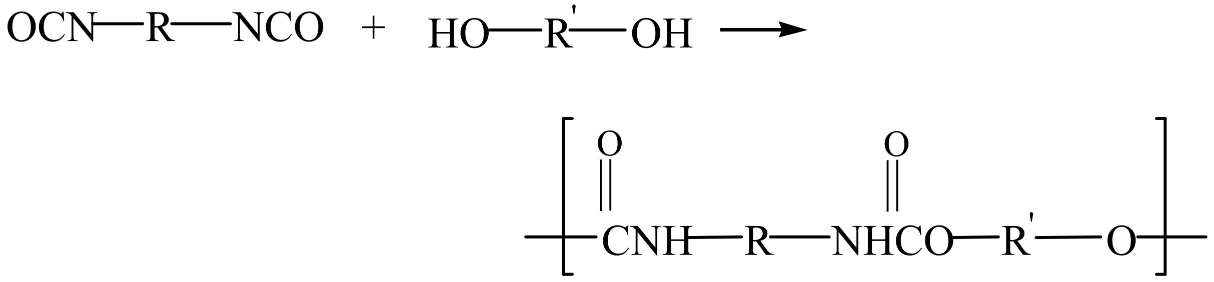
$$\mathrm{HO{-}R{-}CO_2H} \longrightarrow \mathrm{{-}\!\!\left[O{-}R{-}\overset{\overset{\displaystyle O}{\|}}{C}\right]\!\!{-}} + \mathrm{H_2O} \qquad (1.8)$$



$$\mathrm{H_2N{-}R{-}CO_2H} \longrightarrow \mathrm{{-}\!\!\left[NH{-}R{-}\overset{\overset{\displaystyle O}{\|}}{C}\right]\!\!{-}} + \mathrm{H_2O} \qquad (1.10)$$

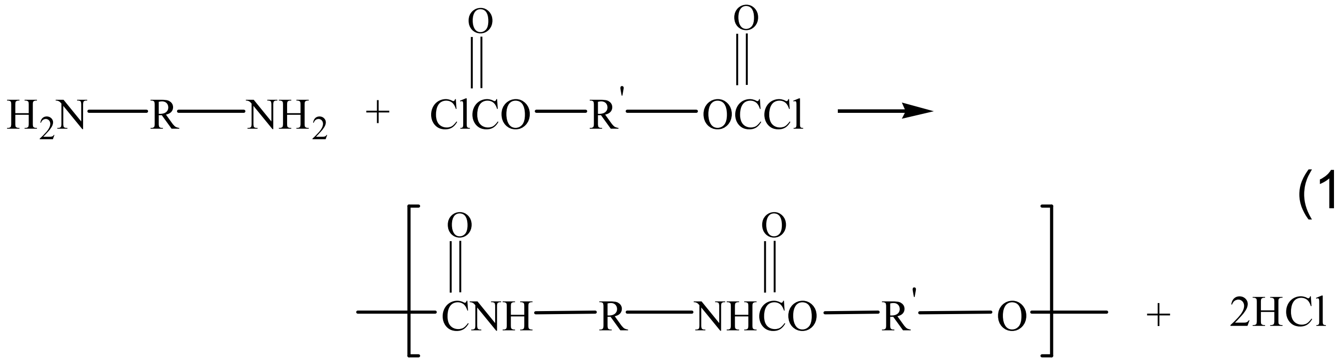
2. Other having two difunctional monomers

$$A-R-A + B-R'-B \longrightarrow \left[R-X-R'-X \right]$$



$$OCN-R-NCO + HO-R'-OH \longrightarrow \left[\overset{O}{\overset{\|}{C}}NH-R-NH\overset{O}{\overset{\|}{C}}O-R'-O \right]$$

(1.11)

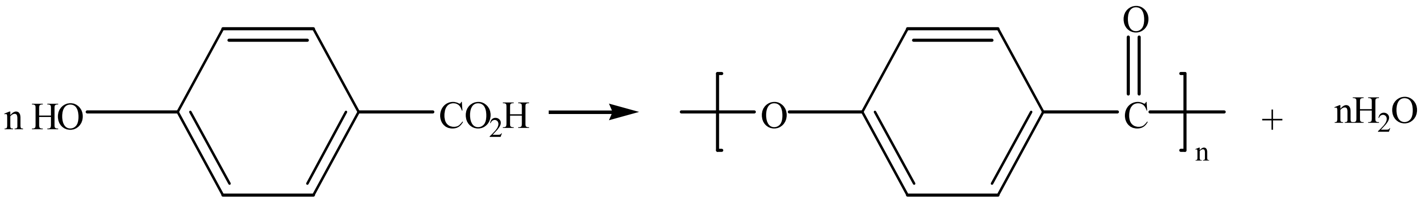


$$H_2N-R-NH_2 + Cl\overset{O}{\overset{\|}{C}}O-R'-O\overset{O}{\overset{\|}{C}}Cl \longrightarrow \left[\overset{O}{\overset{\|}{C}}NH-R-NH\overset{O}{\overset{\|}{C}}O-R'-O \right] + 2HCl$$

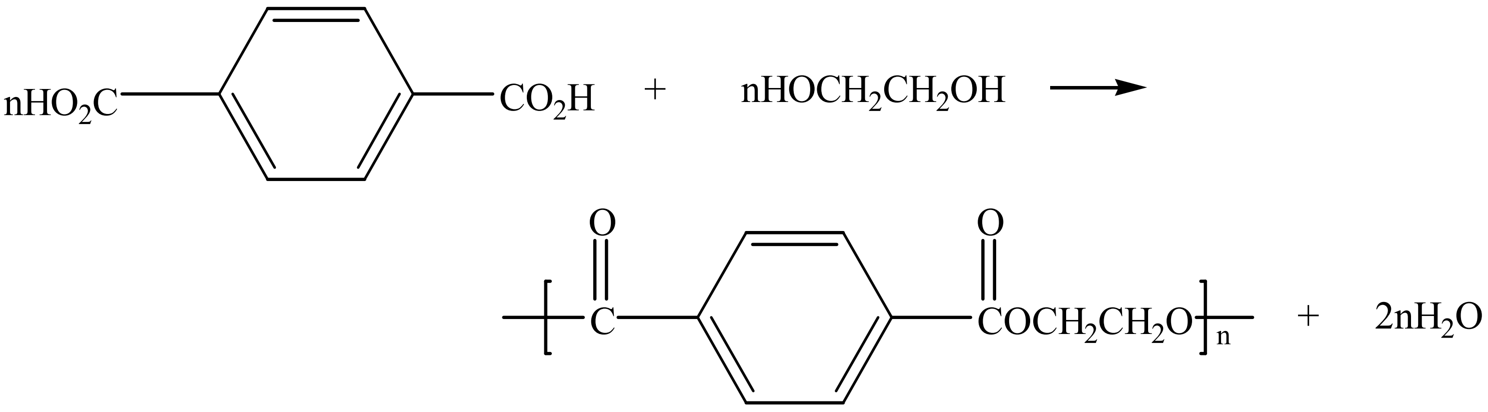
(1.12)

B. Reaction : Condensation reaction using functional group

Example - Polyesterification



(1.3)



(1.4)

C. Carothers equation

(N_O : number of molecules
N : total molecules after a given reaction period.
$N_O - N$: The amount reacted
P : The reaction conversion)

$$P = \frac{N_O - N}{N_O} \qquad \textit{Or} \qquad N = N_O(1 - P)$$

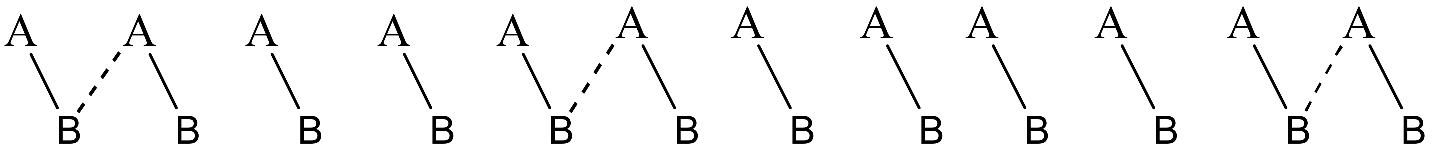
($\overline{DP}$ is the average number of repeating units of all molecules present)

$$\overline{DP} = N_O/N$$

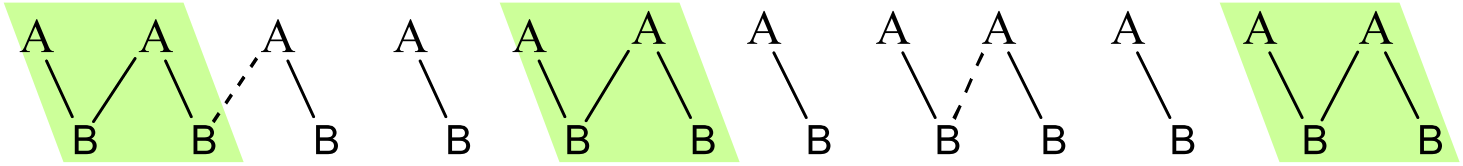
$$\overline{DP} = \frac{1}{1 - P}$$

For example
At 98% conversion → $\overline{DP} = \dfrac{1}{1- 0.98}$

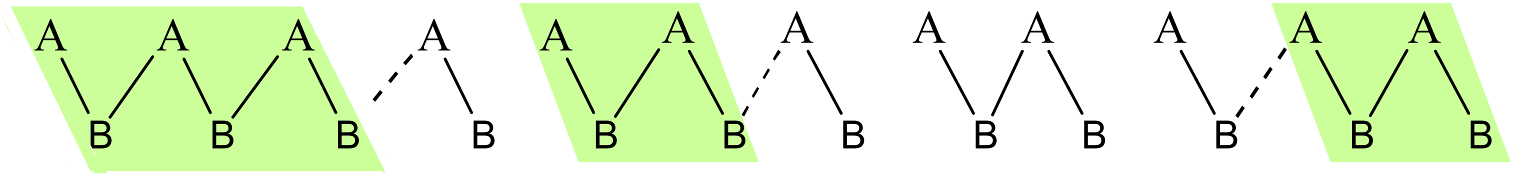
(A) Unreacted monomer



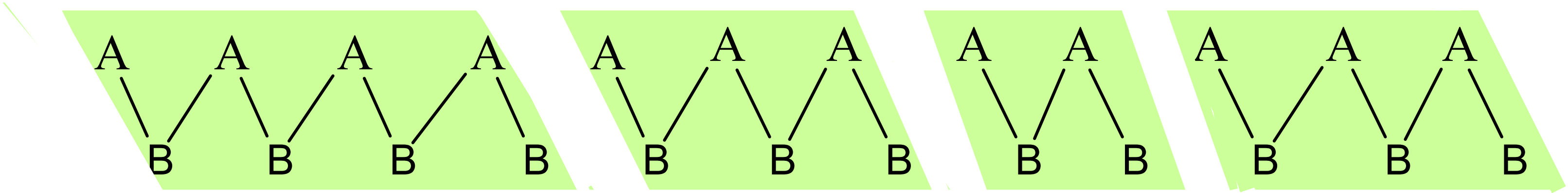
(B) 50% reacted, $\overline{DP}$ = 1.3



(C) 75% reacted, $\overline{DP}$ = 1.7



(D) 100% reacted, $\overline{DP}$ = 3



1.5 Chain-reaction Polymerization

A. Monomer : vinyl monomer

$_{\chi}CH_2{=}CH_2$

B. Reaction : Addition reaction initiated by active species

C. Mechanism :

- **Initiation**

  $R\cdot + CH_2{=}CH_2 \rightarrow RCH_2C{\cdot}H_2$

- **Propagation**

  $RCH_2CH_2\cdot + CH_2{=}CH_2 \rightarrow RCH_2CH_2CH_2C{\cdot}H_2$

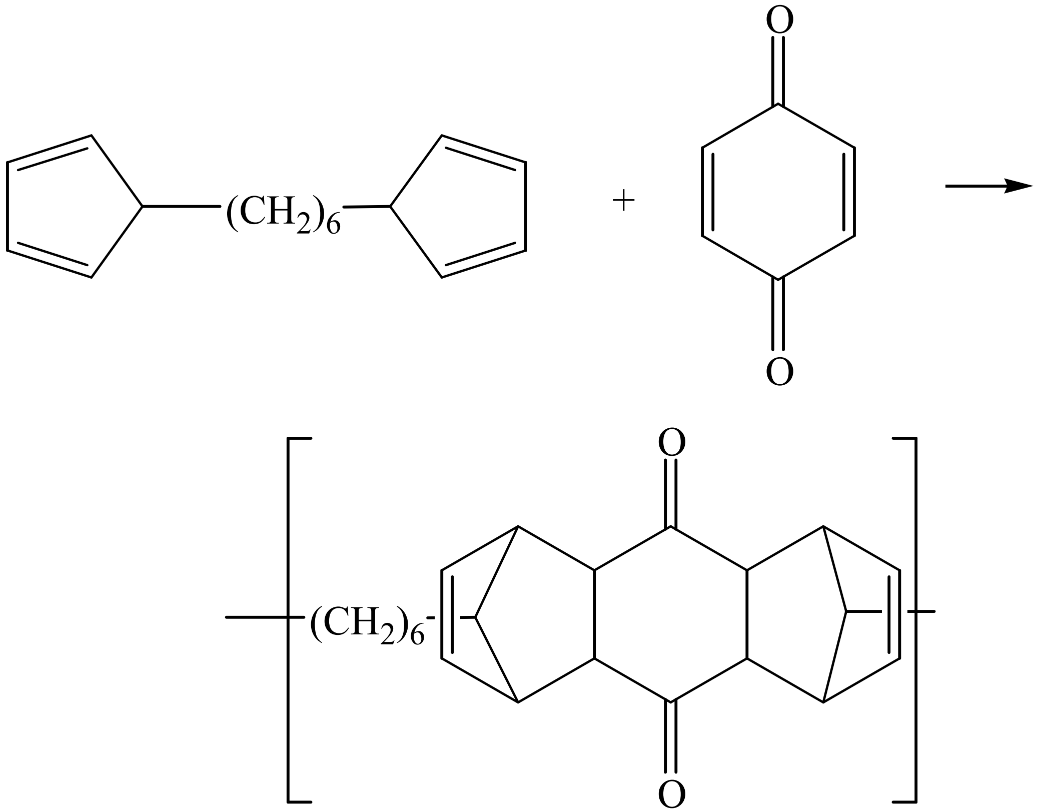
TABLE 1.1 Comparison of Step-Reaction and Chain-Reaction Polymerization

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

[a] $\overline{DP}$, *average degree of polymerization*.

1.6 Step-reaction Addition and Chain-reaction Condensation

A. Step-reaction Addition.



(1.15)

1.6 Step-reaction Addition and Chain-reaction Condensation

B. Chain-reaction Condensation

$$CH_2N_2 \xrightarrow{BF_3} -\!\left[CH_2 \right]\!- \quad + \quad N_2 \qquad (1.16)$$

1.7 Nomenclature

A. Types of Nomenclature

a. Source name : to be based on names of corresponding monomer

Polyethylene, Poly(vinyl chloride), Poly(ethylene oxide)

b. IUPAC name : to be based on CRU, systematic name

Poly(methylene), Poly(1-chloroethylene), Poly(oxyethylene)

c. Functional group name :

Acoording to name of functional group in the polymer backbone

Polyamide, Polyester

1.7 Nomenclature

d. **Trade name** : The commercial names by manufacturer Teflon, Nylon

e. **Abbreviation name** : PVC, PET

f. **Complex and Network polymer** : Phenol-formaldehyde polymer

g. **Vinyl polymer** : Polyolefin

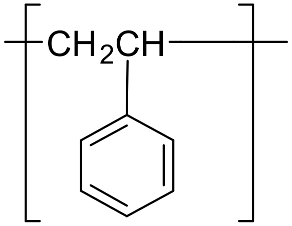
1.7.1 Vinyl polymers

A. Vinyl polymers

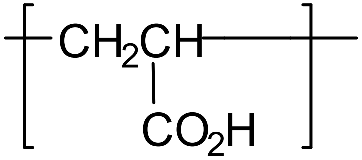
a. **Source name** : Polystyrene, Poly(acrylic acid),
Poly(α-methyl styrene), Poly(1-pentene)

b. **IUPAC name** : Poly(1-phenylethylene), Poly(1-carboxylatoethylene)
Poly(1-methyl-1-phenylethylene), Poly(1-propylethylene)

Polystyrene

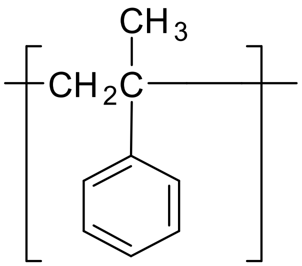


Poly(acrylic acid)

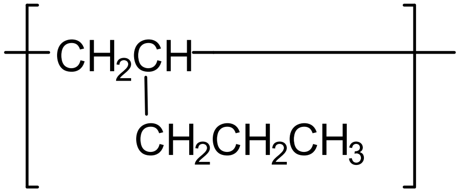


$\left[-\mathrm{CH_2}\underset{\mathrm{CO_2H}}{\underset{|}{\mathrm{CH}}}-\right]$

Poly(α-methylstyrene)



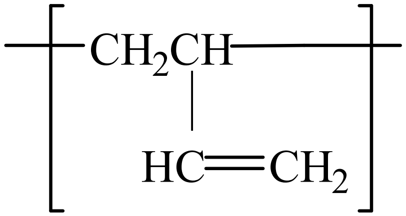
Poly(1-pentene)



$\left[-\mathrm{CH_2}\underset{\mathrm{CH_2CH_2CH_3}}{\underset{|}{\mathrm{CH}}}-\right]$

1.7.1 Vinyl polymers

B. Diene monomers


$$\left[CH_2CH(HC{=}CH_2) \right]$$

1,2-addition

$$\left[CH_2CH{=}CHCH_2 \right]$$

1,4-addition

Source name : 1,2-Poly(1,3-butadiene) 1,4-Poly(1,3-butadiene)

IUPAC name : Poly(1-vinylethylene) Poly(1-butene-1,4-diyl)

cf) Table 1.2

1.7.2 Vinyl copolymer

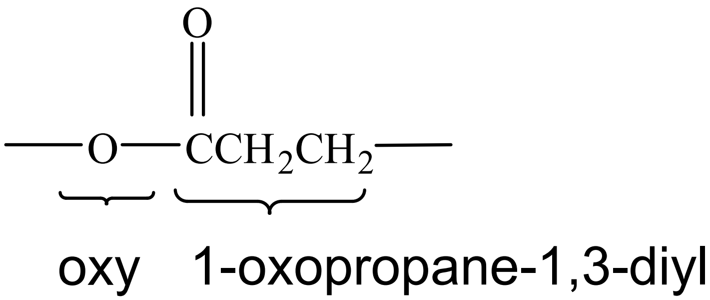
Systematic

Poly[styrene-co-(methyl methacrylate)]
Poly[styrene-*alt*-(methyl methacrylate)]
Polystyrene-*block*-poly(methyl methacrylate)
Polystyrene-*graft*-poly(methyl methacrylate)

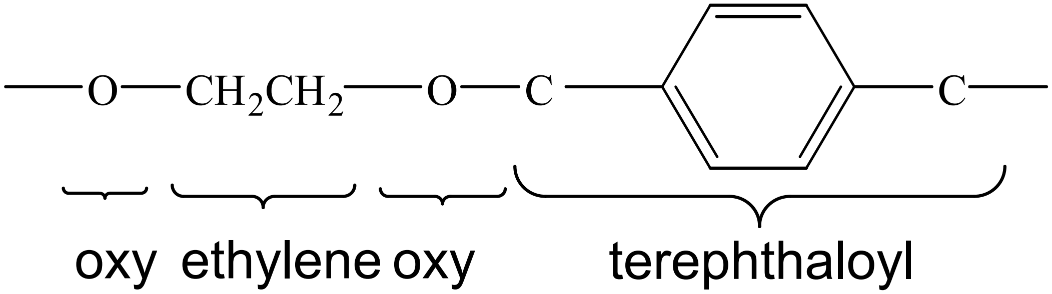
Concise

Copoly(styrene/methyl methacrylate)
Alt-copoly(styrene/methyl methacrylate)
Block-copoly(styrene/methyl methacrylate)
Graft-copoly(styrene/methyl methacrylate)

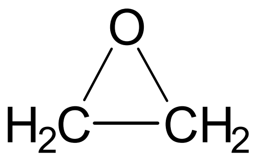
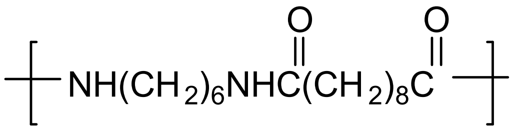
1.7.3 Nonvinyl Polymers



$$-\underbrace{O}_{\text{oxy}}-\underbrace{\overset{O}{\overset{\|}{C}}CH_2CH_2}_{\text{1-oxopropane-1,3-diyl}}-$$



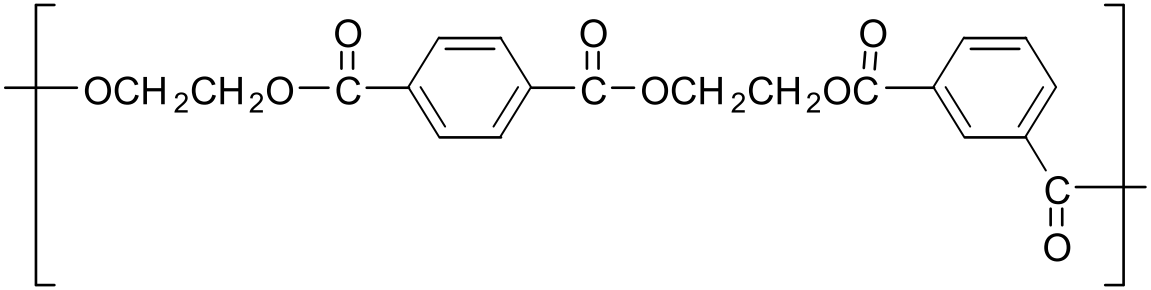
* Representative Nomenclature of Nonvinyl Polymers

Monomer structure	Polymer repeating unit	Source or Common Name	IUPAC name
	$\left[CH_2CH_2O \right]$	Poly(ethylene oxide)	Poly(oxyethylene)
$HOCH_2CH_2OH$	$\left[CH_2CH_2O \right]$	Poly(ethylene glycol)	Poly(oxyethylene)
$H_2N(CH_2)_6NH_2$ $HO_2C(CH_2)_8CO_2H$	 $\left[NH(CH_2)_6NH\overset{O}{\overset{\parallel}{C}}(CH_2)_8\overset{O}{\overset{\parallel}{C}} \right]$	Poly(hexamethylene sebacamide) or Nylon6,10	Poly(iminohexane-1,6-diyliminosebacoyl)

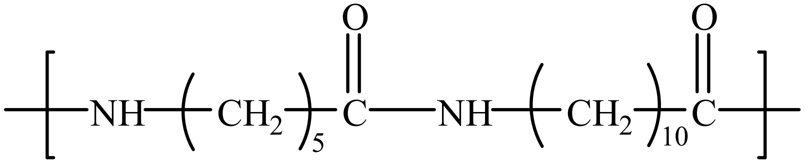
cf) Table 1.3

1.7.4 Nonvinyl copolymers

a. Poly(ethylene terephthalate-*co*-ethylene isophthalate)



b. Poly[(6-aminohexanoic acid)-*co*-(11-aminoundecanoic acid)]



$$\left[NH \left(CH_2 \right)_5 \overset{O}{\overset{\|}{C}} NH \left(CH_2 \right)_{10} \overset{O}{\overset{\|}{C}} \right]$$

1.7.5 End Group

$$\mathrm{H}\!-\!\left[\mathrm{OCH_2CH_2}\right]\!-\!\mathrm{OH}$$

α-Hydro-ω-hydroxypoly(oxyethylene)

1.7.6 Abbreviations

PVC	Poly(vinyl chloride)
HDPE	High-density polyethylene
LDPE	Low-density polyethylene
PET	Poly(ethylene terephthalate)

1.8 Industrial Polymers

a. The world consumption of synthetic polymers
: 150 million metric tons per year.

1) Plastics : 56%
2) Fibers : 18%
3) Synthetic rubber : 11%
4) Coating and Adhesives : 15%

b.Styrene-butadiene copolymer

Synthetic rubber, PET Fiber (polyester)

Latex paint Plastic (bottle)

1.8.1
Plastics

1) Commodity plastics
LDPE, HDPE, PP, PVC, PS cf) Table 1.4

2) Engineering plastics
Acetal, Polyamide, Polyamideimide, Polyarylate,
Polybenzimidazole, etc. cf) Table 1.5

3) Thermosetting plastics
Phenol-formaldehyde, Urea-formaldehyde,
Unsaturated polyester, Epoxy,
Melamine-formaldehyde
cf) Table 1.6

4) Functional plastics
Optics, Biomaterial, etc.

TABLE 1.4 Commodity Plastic

Type	*Abbreviation*	*Major Uses*
Low-density polyethylene	LDPE	Packaging film, wire and cable insulation, toys, flexible bottles 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 packag
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

TABLE 1.5 Principal Engineering Plastics

Type	***Abbreviation***	***Chapter Where Discussed***
Acetal[a]	POM	11
Polyamide[b]	—	13
Polyamideimide	PAI	13
Polyarylate	—	12
Polybenzimidazole	PBI	17
Poltcarbonate	PC	12
Polyeseter[c]	—	12
Polyetheretherketone	PEEK	11
Polyetherimide	PEI	11
Polyimide	PI	13
Poly(phenylene oxide)	PPO	11
Poly(phenylene sulfide)	PPS	11
Polysulfone[d]	—	11

TABLE 1.6 Principal Thermosetting Plastics

Type	*Abbreviation*	*Typical Uses*	*Chapter Where Discussed*
Phenol-formaldehyde	PF	Electrical and electronic equipment, automobile parts, utensil handles, plywood adhesives, particle board binder	1 4
Urea-formaldehyde	UF	Similar to PF polymer; also treatment of textiles, coatings	1 4
Unsaturated polyester	UP	Construction, automobile parts, boat hulls, marine accessories, corrosion-resistant ducting, pipe, tanks, etc., business equipment	12
Epoxy	-	Protective coatings, adhesives, electrical and electronics applications, industrial flooring highway paving materials, composites	11
Melamine-formaldehyde	MF	Similar to UF polymers; decorative panels, counter and table tops, dinnerware	14

1.8.2 Fibers

1) Cellulosic :

Acetate rayon, Viscose rayon

2) Noncellulosic :

Polyester, Nylon(Nylon6,6, Nylon6, etc)
Olefin
(PP, Copolymer(PVC 85%+PAN and others 15%; *vinyon*))

3) Acrylic :

Contain at least 80% acrylonitrile
(PAN 80% + PVC and others 20%)

1.8.3 Rubber (Elastomers)

1) Natural rubber :

cis-polyisoprene

2) Synthetic rubber :

Styrene-butadiene, Polybutadiene,
Ethylene-propylene(EPDM), Polychloroprene, Polyisoprene,
Nitrile, Butyl, Silicone, Urethane

3) Thermoplastic elastomer :

Styrene-butadiene block copolymer
(SB or SBS)

TABLE 1.7 Principal Synthetic Fibers

Type	*Description*
Cellulosic	
Acetate rayon	Cellulose acetate
Viscose rayon	Regenerated cellulose
Noncellulosic	
Polyester	Principally poly(ethylene terephthalate)
Nylon	Includes nylon 66, nylon 6, and a variety of other aliphatic and aromatic polyamides
Olefin	Includes polypropylene and copolymers of vinyl chloride, with lesser amounts of acrylonitrile, vinyl acetate, or vinylidene chloride (copolymers consisting of more than 85% vinyl chloride are called *vinyon* fibers)
Acrylic	Contain at least 80% acrylonitrile; included are *modacrylic* fibers comprising acrylonitrile and about 20% vinyl chloride or

1.8.4 Coating and Adhesives

1) **Coating** :

Lacquer, Vanishes, Paint (Oil or Latex), Latex

2) **Adhesives** :

Solvent based, Hot melt, Pressure sensitive, etc.
Acrylate, Epoxy, Urethane, Cyanoacrylate

TABLE 1.8 Principal Types of Synthetic Rubber

Type	*Description*
Styrene-butadiene	Copolymer of the two monomers in various proportions depending c properties desired; called SBR for styrene-butadiene rubber
Polybutadiene	Consists almost entirely of the *cis*-1,4 polymer
Ethylene-propylene	Often abbreviated EPDM for ethylene-propylene-diene monomer; made up principally of ethylene and propylene units with small amo of a diene to provide unsaturation
Polychloroprene	Principally the *trans*-1,4polymer, but also some *cis*-1,4 and 1,2 poly also known as *neoprene* rubber
Polyisoprene	Mainly the *cis*-1,4 polymer; sometimes called “synthetic natural rubb
Nitrile	Copolymer of acrylonitrile and butadiene, mainly the latter
Butyl	Copolyner of isobutylene and isoprene, with only small amounts of t Latter
Silicone	Contains inorganic backbone of alternating oxygen and methylated atoms; also called polysiloxane (Chap. 15)
Urethane	Elastomers prepared by linking polyethers through urethane groups (Chap. 13)

1.9 Polymer Recycling

a. Durability of polymer property

1) Advantage : Good materials for use

2) Disadvantage : Environmental problem

b. Treatment of waste polymer : Incinerate,
Landfill, Recycling

ex) Waste Tire : Paving materials
Waste PET : To make monomer (hydrolysis)
To make polyol (glycolysis)

TABLE 1.9 Plastics Recycling Code[a]

Number	*Letters*	*Plastic*
1	PETE[b]	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

[a] Adopted by the Society of the Plastics Industry (SPI).

[b] PET is the more widely accepted abbreviation.

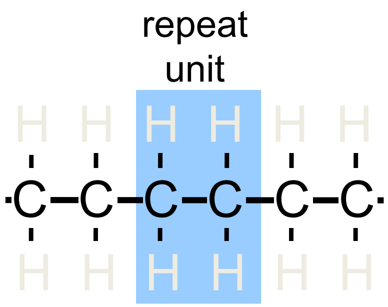
Polymers

What is a polymer?

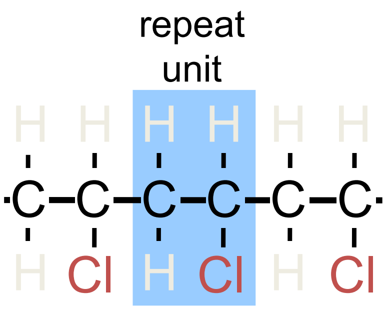
Very Large molecules structures chain-like in nature.

Poly **mer**

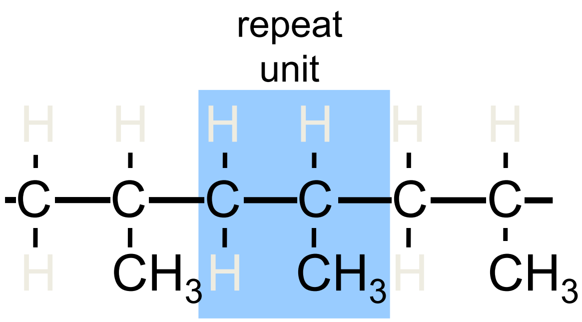
many **repeat unit**



Polyethylene (PE)



Polyvinyl chloride (PVC)



Polypropylene (PP)

Adapted from Fig. 14.2, *Callister 7e.*

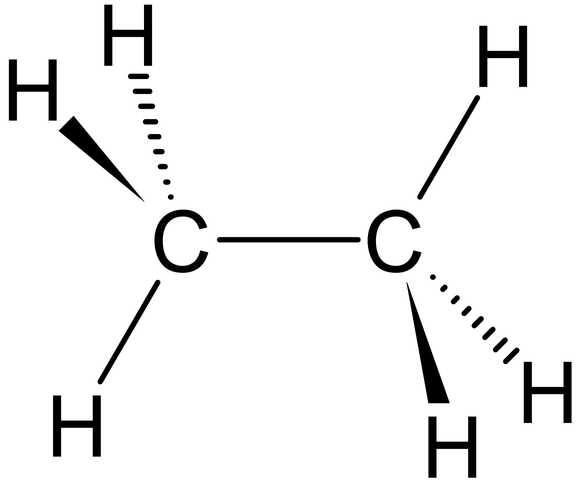
Ancient Polymer History

- **Originally natural polymers were used**
  - **Wood**
  - **Cotton**
  - **Leather**
  - **Rubber**
  - **Wool**
  - **Silk**

Polymer Composition

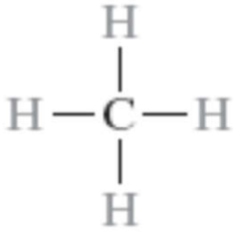
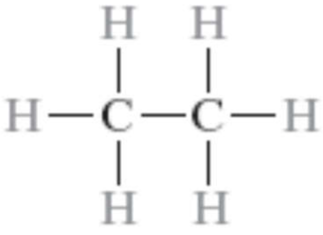
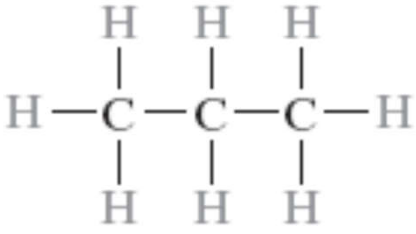
Most polymers are hydrocarbons
  – i.e. made up of H and C

- **Saturated hydrocarbons**
  - **Each carbon bonded to four other atoms**



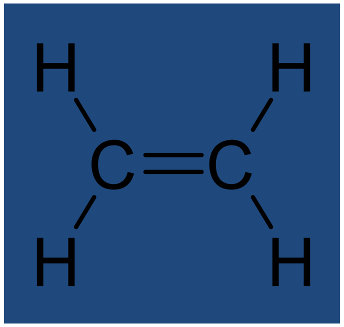
C_nH_{2n+2}

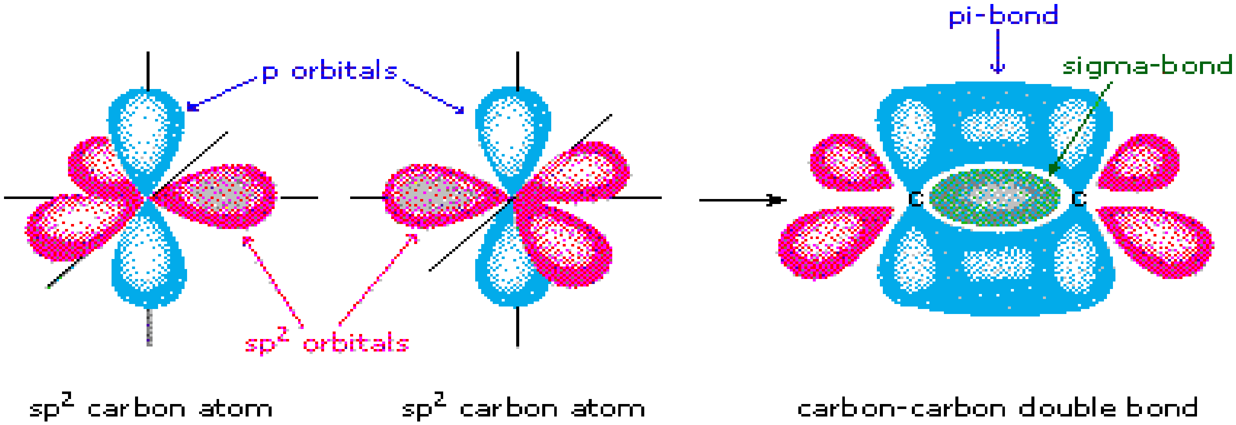
Table 14.1 Compositions and Molecular Structures for Some of the Paraffin Compounds: C_nH_{2n+2}

Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4	 $\begin{array}{ccc} & H & \\ & \vert & \\ H- & C & -H \\ & \vert & \\ & H & \end{array}$	−164
Ethane	C_2H_6	 $\begin{array}{cccc} & H & H & \\ & \vert & \vert & \\ H- & C- & C & -H \\ & \vert & \vert & \\ & H & H & \end{array}$	−88.6
Propane	C_3H_8	 $\begin{array}{ccccc} & H & H & H & \\ & \vert & \vert & \vert & \\ H- & C- & C- & C & -H \\ & \vert & \vert & \vert & \\ & H & H & H & \end{array}$	−42.1
Butane	C_4H_{10}		−0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

Unsaturated Hydrocarbons

- **Double & triple bonds relatively reactive – can form new bonds**
  - **Double bond – ethylene or ethene - C_nH_{2n}**





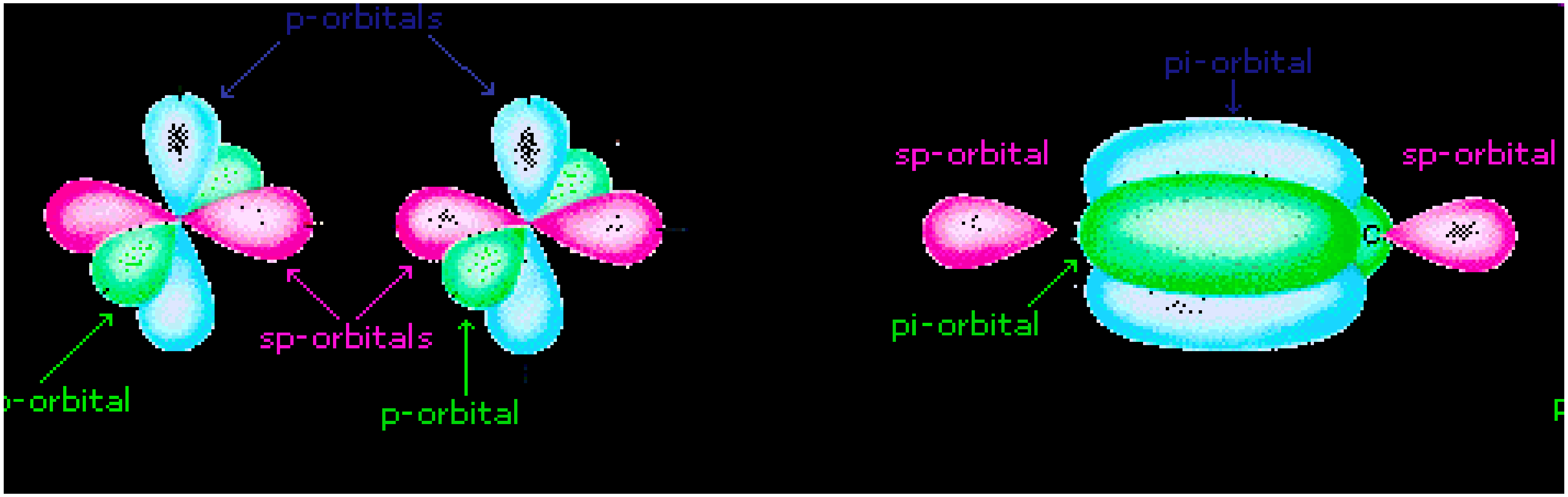
B Formation of σ- and π- molecular orbitals from two sp² hybridized carbon atoms

- **4-bonds, but only 3 atoms bound to C's**

Unsaturated Hydrocarbons

- **Triple bond – acetylene or ethyne - C_nH_{2n-2}**

$H{-}C{\equiv}C{-}H$

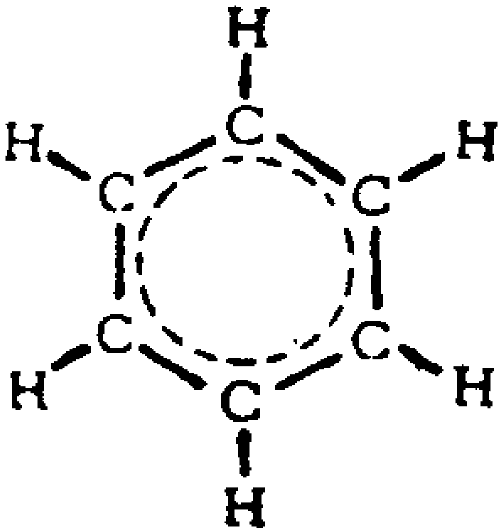


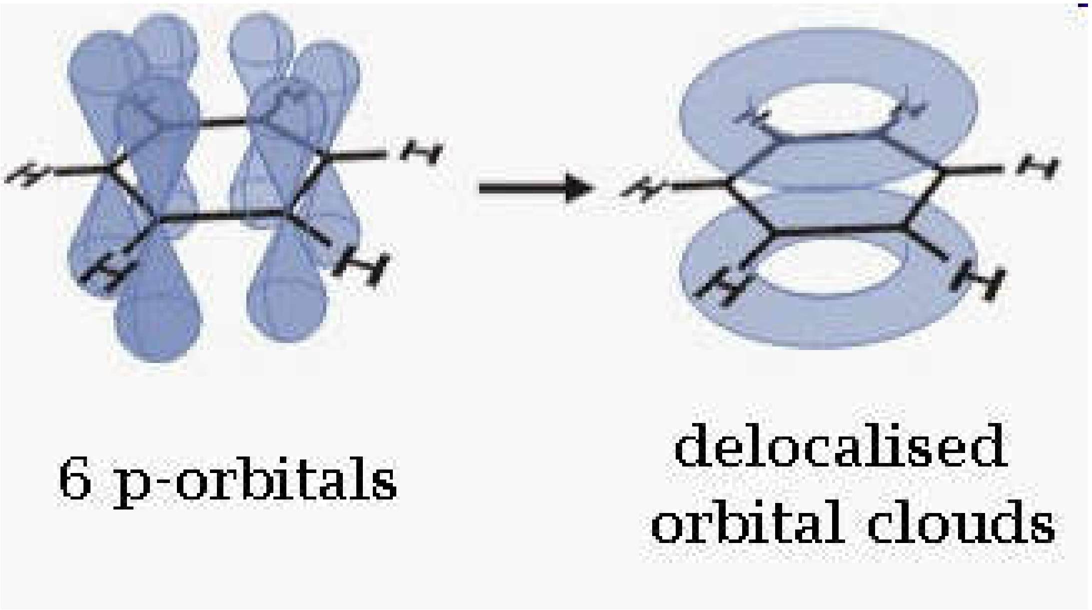
Unsaturated Hydrocarbons

- An **aromatic hydrocarbon** (abbreviated as AH) or **arene** is a hydrocarbon, of which the molecular structure incorporates one or more planar sets of six carbon atoms that are connected by delocalised electrons numbering the same as if they consisted of alternating single and double covalent bonds

Unsaturated Hydrocarbons

- Benzene, $C6H6$, is the simplest and first recognized aromatic hydrocarbon





Unsaturated Hydrocarbons

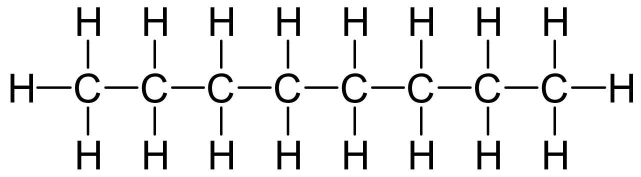
- What is actually found is that all of the bond lengths in the benzene rings are 1.397 angstroms
- This is roughly intermediate between the typical lengths of single bonds (~1.5 angstroms) and double bonds (~1.3 angstroms)

Isomerism

- **Isomerism**
  - two compounds with same chemical formula can have quite different structures/atomic arrangement

Ex: C_8H_{18}

- **n-octane**



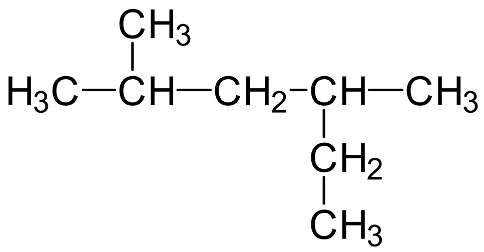
$$\begin{array}{cccccccccc} & H & H & H & H & H & H & H & H & \\ & | & | & | & | & | & | & | & | & \\ H- & C- & C- & C- & C- & C- & C- & C- & C & -H \\ & | & | & | & | & | & | & | & | & \\ & H & H & H & H & H & H & H & H & \end{array}$$

$= H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

⇓

$H_3C\left(CH_2\right)_6CH_3$

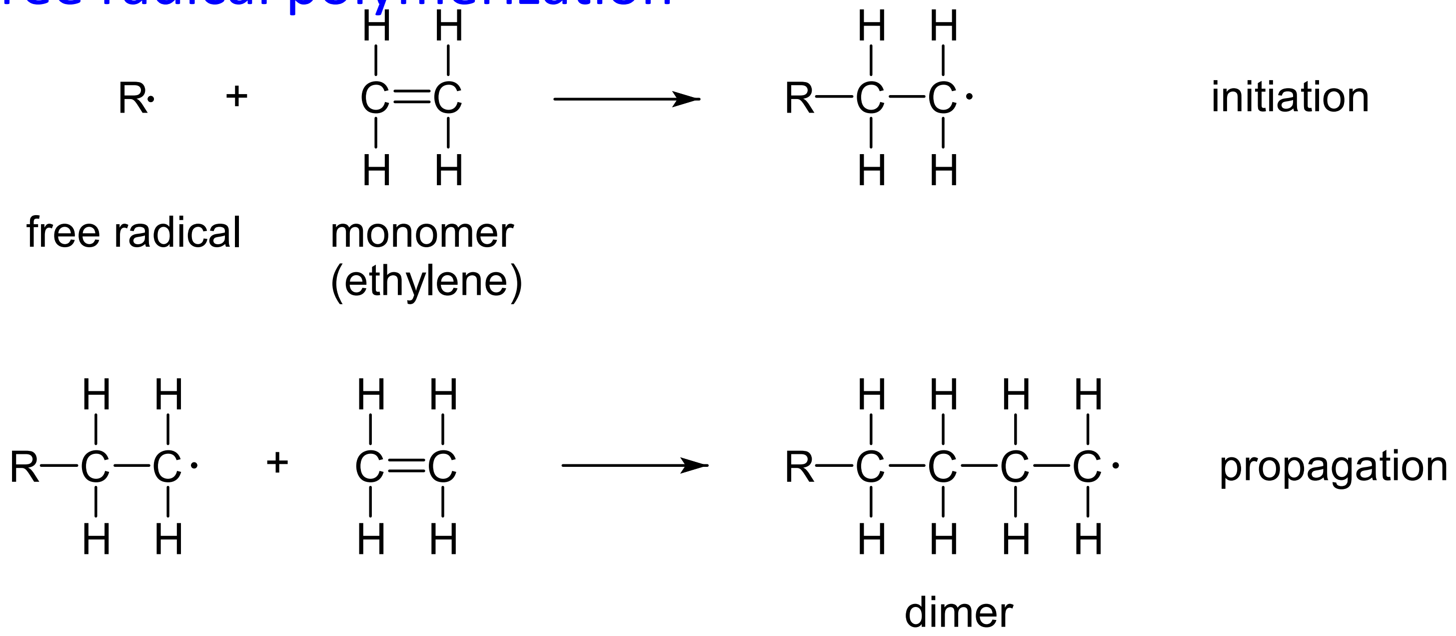
- **2-methyl-4-ethyl pentane (isooctane)**



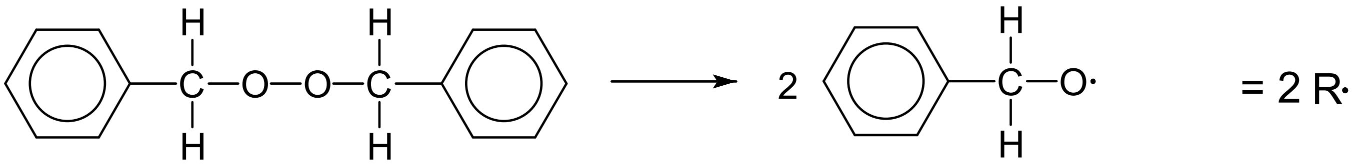
$$\begin{array}{lllll} & CH_3 & & & \\ & | & & & \\ H_3C- & CH- & CH_2- & CH- & CH_3 \\ & & & | & \\ & & & CH_2 & \\ & & & | & \\ & & & CH_3 & \end{array}$$

Chemistry of Polymers

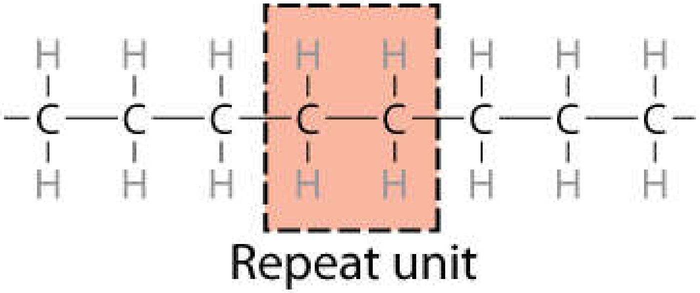
- Free radical polymerization



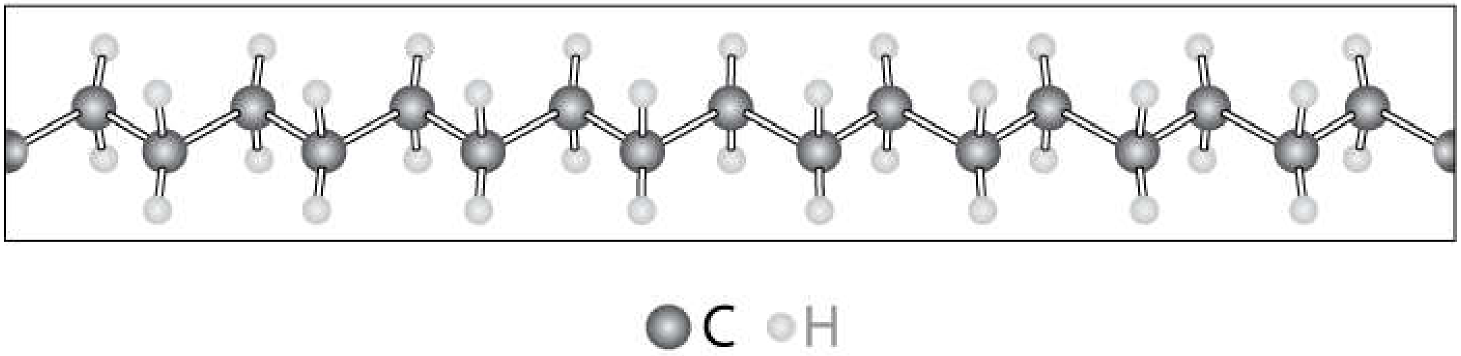
- Initiator: example - benzoyl peroxide



Chemistry of Polymers



Adapted from Fig. 14.1, *Callister 7e.*



Note: polyethylene is just a long HC

- paraffin is short polyethylene

Bulk or Commodity Polymers

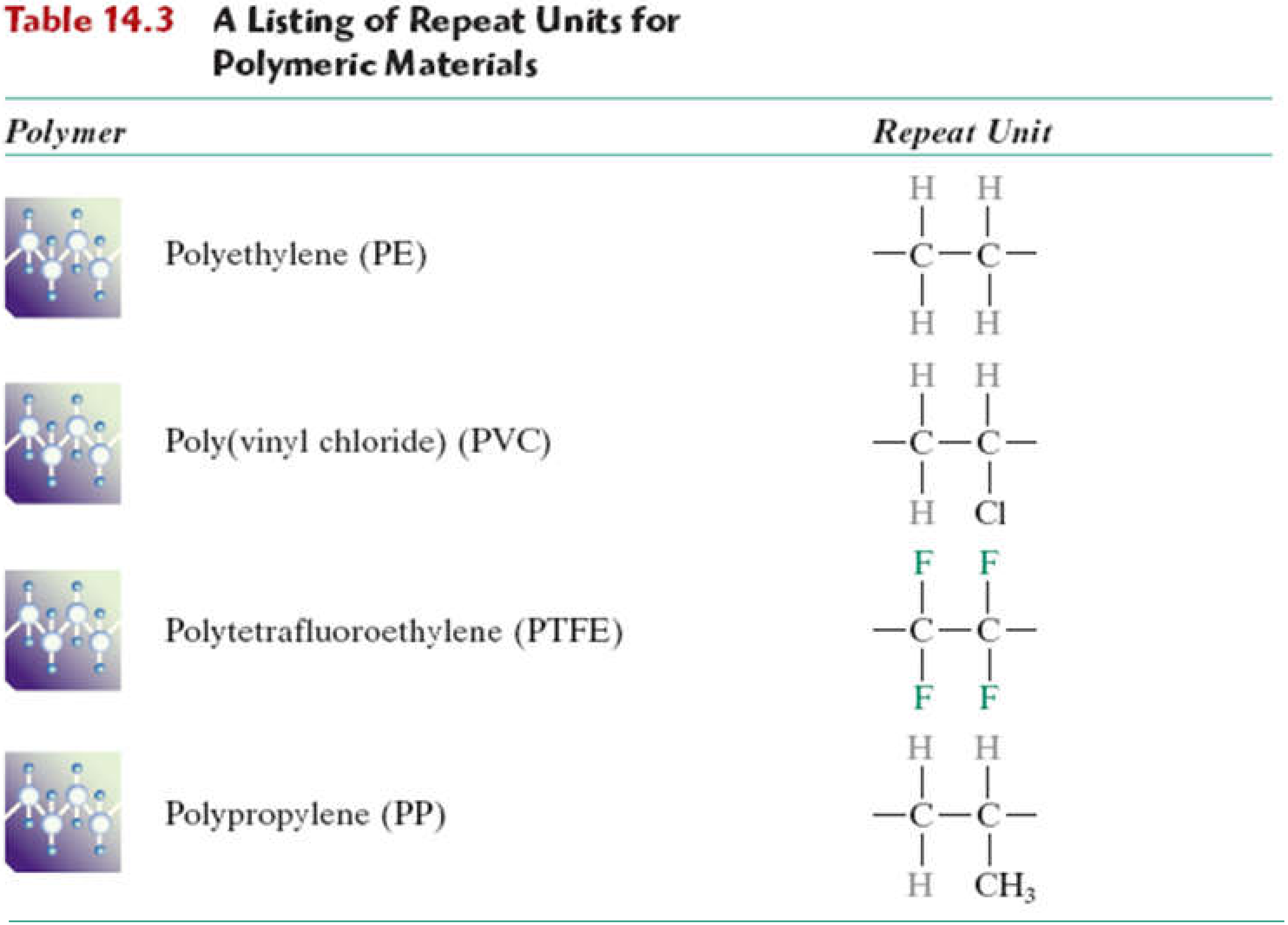
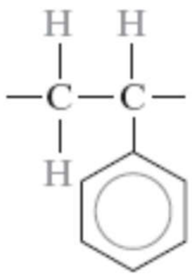
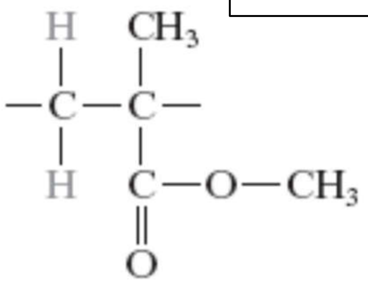
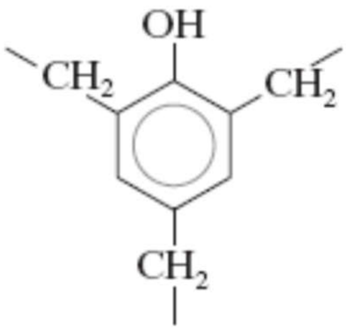
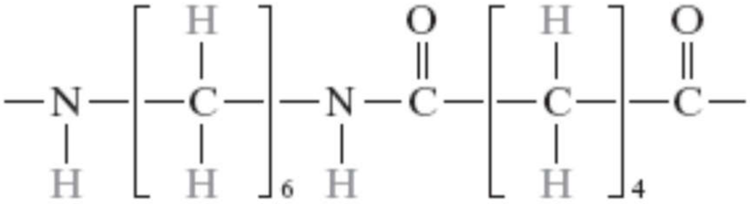
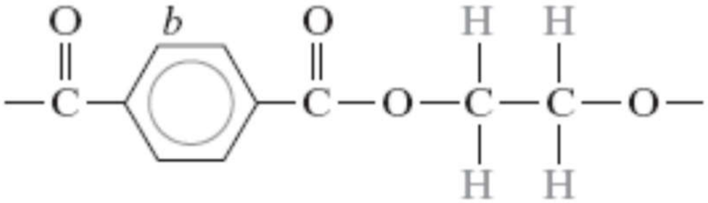
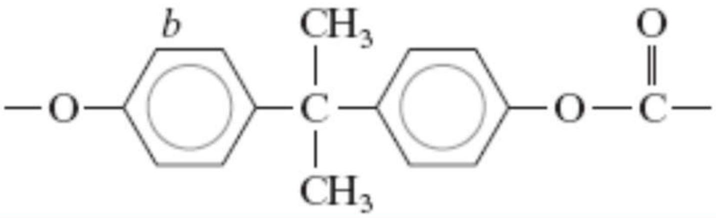


Table 14.3 **A Listing of Repeat Units for Polymeric Materials**

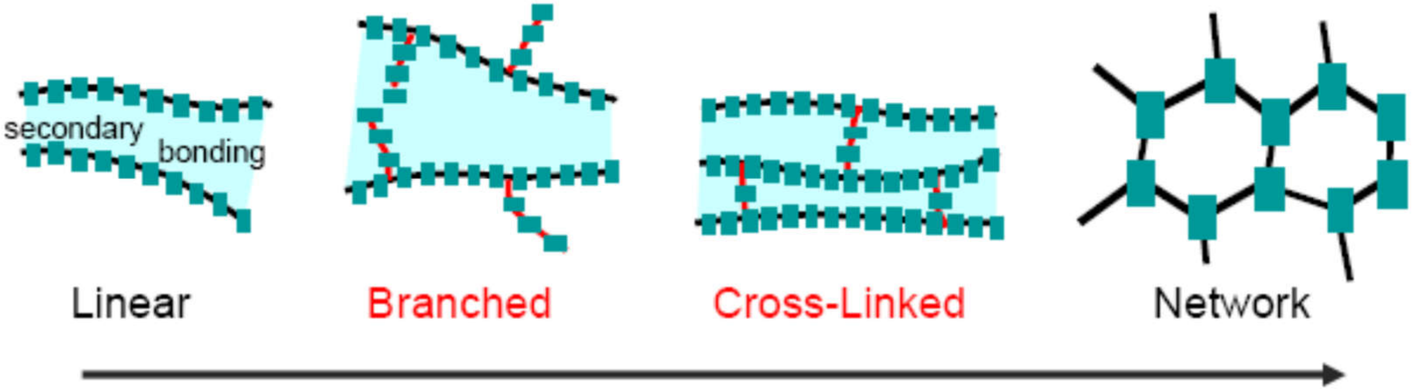
Polymer	*Repeat Unit*
Polyethylene (PE)	$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$
Poly(vinyl chloride) (PVC)	$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-$
Polytetrafluoroethylene (PTFE)	$-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-$
Polypropylene (PP)	$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{CH_3}{C}}-$

Polymer	***Repeat Unit***
Polystyrene (PS)	
Poly(methyl methacrylate) (PMMA)	 $-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{\overset{\|}{\underset{O}{\overset{\|}{C}}}-O-CH_3}{C}}-$
Phenol-formaldehyde (Bakelite)	

Polymer	*Repeat Unit*
Poly(hexamethylene adipamide) (nylon 6,6)	 $-\underset{\mathrm{H}}{\underset{\vert}{\mathrm{N}}}-\left[-\underset{\mathrm{H}}{\underset{\vert}{\overset{\mathrm{H}}{\overset{\vert}{\mathrm{C}}}}}-\right]_6-\underset{\mathrm{H}}{\underset{\vert}{\mathrm{N}}}-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}-\left[-\underset{\mathrm{H}}{\underset{\vert}{\overset{\mathrm{H}}{\overset{\vert}{\mathrm{C}}}}}-\right]_4-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}-$
Poly(ethylene terephthalate) (PET, a polyester)	
Polycarbonate (PC)	

Molecular Structures

- Covalent chain configurations and strength:



Direction of increasing strength

Adapted from Fig. 14.7, *Callister 7e.*

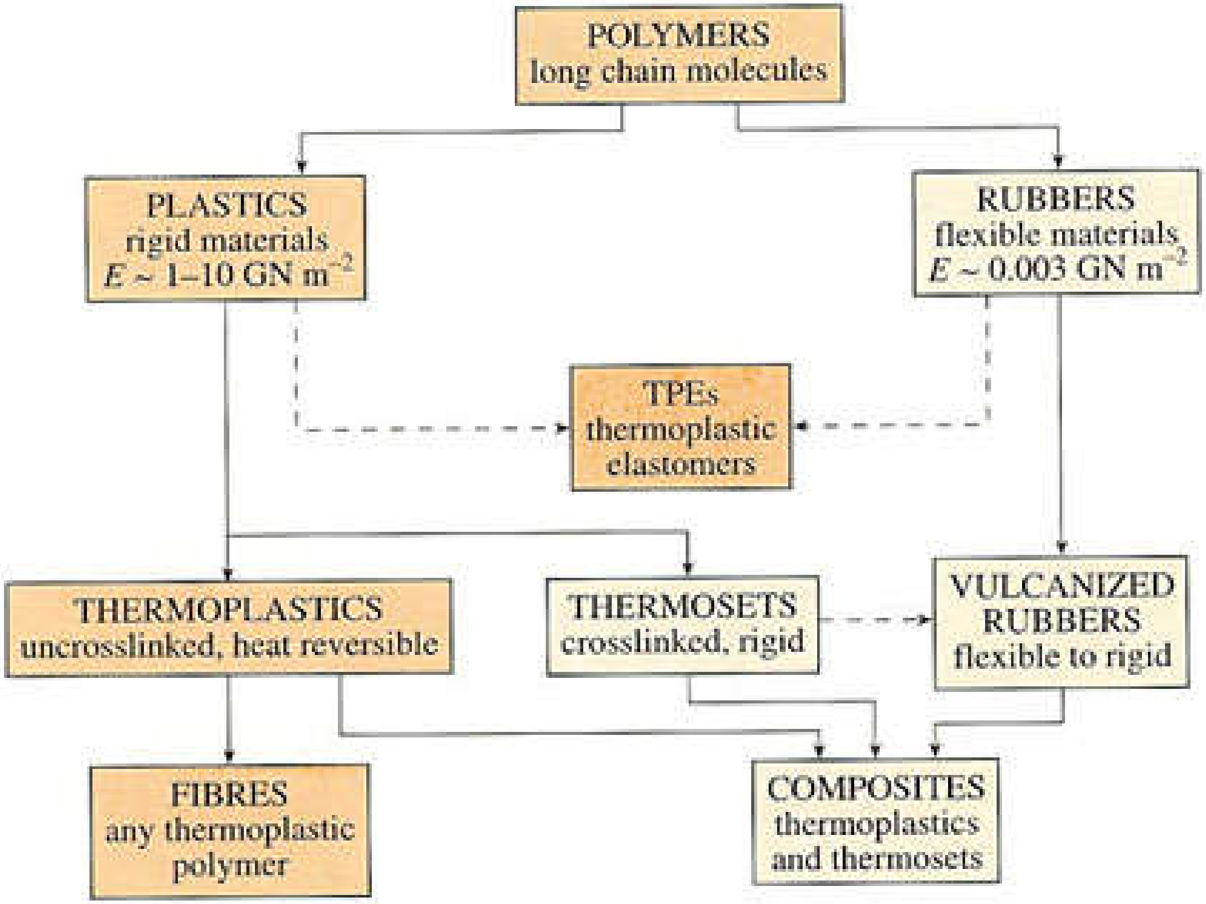
Range of Polymers

- Traditionally, the industry has produced two main types of synthetic polymer – plastics and rubbers.
- Plastics are (generally) rigid materials at service temperatures
- Rubbers are flexible, low modulus materials which exhibit long-range elasticity.

Range of Polymers

- Plastics are further subdivided into thermoplastics and thermosets

Range of Polymers



POLYMERS
long chain molecules

PLASTICS
rigid materials
$E \sim 1\text{–}10$ GN m^{-2}

RUBBERS
flexible materials
$E \sim 0.003$ GN m^{-2}

TPEs
thermoplastic
elastomers

THERMOPLASTICS
uncrosslinked, heat reversible

THERMOSETS
crosslinked, rigid

VULCANIZED RUBBERS
flexible to rigid

FIBRES
any thermoplastic
polymer

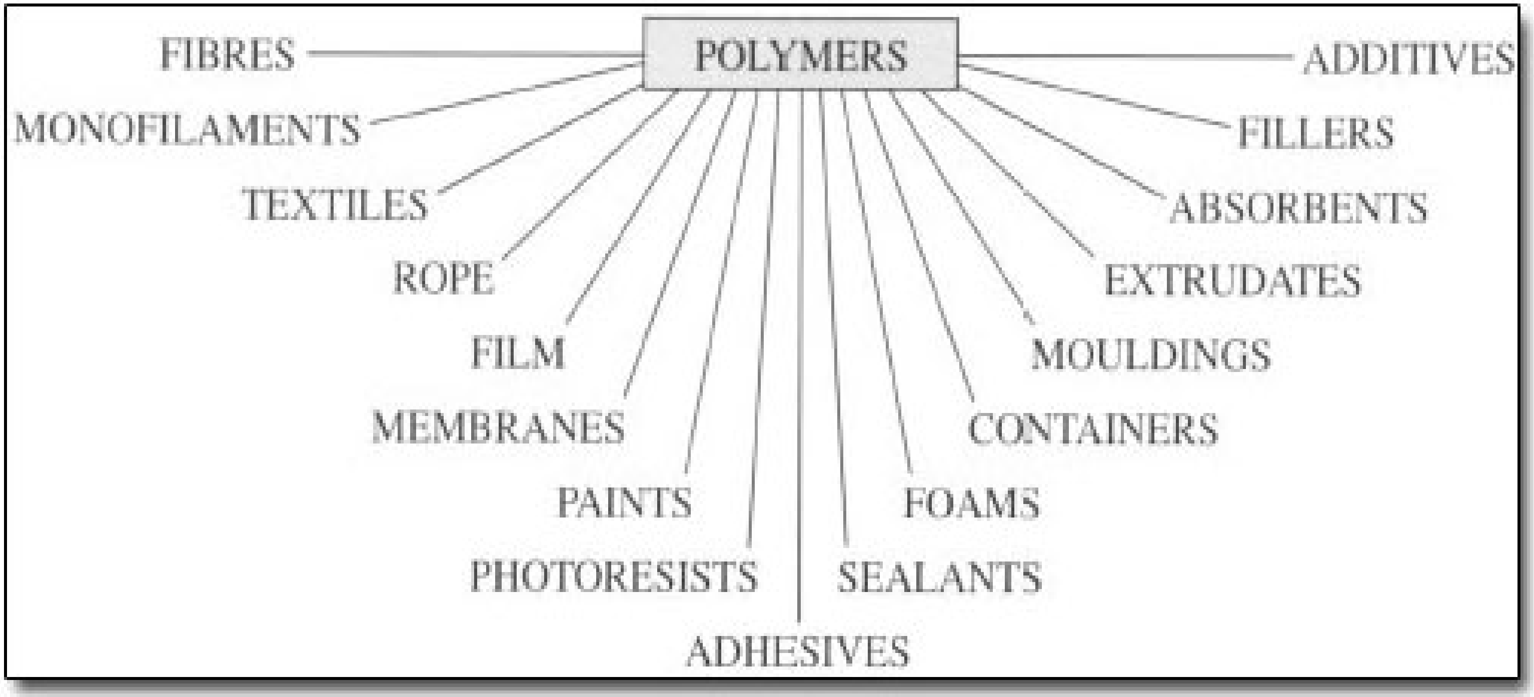
COMPOSITES
thermoplastics
and thermosets

Thermoplastics & Thermosetting polymers

- Thermoplastics polymers: soften when heated and harden when cooled and vice versa
- Structure Example: linear, branched:
- Polyethylene, polystyrene, PVC, Poly (ethylene terephthalate)
- Thermosetting polymers: permanently hard (do not soften when heated)
- Made from network polymers: covalent bond resist motion at high temperature prevent.
- Epoxies, phenolics, and some polyester resins.

Range of Polymers

- Another way of classifying polymers is in terms of their form or function



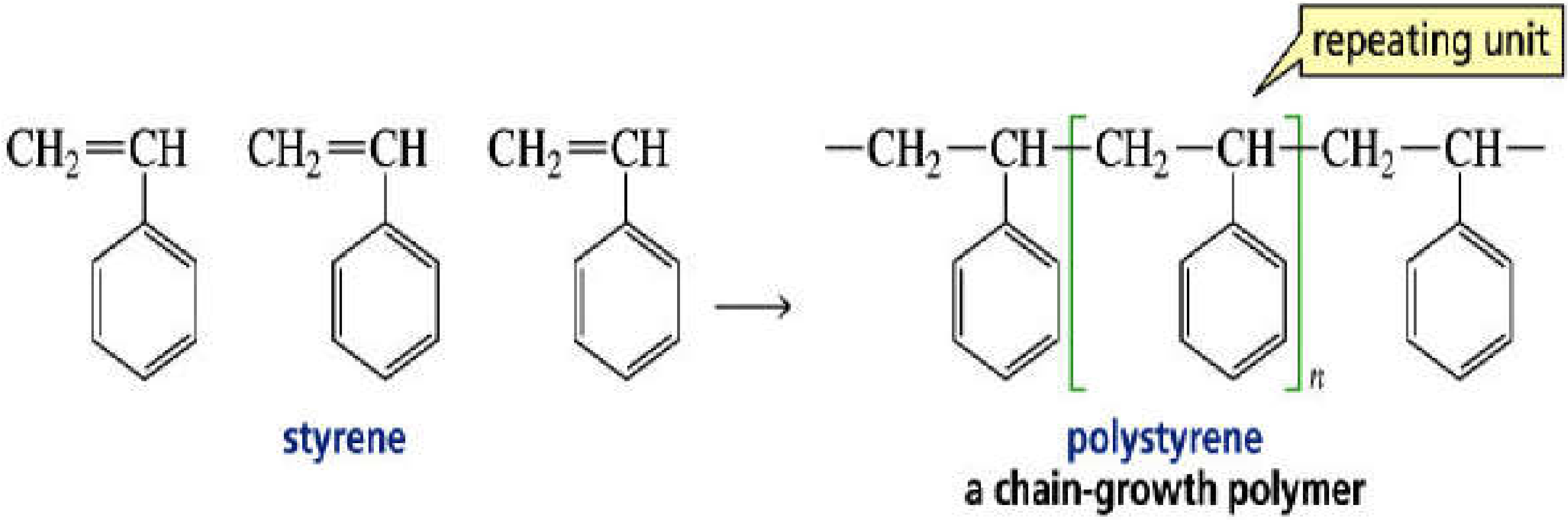
Synthesis of Polymers

Synthesis of Polymers

- There are a number different methods of preparing polymers from suitable monomers, these are
  - step-growth (or condensation) polymerisation
  - addition polymerisation
  - insertion polymerisation.

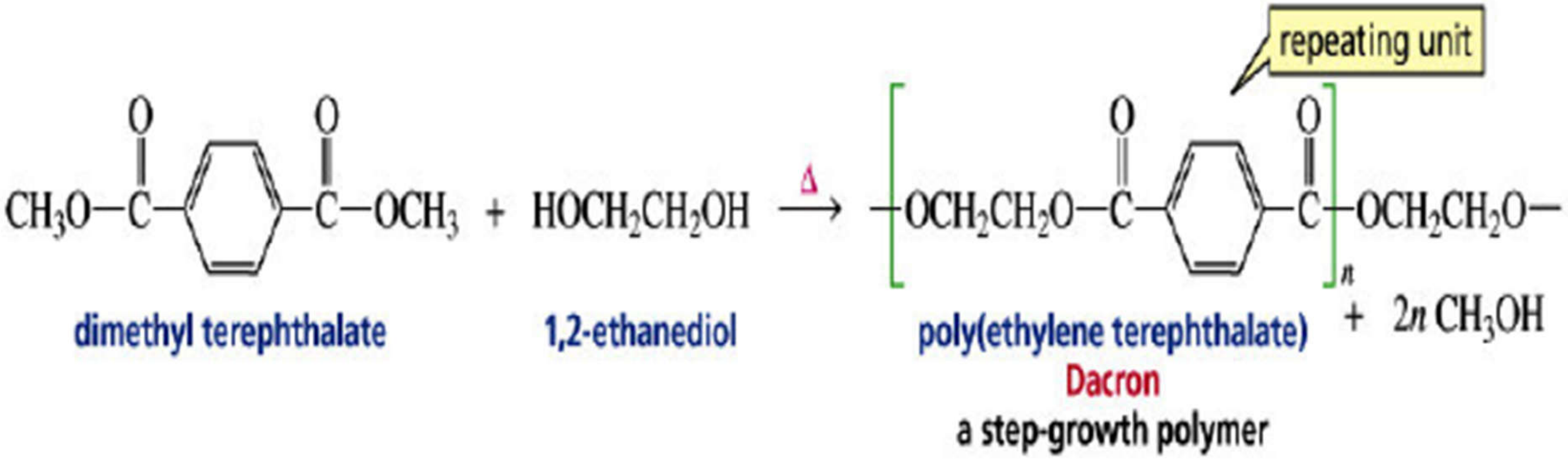
Types of Polymerization

- Chain-growth polymers, also known as addition polymers, are made by chain reactions



Types of Polymerization

- Step-growth polymers, also called condensation polymers, are made by combining two molecules by removing a small molecule



Addition Vs. Condensation Polymerization

- Polymerisation reactions can generally be written as

  $$\text{x-mer} + \text{y-mer} \longrightarrow \text{(x +y)-mer}$$

- In a reaction that leads to **condensation polymers**, x and y may assume any value
- i.e. chains of any size may react together as long as they are capped with the correct functional group

Addition Vs. Condensation Polymerization

- In **addition polymerization** although x may assume any value, y is confined to unity
- i.e. the growing chain can react only with a monomer molecule and continue its growth

Thermodynamics

- Thermodynamics of polymerization determines the position of the equilibrium between polymer and monomer(s).
- The well known thermodynamic expression:

$$\Delta G = \Delta H - T\Delta S$$

yields the basis for understanding polymerization/depolymerization behavior.

Thermodynamics

- For polymerization to occur (i.e., to be thermodynamically feasible), the Gibbs free energy of polymerization $\mathbf{\Delta G_p < 0}$.
- If $\mathbf{\Delta G_p > 0}$, then depolymerization will be favored.

Thermodynamics

- Standard enthalpy and entropy changes, $\Delta H^o p$ and $\Delta S^o p$ are reported for reactants and products in their appropriate standard states. Generally:
  - Temperature = 25^oC = 298K
  - Monomer – pure, bulk monomer or 1 M solution
  - Polymer – solid amorphous or slightly crystalline

Thermodynamics

- Polymerization is an association reaction such that many monomers associate to form the polymer
- Thus: $\Delta Sp < 0$ for nearly all polymerization processes

Thermodynamics

- Since depolymerization is almost always <u>entropically</u> favored, the $\Delta \mathbf{H_p}$ must then be sufficiently <u>negative</u> to compensate for the unfavorable entropic term.

- Only then will polymerization be thermodynamically favored by the resulting negative ΔGp.

Thermodynamics

In practice:

- Polymerization is favored at low temperatures: TΔSp is small

- Depolymerization is favored at high temperatures: TΔSp is large

Thermodynamics

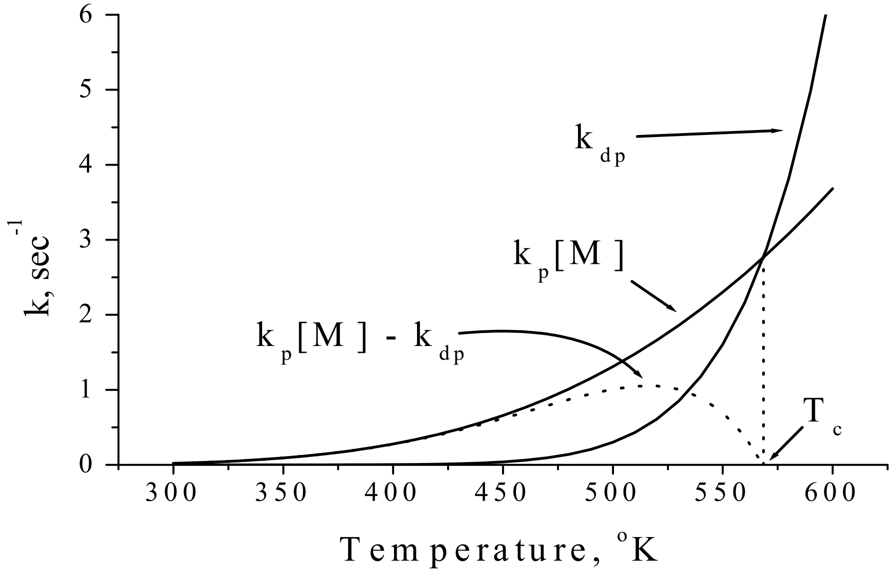
- Therefore, thermal instability of polymers results when $\mathbf{T\Delta S_p}$ overrides $\mathbf{\Delta H_p}$ and thus $\mathbf{\Delta G_p > O}$; this causes the system to spontaneously depolymerize (<u>if kinetic pathway exists</u>).

Thermodynamics

- the activation energy for the depropagation reaction is higher,
- Compared to the propagation reaction its rate increases more with increasing temperature
- As shown below, this results in a ceiling temperature.

Thermodynamics

- ceiling temperature
  - the temperature at which the propagation and depropagation reaction rates are exactly equal at a given monomer concentration



Thermodynamics

- At long chain lengths, the chain propagation reaction

$$-P_n^* + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} -P_{n+1}^*$$

- is characterized by the following equilibrium expression:

$$\frac{k_p}{k_{dp}} = \frac{[-P_{n+1}^*]}{[-P_n^*][M]} \cong \frac{1}{[M]_c}$$

Thermodynamics

- The standard-state enthalpy and entropy of polymerization are related to the standard-state monomer concentration, $[M]_o$ (usually neat liquid or 1 M solution) as follows:

$$\Delta G = \Delta H^o - T\Delta S^o + RT \ln \frac{[M]_o}{[M]}$$

Thermodynamics

- At equilibrium, $\Delta G = 0$, and $T = T_c$ (assuming that ΔH_p^o and ΔS_p^o are independent of temperature).

$$\Delta H^o - T_c \Delta S^o = -RT_c \ln \frac{[M]_o}{[M]_c}$$

- Or:

$$T_c = \frac{\Delta H^o}{\Delta S^o + R \ln \frac{[M]_c}{[M]_o}}$$

Thermodynamics

- Or:

$$\ln\frac{[\mathrm{M}]_c}{[\mathrm{M}]_o}=\frac{\Delta H^o}{RT_c}-\frac{\Delta S^o}{R}$$

Thermodynamics

- At $[M]_c = [M]_o$, $T_c = \Delta H_p^o / \Delta S_p^o$

Specific Examples of Monomer - Polymer Equilibrium

	kcal/mol	**cal/mol-deg**	**(ΔH/ΔS)**
Monomer	ΔH_p	ΔS_p	$T_c(^oC)$
Ethylene	-21.2	-24	610
Isobutylene	-12.9	-28	175
Styrene	-16.7	-25.0	395
α-methyl styrene	-8.4	-24	66
2,4,6-trimethyl styrene	-16.7	---	---
TFE	-37	-26.8	1100

Thermodynamics

- Notice the large variation in the -ΔH values.
  - ethylene > isobutylene - attributed to steric hinderance along the polymer chain, which decreases the exothermicity of the polymerization reaction.
  - ethylene > styrene > α-metylstyrene - also due to increasing steric hinderance along the polymer chain.
  - Note, however, that 2,4,6-trimethylstyrene has the same -ΔH value as styrene. Clearly, the major effect occurs for substituents directly attached to the polymer backbone.

Types of Addition Polymerization

- Free Radical
- Cationic
- Anionic

Free Radical Polymerization

- Usually, many low molecular weight alkenes undergo rapid polymerization reactions when treated with small amounts of a radical initiator.
- For example, the polymerization of ethylene

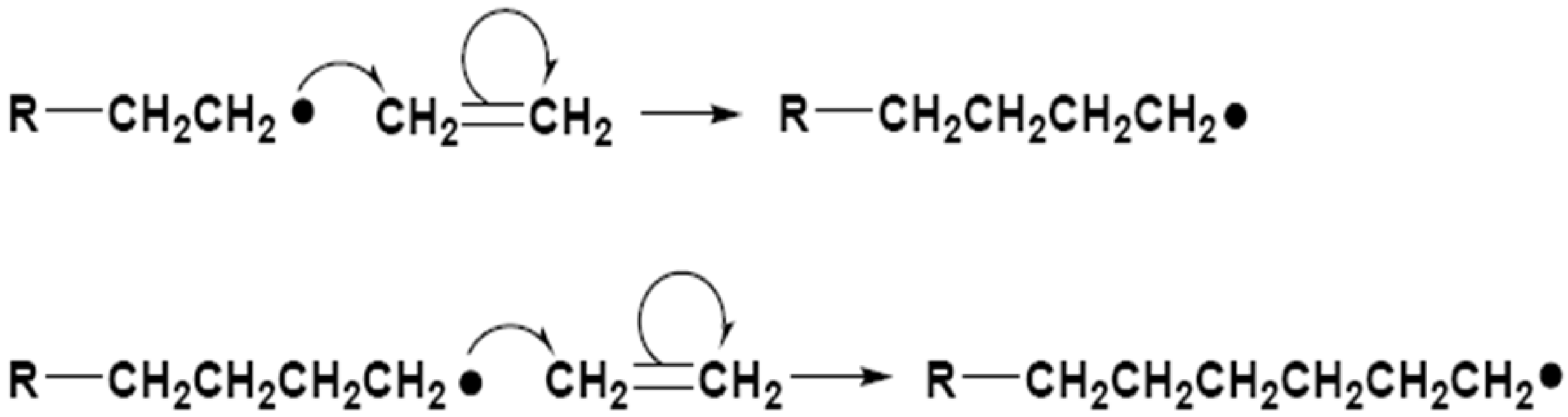
Free Radical Polymerization

step 1: Initiation

$$R\text{-}R \longrightarrow 2R\bullet$$

Free Radical Polymerization

step 2: Propagation



$R{-}CH_2CH_2\bullet \quad CH_2{=}CH_2 \longrightarrow R{-}CH_2CH_2CH_2CH_2\bullet$

$R{-}CH_2CH_2CH_2CH_2\bullet \quad CH_2{=}CH_2 \longrightarrow R{-}CH_2CH_2CH_2CH_2CH_2CH_2\bullet$

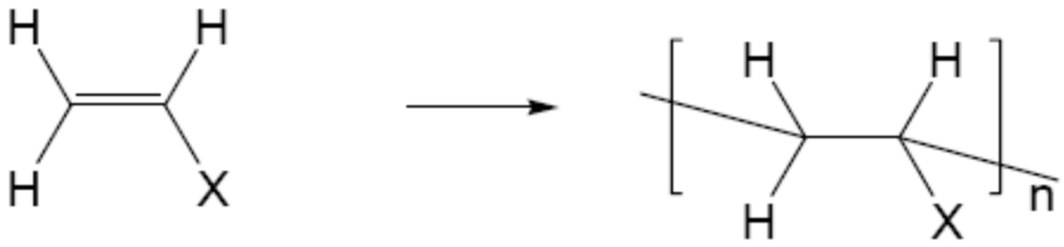
Free Radical Polymerization

step 3: Termination

$$2\ R{-}(CH_2CH_2)_nCH_2CH_2\bullet \longrightarrow R{-}(CH_2CH_2)_nCH_2CH_2{-}CH_2CH_2(CH_2CH_2)_nR$$

$$2\ R{-}(CH_2CH_2)_nCH_2CH_2^{\bullet} \longrightarrow R{-}(CH_2CH_2)_nCH{=}CH_2 + R{-}(CH_2CH_2)_nCH_2CH_3$$

Thermodynamic considerations for the free radical polymerization



X = Cl, CN etc

Gibbs free energy change: $\Delta G = \Delta H - T\Delta S$

$\Delta S < 0$ (polymer is a state of higher order)

$\Delta H < 0$ (σ-bond is stronger than π-bond)

Chemically stable polymers: $\Delta G < 0$

“Ceiling“ temperature: $\Delta H = T\Delta S$

$T > T_{ceiling}$ depolymerization is thermodynamically favourable

Thermodynamic considerations for the free radical polymerization

Chain growth

- Activation energy for chain growth much lower than for initiation.
- i.e. Growth velocity less temperature dependent than initiation

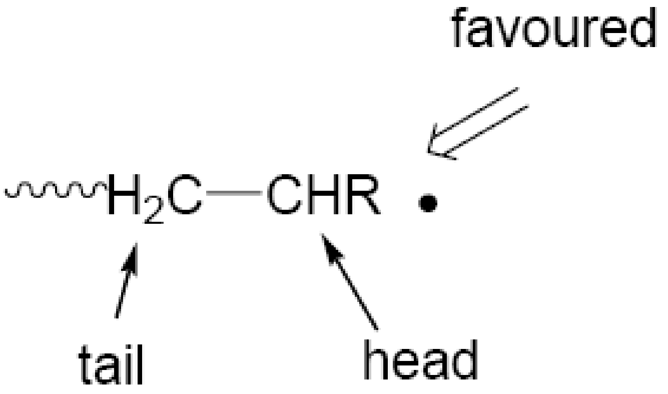
Thermodynamic considerations for the free radical polymerization

Vinyl polymers $\sim\sim HC{=}CH_2$ vinyl rest

$\sim\sim HC{=}CHR$ R eg Cl, CN, phenyl

Alternatives

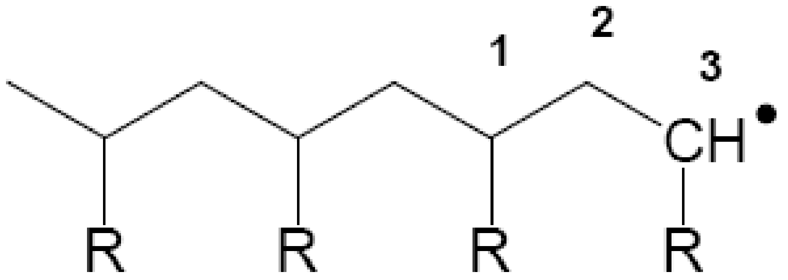
$\sim\sim RHC{-}CH_2\bullet$



Thermodynamic considerations for the free radical polymerization

Resonance effect: R more electronegative than H

⟹ Substituents are incorporated in 1,3 position (head-to-tail linkage):



Macromonomer/Comonomer Copolymerization
Kinetics : free radical

$$\frac{\mathrm{d}[A]}{\mathrm{d}[M]} = \frac{[A](r_a[A]+[M]}{[M]\mathrm{r}_{\mathrm{M}}([M]+[A]}$$

$$\frac{\mathrm{d}[A]}{\mathrm{d}[M]} = \frac{r_a[A]}{[M]}$$

⟶

Ionic Polymerization

- Ionic polymerization is more complex than free-radical polymerization

Ionic Polymerization

- Whereas free radical polymerization is non-specific, the type of ionic polymerization procedure and catalysts depend on the nature of the substituent (R) on the vinyl (ethenyl) monomer.

Ionic Polymerization

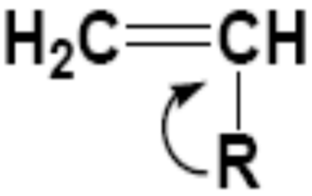
- Cationic initiation is therefore usually limited to the polymerization of monomers where the R group is electron-donating
- This helps stabilise the delocation of the positive charge through the p orbitals of the double bond

Ionic Polymerization

- Anionic initiation, requires the R group to be electron withdrawing in order to promote the formation of a stable carbanion (ie, -M and -I effects help stabilise the negative charge).

Ionic Polymerization

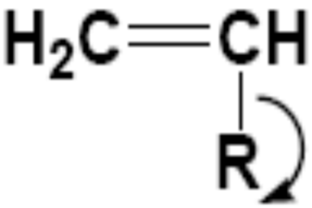
Cationic



$H_2C{=}CH{-}R$

R - Electron donating

Anionic



$H_2C{=}CH{-}R$

R - Electron withdrawing

Ionic Polymerization

(i) Initiation can occur in one of the four following ways:

(a) $M + I^{\oplus} \xrightarrow[\text{Cationic}]{} MI^{\oplus}$

(b) $M + I^{\ominus} \xrightarrow[\text{Anionic}]{} MI^{\ominus}$

(c) $M + e^{\ominus} \xrightarrow[\text{Anionic}]{} M^{\ominus}$

(c) $M - e^{\ominus} \xrightarrow[\text{Cationic}]{} M^{\oplus}$

Ionic Polymerization

- M is a Monomer Unit.
- As these ions are associated with a counter-ion or gegen-ion the solvent has important effects on the polymerization procedure.

Ionic Polymerization

(ii) Chain Propagation depends on :

- Ion separation
- The nature of the Solvent
- Nature of the counter Ion

Anionic Polymerization

- Involves the polymerization of monomers that have strong electron-withdrawing groups, eg, acrylonitrile, vinyl chloride, methyl methacrylate, styrene etc. The reactions can be initiated by methods (b) and (c) as shown in the sheet on ionic polymerization

Anionic Polymerization

- eg, for mechanism (b)

$$CX \longrightarrow C^{\oplus} + X^{\ominus}$$

$$X^{\ominus} + M \longrightarrow MX^{\ominus}$$

Anionic Polymerization

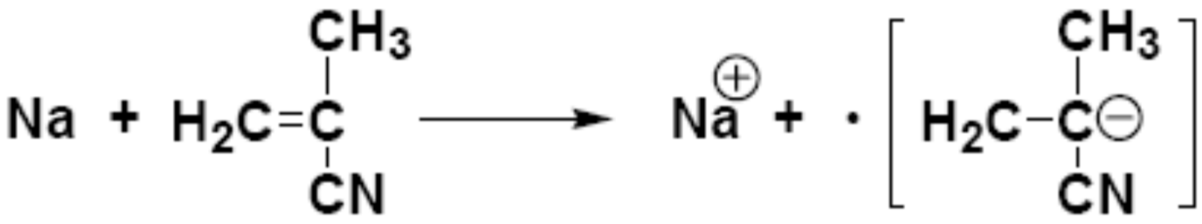
- The gegen-ion may be inorganic or organic and typical initiators include KNH2, n-BuLi, and Grignard reagents such as alkyl magnesium bromides

Anionic Polymerization

- If the monomer has only a weak electron-withdrawing group then a strong base initiator is required, eg, butyllithium; for strong electron-withdrawing groups only a weak base initiator is required, eg, a Grignard reagent.

Anionic Polymerization

- Initiation mechanism (c) requires the direct transfer of an electron from the donor to the monomer in order to form a radical anion.
- This can be achieved by using an alkali metal eg.,

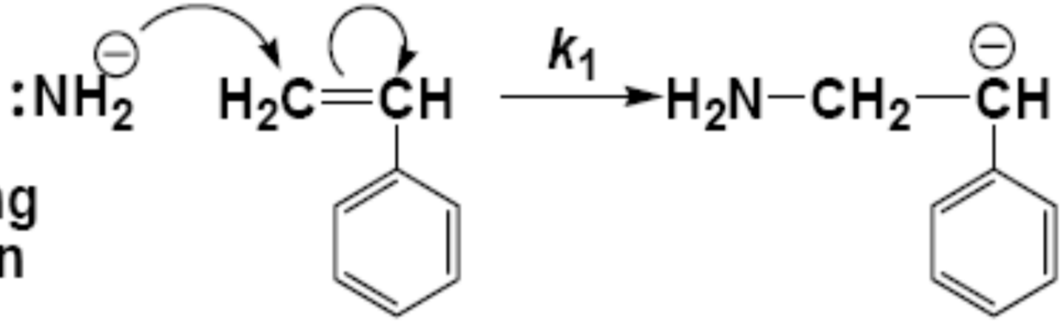


$$\mathrm{Na} + \mathrm{H_2C{=}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CN}}{\mathrm{C}}} \longrightarrow \mathrm{Na}^{\oplus} + \cdot\left[\mathrm{H_2C{-}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CN}}{\mathrm{C}}}{}^{\ominus}\right]$$

Anionic Polymerization of Styrene

(i) Initiation

$$KNH_2 \rightleftharpoons \overset{\oplus}{K} + :\overset{\ominus}{N}H_2$$

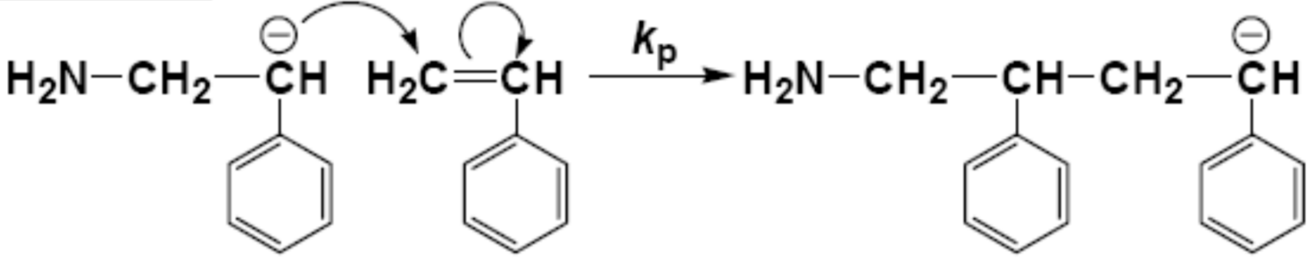


Rate determining step in initiation

Rate $v_1 = k_1[NH_2^{\ominus}][M]$

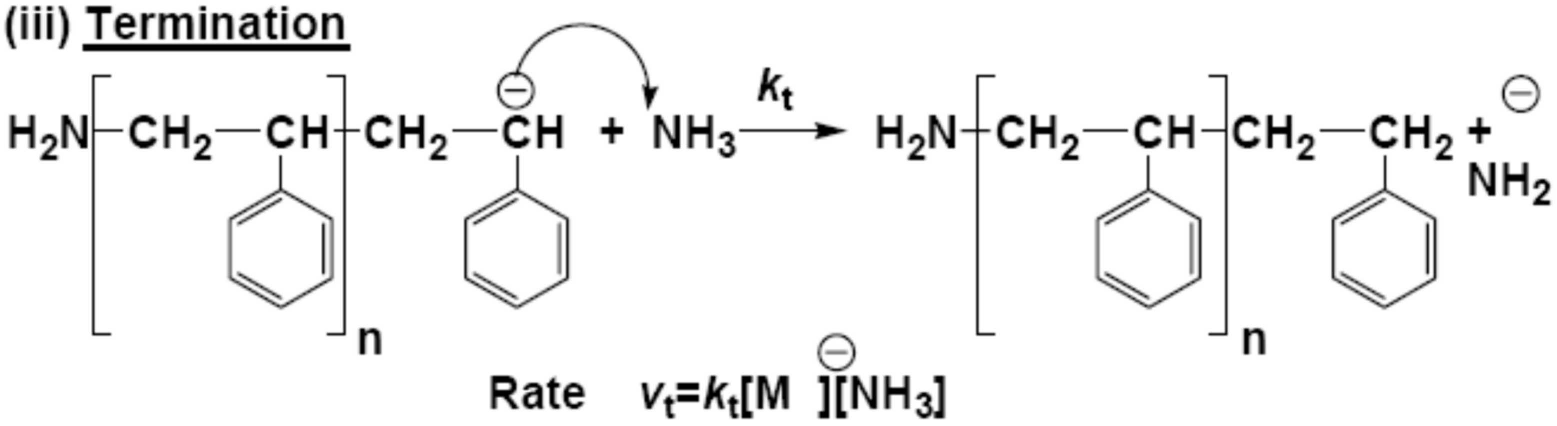
Anionic Polymerization of Styrene

(ii) Propagation



Rate $v_p = k_p[M^{\ominus}][M]$

Anionic Polymerization of Styrene



Anionic Polymerization of Styrene

Assuming steady state conditions, the concentration of propagating species is:

$$[M^{\ominus}] = \frac{k_1[NH_2^{\ominus}][M]}{k_t[NH_3]} \qquad \text{which gives} \qquad v_p = \frac{k_p k_1[NH_2^{\ominus}][M]^2}{k_t[NH_3]}$$

and the length of the polymer chains depends on the number of initiations

Anionic Polymerization of Styrene

Thus $$\langle x_n \rangle = \frac{k_p[M]}{k_t[NH_3]}$$

The activation energy for transfer is larger than for propagation, and so the chain length decreases with increasing temperature.

Anionic Kinetics

- A general description of the kinetics is complicated however some useful approximations may be attained.

Anionic Kinetics — approximations

1. The rate of polymerization will be proportional to the product of the monomer concentration of growing chain ends.
2. Under conditions of negligible association each initiator molecule will start a growing chain
3. In the absence of terminating impurities the number of growing chain ends will always equal the number of initiator molecules added

Anionic Kinetics

1. If propagation is rate controling

- $r_p = \frac{-d[M]}{dt} = k_p[M][I_0]$ (11-1)

Anionic Kinetics

2. In BuLi polymerization at high concentrations in non polar solvents, the chain ends are present almost exclusively as inactive dimmers, which dissociate slightly according to the equilibrium

$$\left(BuM_x^-Li^+\right)_2 \xleftrightarrow{k} 2BuM_x^-Li^+$$

Anionic Kinetics

- Where K= $\left[BuM_x^- Li^+\right]^2 / \left[\left(BuM_x^- Li^+\right)_2\right] \langle\langle 1$

3. The concentration of active chain ends is then

$$\left[BuM_x^- Li^+\right] = K^{1/2}\left[\left(BuM_x^- Li^+\right)_2\right]^{1/2} \quad (11\text{-}3)$$

- Now it takes two initiator molecules to make one inactive chain dimmer, so

$$\left[\left(BuM_x^- Li^+\right)_2\right] = \frac{[BuLi]}{2} = \frac{[I_0]}{2} \quad (11\text{-}4)$$

Anionic Kinetics

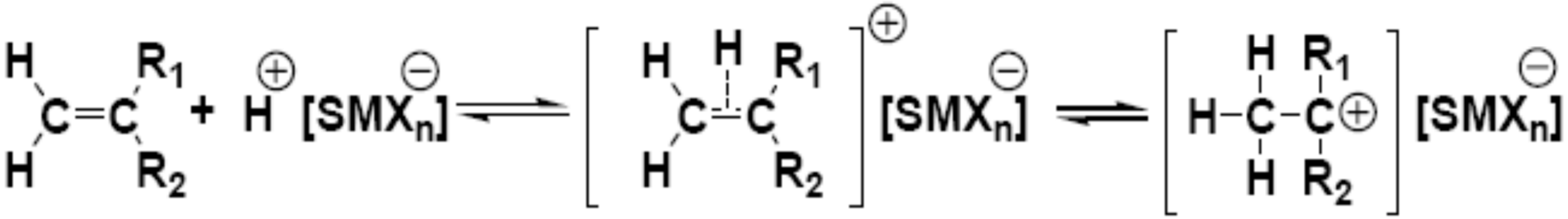
- The rate of polymerisation then becomes

$$r_p = \frac{-d[M]}{dt} = k_p K^{1/2}\left(\frac{[I_0]}{2}\right)^{1/2} \qquad (11\text{-}5)$$

- The low value of K, reflecting the presence of most chain ends in the inactive association state, gives rise to the low rates of polymerisation in nonpolar solvents. At very high concentrations, association may be even greater and the rate essentially independent of $[I_0]$

Cationic Polymerization

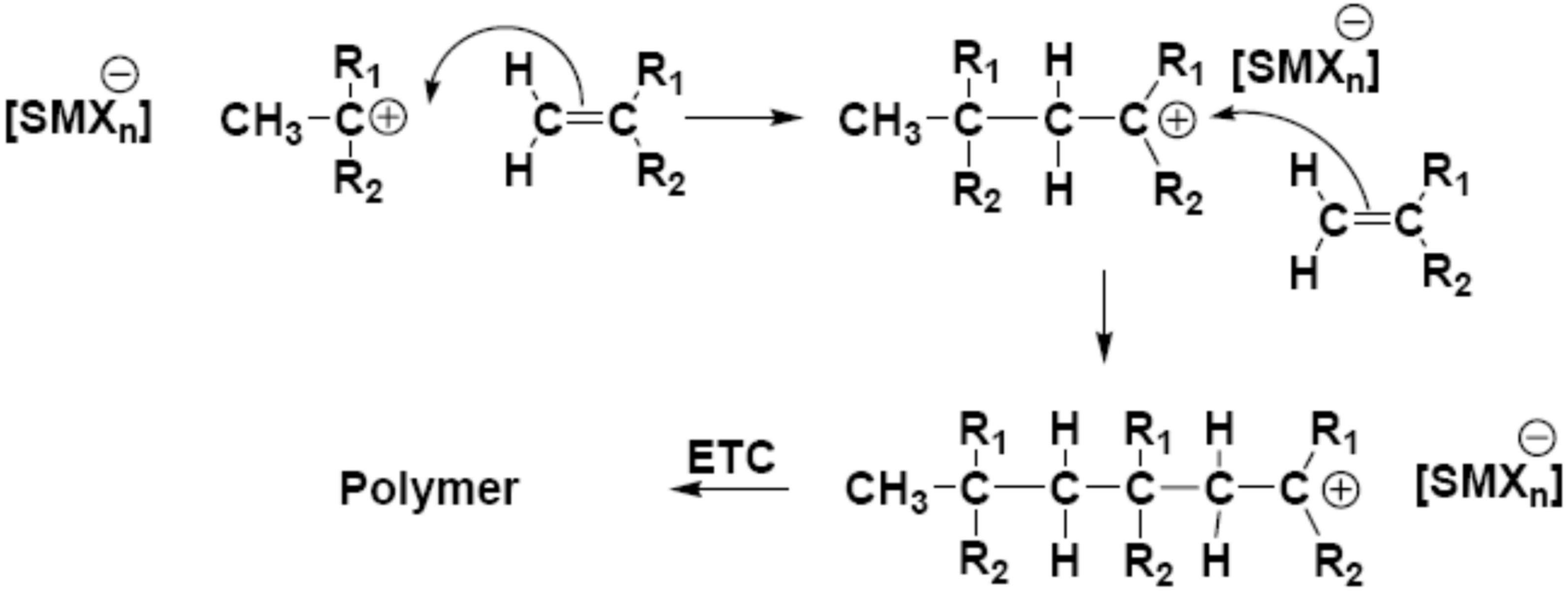
(i) **Initiation**



Cationic Polymerization

- (ii) PropagationChain growth takes place through the repeated addition of a monomer in a head-to-tail manner to the ion with retention of the ionic character throughout

Cationic Polymerization



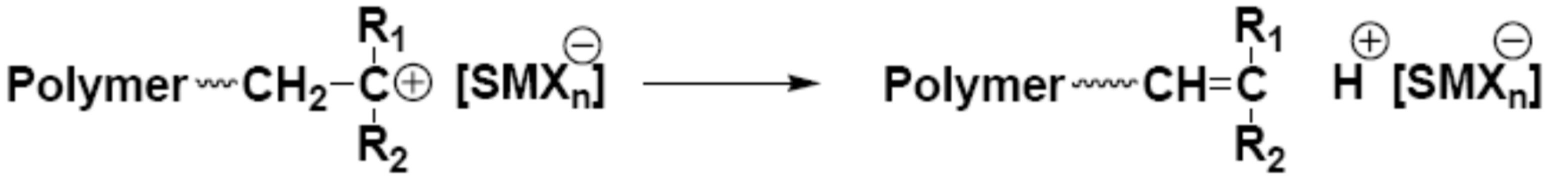
Cationic Polymerization

(iii) Termination

Termination of cationic polymerization reactions are less well-defined than in free-radical processes. Two possibilities exist as follows:

Cationic Polymerization

(a) Unimolecular rearrangement of the ion pair



$$\text{Polymer}\sim CH_2-\underset{R_2}{\overset{R_1}{C}}{}^{\oplus}\ [SMX_n]^{\ominus} \longrightarrow \text{Polymer}\sim CH=\underset{R_2}{\overset{R_1}{C}}\ \overset{\oplus}{H}\ [SMX_n]^{\ominus}$$

Cationic Polymerization

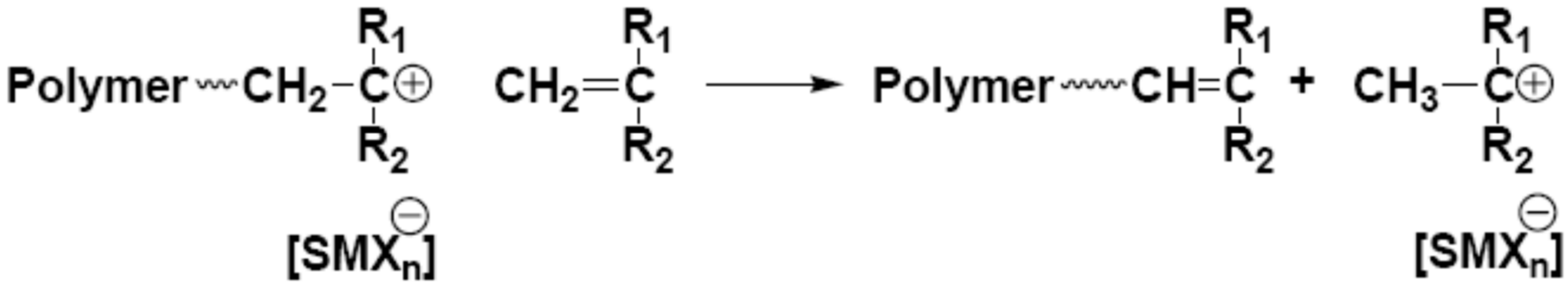
- Hydrogen abstraction occurs from the growing chain to regenerate the catalyst-co-catalyst complex.
- Covalent combination of the active centre with a catalyst-co-catalyst complex fragment may occur giving two inactive species.

Cationic Polymerization

- The kinetic chain is terminated and the initiator complex is reduced - a more effective route to reaction termination.

Cationic Polymerization

(b) Bimolecular transfer reaction with the monomer



$$\underset{[SMX_n]^{\ominus}}{\text{Polymer}\sim CH_2-\overset{R_1}{\underset{R_2}{C}}{}^{\oplus}} \quad CH_2=\overset{R_1}{\underset{R_2}{C}} \longrightarrow \text{Polymer}\sim CH=\overset{R_1}{\underset{R_2}{C}} + \underset{[SMX_n]^{\ominus}}{CH_3-\overset{R_1}{\underset{R_2}{C}}{}^{\oplus}}$$

Reformation of the monomer-initiator complex, ensuring that the kinetic chain is not terminated by the reaction.

Cationic Polymerization

- The kinetics of these reactions is not well understood, but they proceed very rapidly at extremely low temperatures.

Polymerization Processes

- **TWO USEFUL DISTINCTIONS ;**
  - **BETWEEN** BATCH **AND** CONTINUOUS
  - **AND BETWEEN** SINGLE - PHASE **AND** MULTI - PHASE
- **SINGLE - PHASE**
  - **Bulk or Melt Polymerization**
  - **Solution Polymerization**

Polymerization Processes

Bulk Polymerization

- The simplest technique
- Gives the highest-purity polymer
- Only monomer, a monomer soluble initiator and perhaps a chain transfer agent are used
- This process can be used for many free radical polymerizations and some step-growth (condensation) polymerisation.

Polymerization Techniques

These include:

- Bulk Polymerization
- Solution Polymerization
- Suspension Polymerization
- Emulsion Polymerization

Bulk Polymerization

Advantages:

- High yield per reactor volume
- Easy polymer recovery
- The option of casting the polymerisation mixture into final product form

Bulk Polymerization

Limitations:

- Difficulty in removing the last traces of monomer
- The problem of dissipating heat produced during the polymerization
  - In practice, heat dissipated during bulk polymerization can be improved by providing special baffles

Solution Polymerization

- **Definition:** A polymerization process in which the monomers and the polymerization initiators are dissolved in a nonmonomeric liquid solvent at the beginning of the polymerization reaction. The liquid is usually also a solvent for the resulting polymer or copolymer.

Solution Polymerization

- Heat removed during polymerization can be facilitated by conducting the polymerization in an organic solvent or water

Solution Polymerization

- Solvent Requirements:
- Both the initiator and the monomer be soluble in it
- The solvent have acceptable chain transfer characteristics and suitable melting and boiling points for the conditions of the polymerization and subsequent solvent-removal step.

Solution Polymerization

- Solvent choice may be influenced by other factors such as flash point, cost and toxicity
- Reactors are usually stainless steel or glass lined

Solution Polymerization

Disadvantages:

- small yield per reactor volume
- The requirements for a separate solvent recovery step

Suspension Polymerization

- **Definition:** A polymerization process in which the monomer, or mixture of monomers, is dispersed by mechanical agitation in a liquid phase, usually water, in which the monomer droplets are polymerized while they are dispersed by continuous agitation. Used primarily for PVC polymerization

Suspension Polymerization

- If the monomer is insoluble in water, bulk polymerization can be carried out in suspended droplets, i.e., monomer is mechanically dispersed.
- The water phase becomes the heat transfer medium.

Suspension Polymerization

- So the heat transfer is very good. In this system, the monomer must be either
  - 1) insoluble in water or
  - 2) only slightly soluble in water, so that when it polymerizes it becomes insoluble in water.

Suspension Polymerization

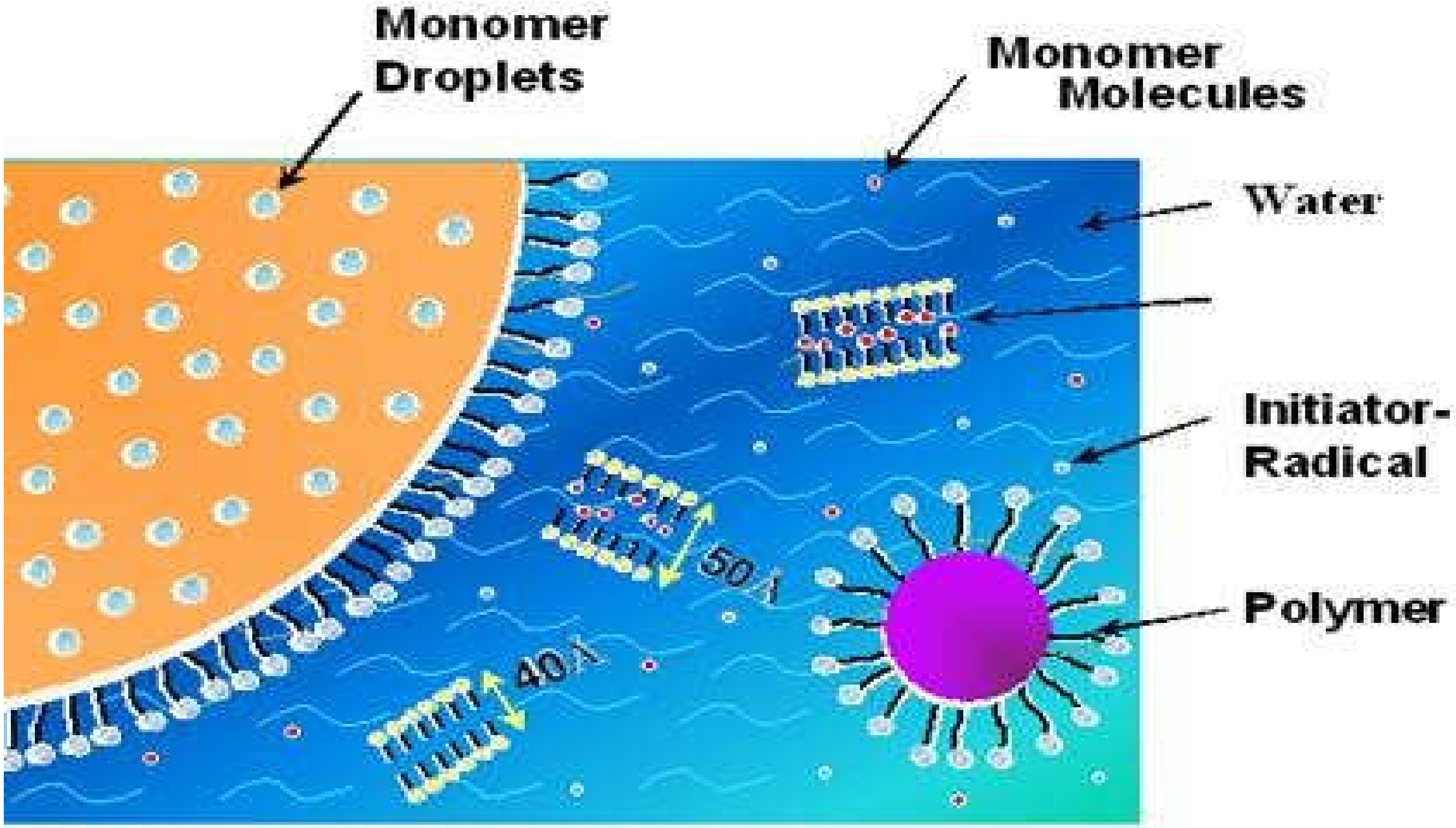
- The behavior inside the droplets is very much like the behavior of bulk polymerization
- Since the droplets are only 10 to 1000 microns in diameter, more rapid reaction rates can be tolerated (than would be the case for bulk polymerization) without boiling the monomer.

Emulsion Polymerization

- **Emulsion polymerization** is a type of radical polymerization that usually starts with an emulsion incorporating water, monomer, and surfactant.

Emulsion Polymerization

- The most common type of emulsion polymerization is an oil-in-water emulsion, in which droplets of monomer (the oil) are emulsified (with surfactants) in a continuous phase of water.
- Water-soluble polymers, such as certain polyvinyl alcohols or hydroxyethyl celluloses, can also be used to act as emulsifiers/stabilizers.



Emulsion Polymerization – Schematic

Emulsion Polymerization

Advantages of emulsion polymerization include:

- High molecular weight polymers can be made at fast polymerization rates. By contrast, in bulk and solution free radical polymerization, there is a tradeoff between molecular weight and polymerization rate.
- The continuous water phase is an excellent conductor of heat and allows the heat to be removed from the system, allowing many reaction methods to increase their rate.

Emulsion Polymerization

Advantages Continued:

- Since polymer molecules are contained within the particles, viscosity remains close to that of water and is not dependent on molecular weight.
- The final product can be used as is and does not generally need to be altered or processed.

Emulsion Polymerization

Disadvantages of emulsion polymerization include:

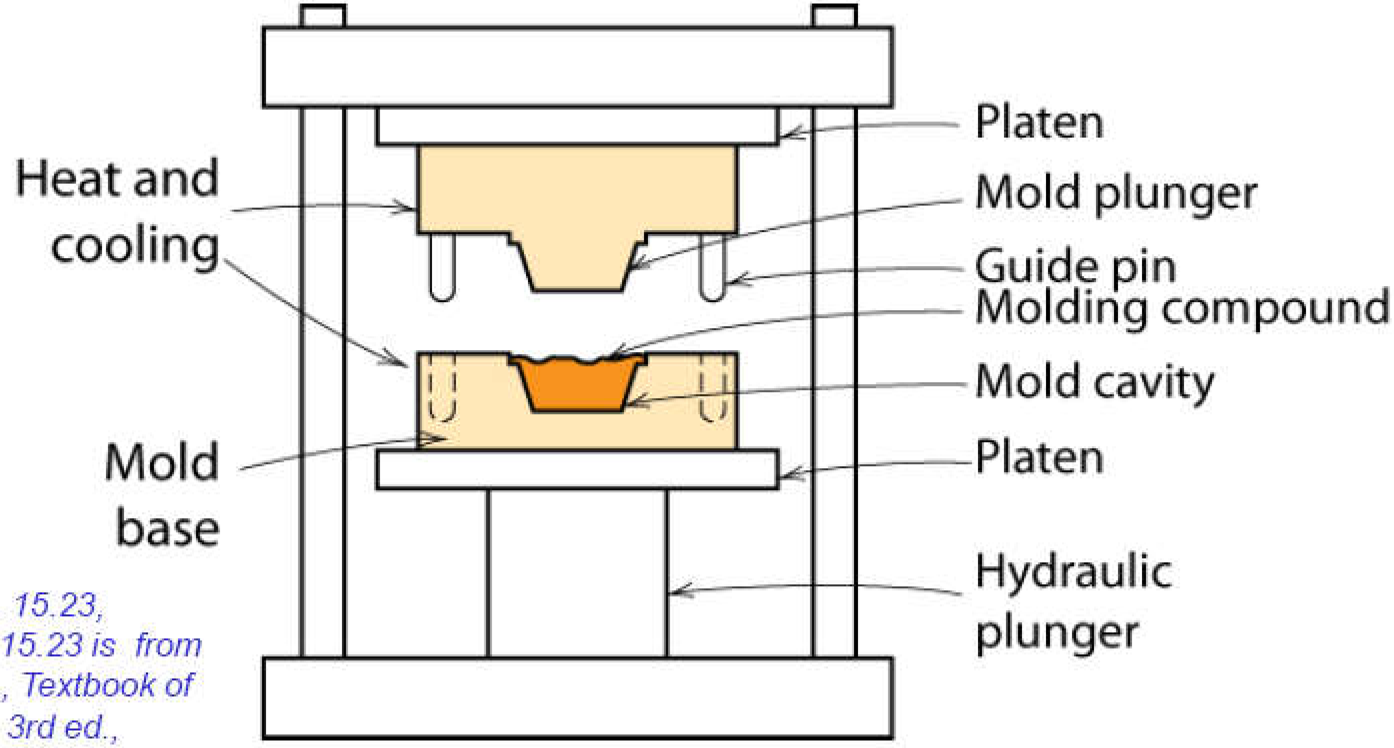
- For dry (isolated) polymers, water removal is an energy-intensive process
- Emulsion polymerizations are usually designed to operate at high conversion of monomer to polymer. This can result in significant chain transfer to polymer.

Fabrication Methods

1

Processing Plastics - Molding

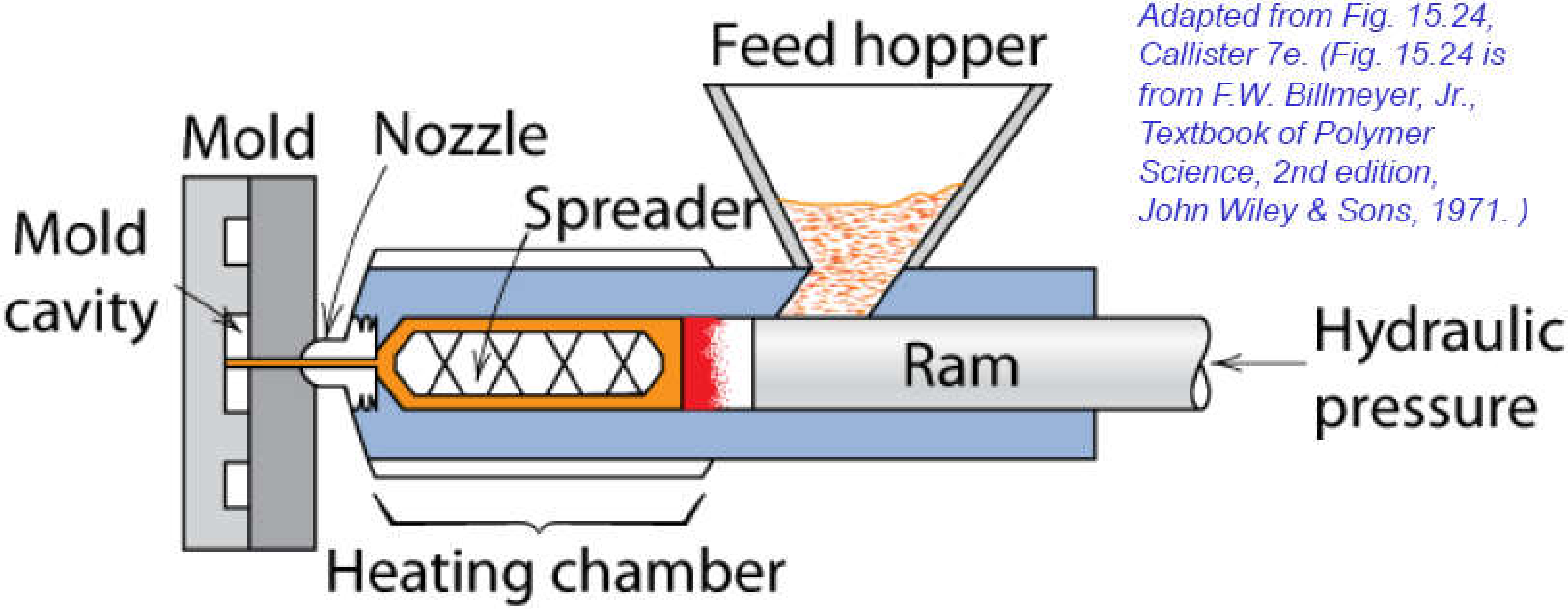
- **Compression and transfer molding**
  - thermoplastic or thermoset



Adapted from Fig. 15.23, Callister 7e. (Fig. 15.23 is from F.W. Billmeyer, Jr., Textbook of Polymer Science, 3rd ed., John Wiley & Sons, 1984.)

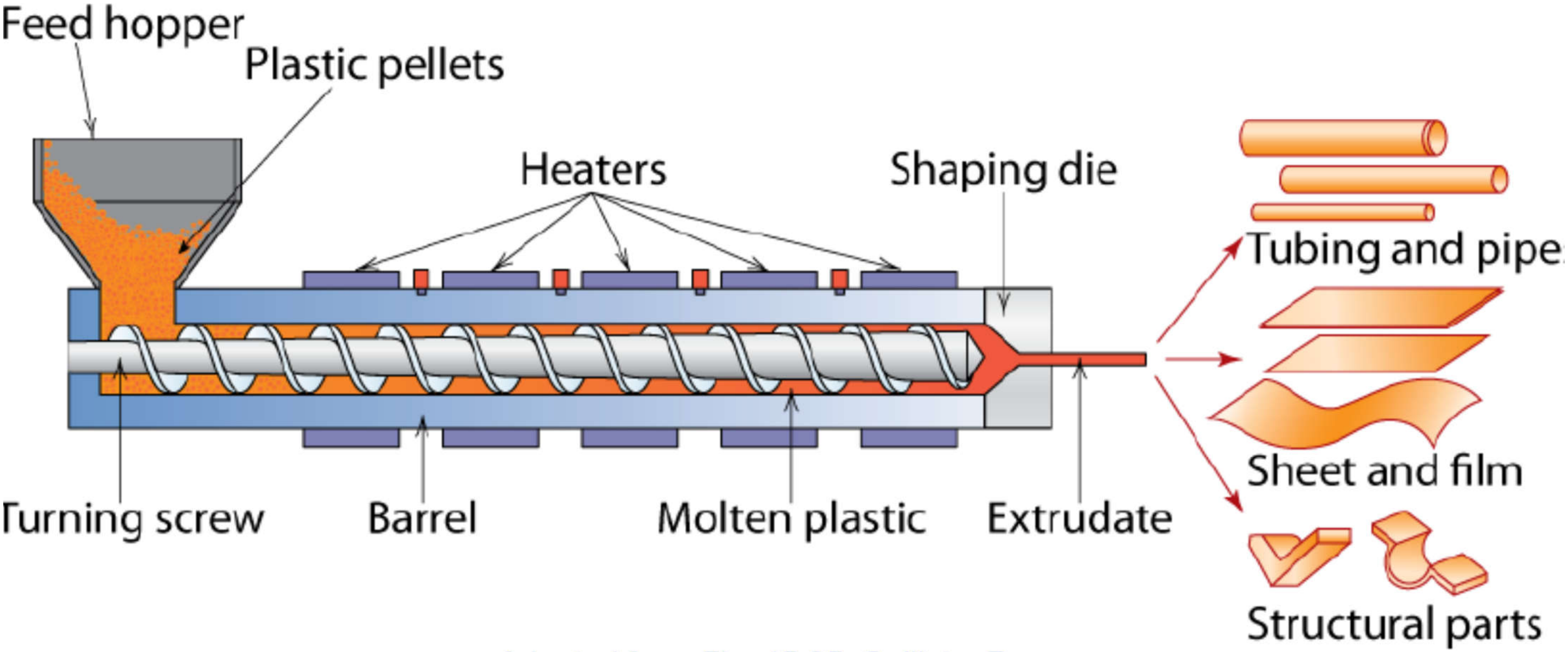
Processing Plastics - Molding

- **Injection molding**
  - **thermoplastic & some thermosets**



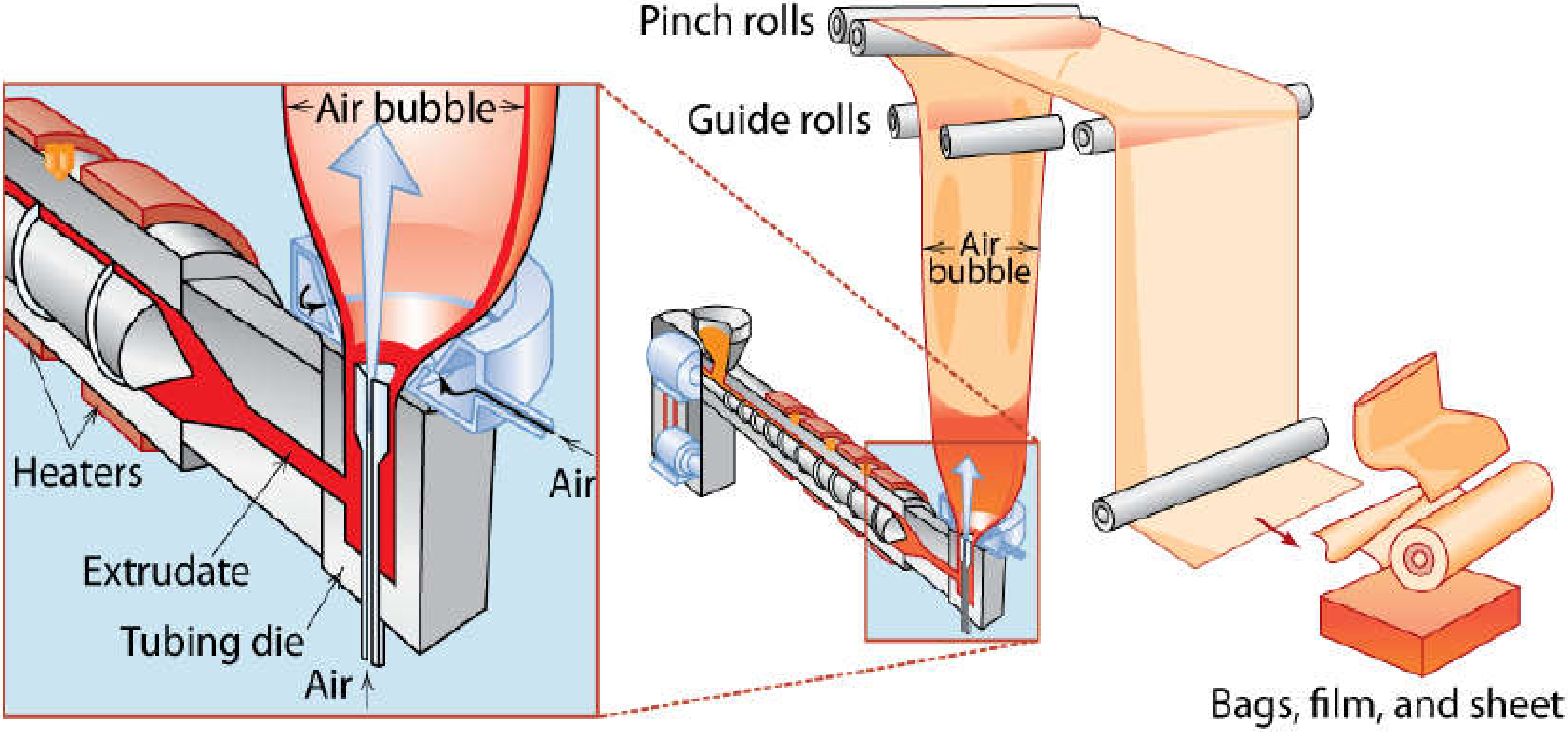
Adapted from Fig. 15.24, Callister 7e. (Fig. 15.24 is from F.W. Billmeyer, Jr., Textbook of Polymer Science, 2nd edition, John Wiley & Sons, 1971.)

Processing Plastics – Extrusion



Adapted from Fig. 15.25, Callister 7e. (Fig. 15.25 is from Encyclopædia Britannica, 1997.)

Blown-Film Extrusion



Adapted from Fig. 15.26, Callister 7e. (Fig. 15.26 is from Encyclopædia Britannica, 1997.)

Example

- Suggest a polymer and fabrication process suitable to produce the following items. Support your choice by contrasting it with other possible alternatives.
  - Car bumper
  - Carry bag
  - Machine gear
  - Shower curtain
  - Tooth brush stand

Solution

- **i) Car bumper**
- ***Polyurethane*** is one of the suitable materials for **car bumpers**. another suitable material is **PP**. Reaction injection molding process is suitable to produce polyurethane bumpers. Polyurethane is molded by mixing of highly reactive liquids (isocyanateandpolyol). Because the materials are very reactive liquids, Other molding processes such as injection molding and compression molding can not be used for this purpose. However, injection molding and compression molding methods can be used to make PP bumpers.

Solution

- **ii) Carry bag**
- **Polyethylene (PE)**is used widely for making carry bags. Blown film extrusion methodis best suitable to produce carry bags. Calendering method also can be applied for the same purpose. However, considering the production rate and thickness range that can be produced, blown film extrusion method is ideal to produce carry bags.

THANK YOU

ANY QUESTIONS ?