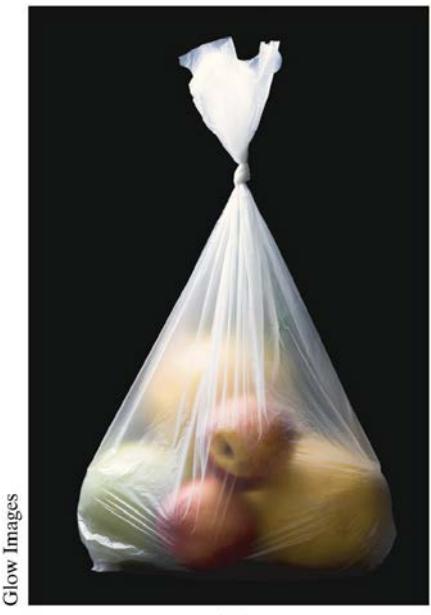
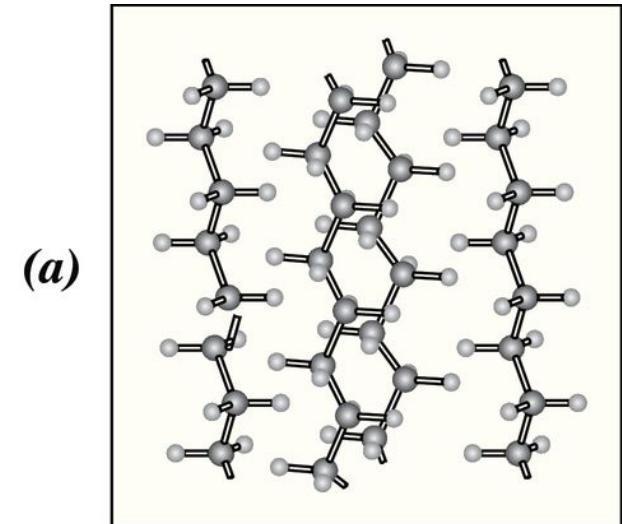


# Chapter 4:

## Polymer Structures

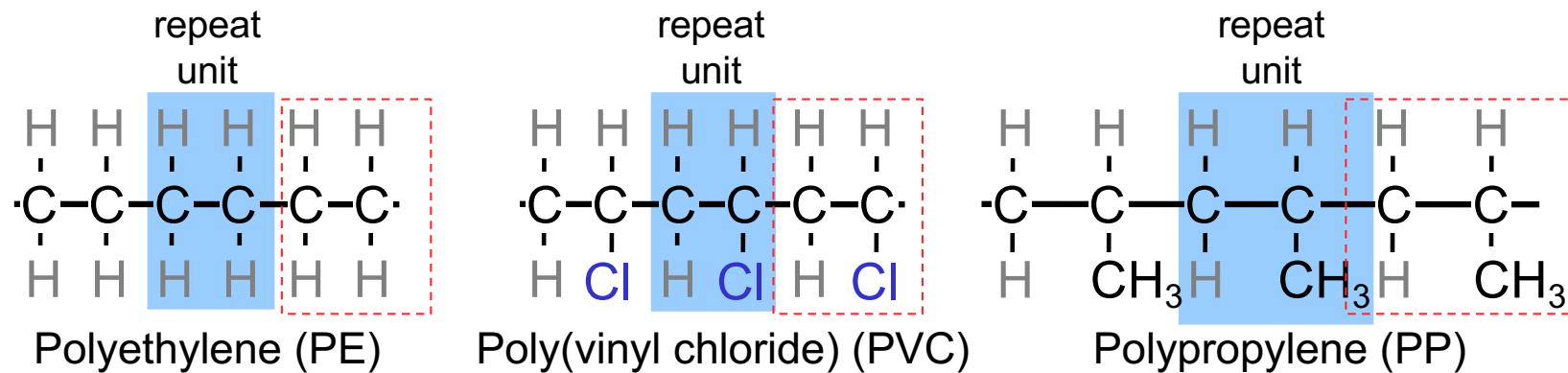
### ISSUES TO ADDRESS...

- What are the general structural and chemical characteristics of **polymer molecules**?
- What are some of the common polymeric materials, and how do they differ chemically?
- How is the crystalline state in polymers different from that in metals and ceramics ?



# What is a Polymer?

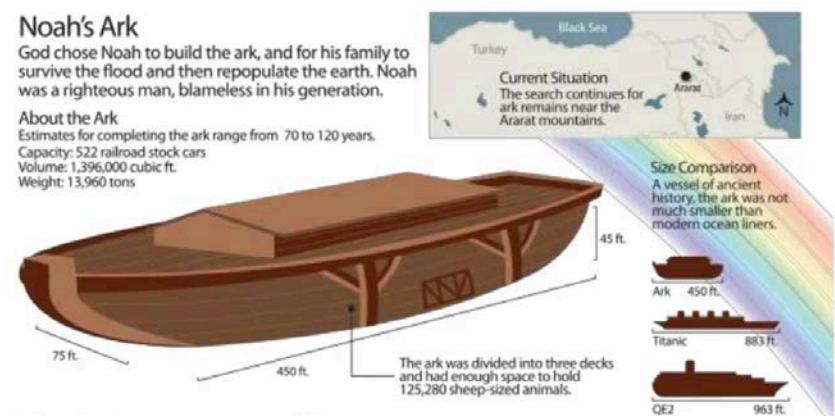
Poly      mer      聚合物  
many      repeat unit



Adapted from Fig. 4.2, Callister & Rethwisch 5e.

# Ancient Polymers

- Originally natural polymers were used
  - Wood
  - Cotton
  - Leather
  - Rubber
  - Wool
  - Silk
- Oldest known uses
  - Rubber balls used by Incas
  - Noah used pitch  
(a natural polymer)  
for the ark

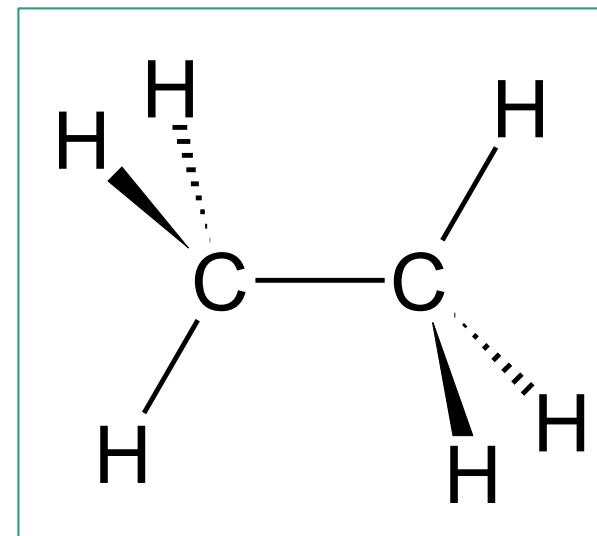


# Polymer Composition

Most polymers are **hydrocarbons**

- i.e., made up of **H** and **C**

- **Saturated** hydrocarbons
  - Each **carbon** singly bonded to **four other atoms**
  - Example:
    - Ethane,  $\text{C}_2\text{H}_6$

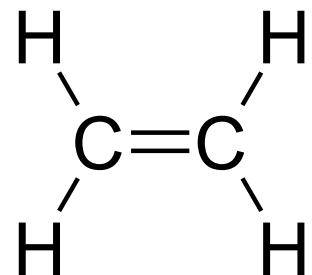


# Unsaturated Hydrocarbons

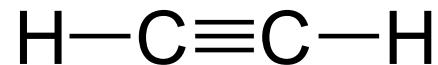
- Double & triple bonds somewhat **unstable** –  
→ can form new bonds

— **Double bond** found in ethylene or ethene -  $C_2H_4$

不飽和



— **Triple bond** found in acetylene or ethyne -  $C_2H_2$



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

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

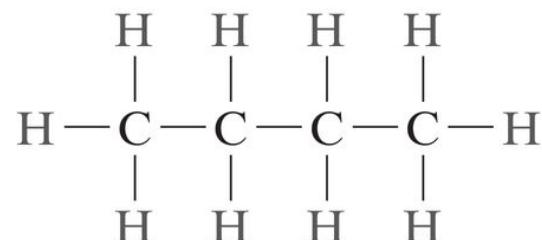
# Isomerism (異構性)

- **Isomerism**

- two compounds with same chemical formula can have quite **different structures**

Butane 丁烷

4C

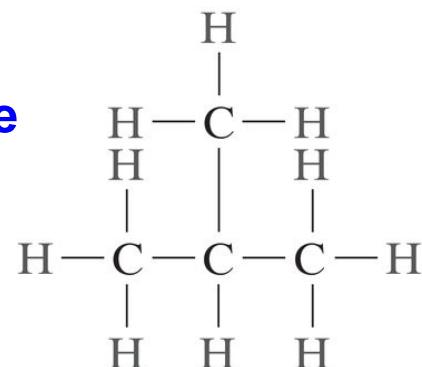


C<sub>4</sub>H<sub>10</sub>

bp. -0.5 °C

Isobutane

異丁烷



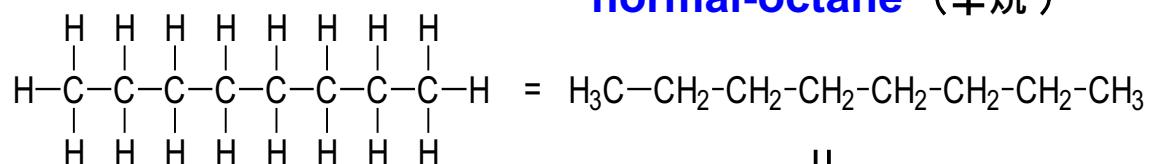
bp. -12.3 °C

4C

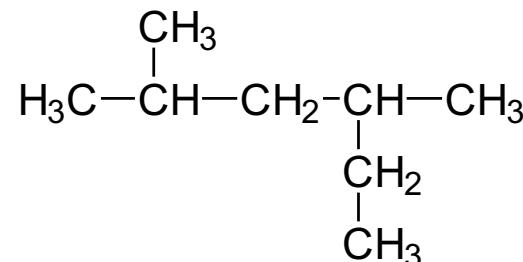
for example: C<sub>8</sub>H<sub>18</sub>

8C

normal-octane (辛烷)



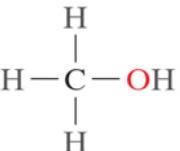
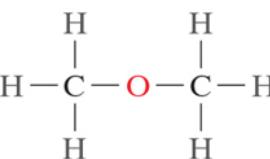
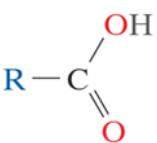
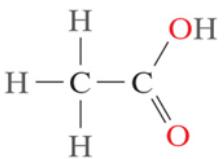
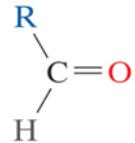
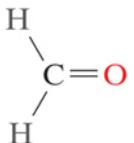
2,4-dimethylhexane (二甲基丙烷)



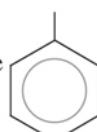
WILEY

Chapter 4 -

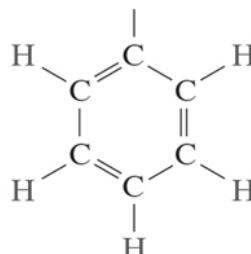
# Hydrocarbon groups

<i>Family</i>	<i>Characteristic Unit</i>	<i>Representative Compound</i>	
Alcohols	$\text{R}-\text{OH}$		Methyl alcohol 甲醇
Ethers	$\text{R}-\text{O}-\text{R}'$		Dimethyl ether 二甲基醚
Acids			Acetic acid 醋酸
Aldehydes			Formaldehyde 甲醛
Aromatic hydrocarbons <sup>a</sup>			Phenol 酚

<sup>a</sup>The simplified structure

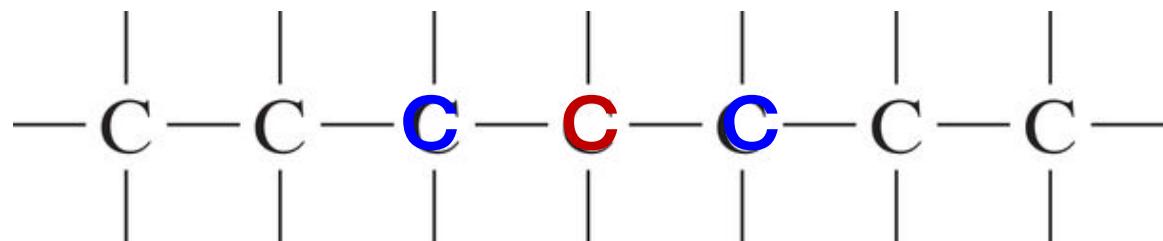


denotes a phenyl group,



# Macromolecules (巨分子)

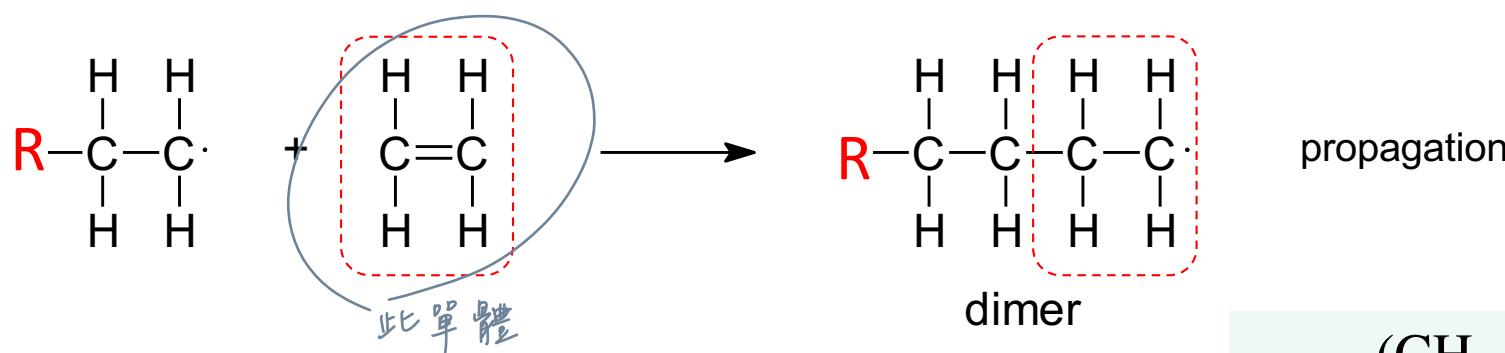
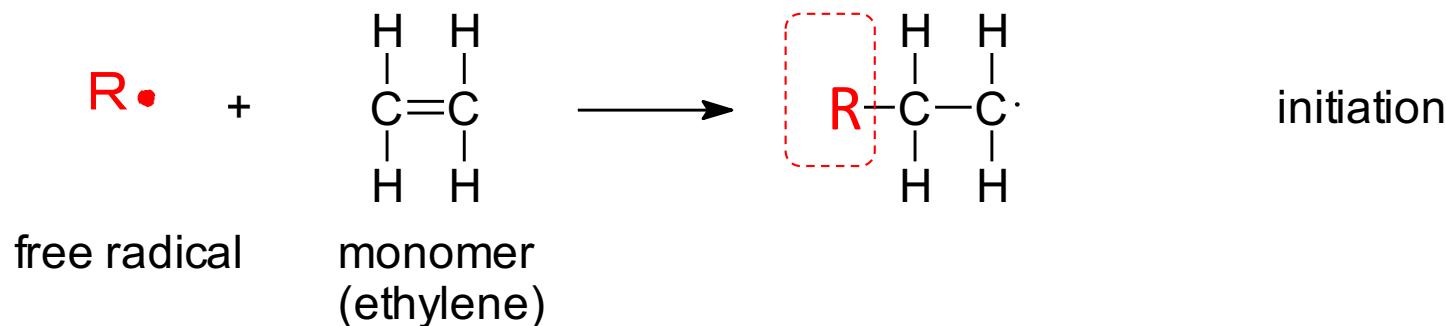
- Each molecule, the atoms are bound together by **covalent** interatomic bonds
- Each **C** singly bonds to two adjacent **C** on either side
- Two remaining valence electrons maybe involved in side bonding with adjacent



# Polymerization & Polymer Chemistry

聚合 → 雙、三鍵

- Free radical polymerization

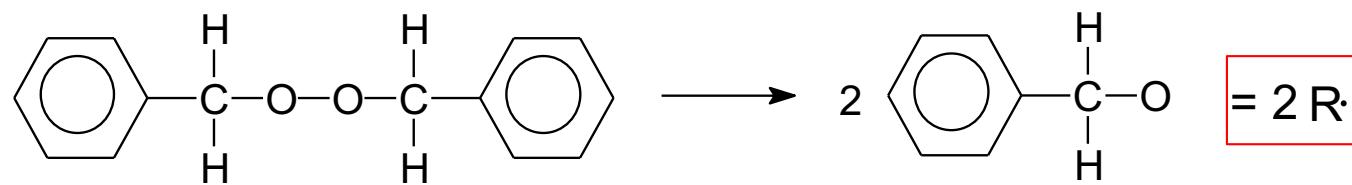


$-(CH_2-CH_2)_n-$

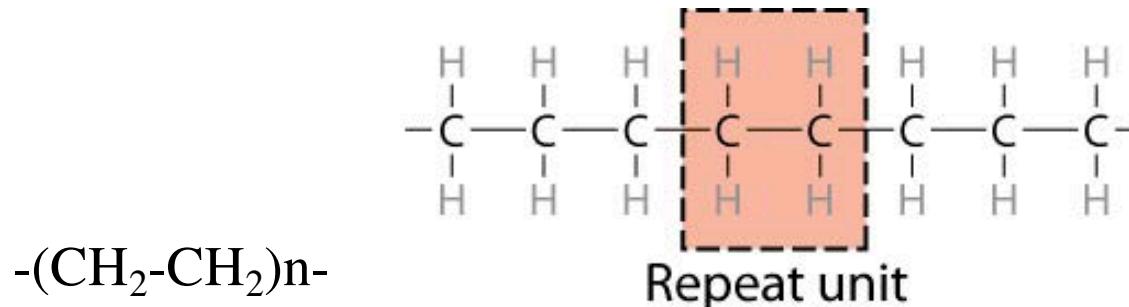
n: repeat number

- Initiator: example - benzoyl peroxide

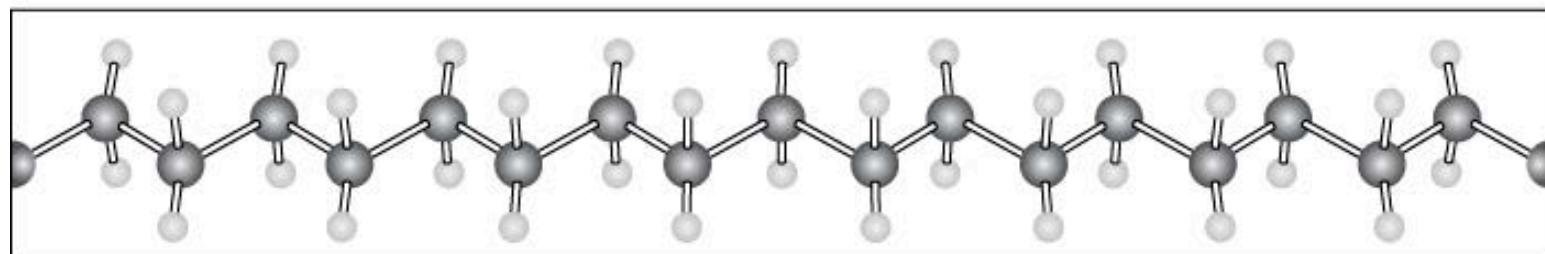
過氧化苯甲醯



# Chemistry and Structure of Polyethylene



n: repeat number



鏈齒狀 10<sup>9</sup> :



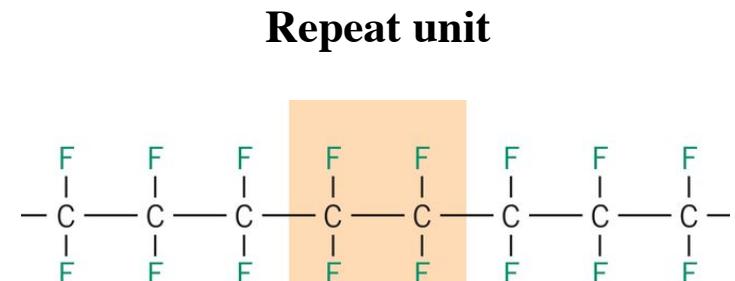
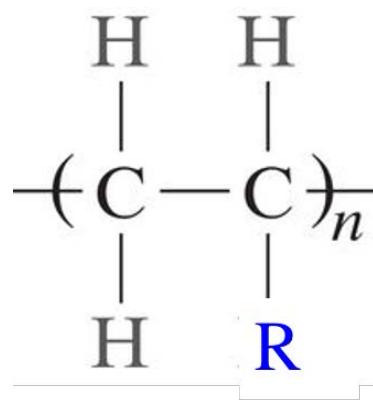
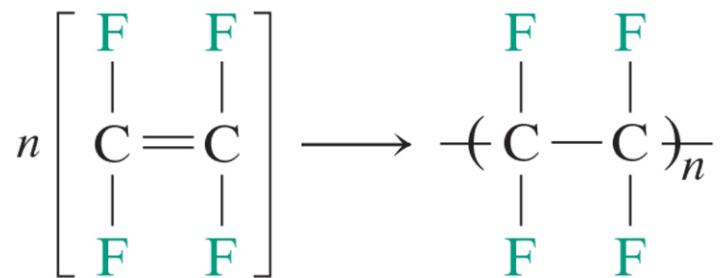
Zigzag  
backbone

Polyethylene is a long-chain hydrocarbon

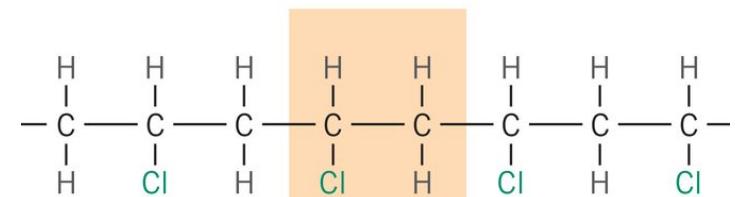
- paraffin wax for candles is short polyethylene
- (n=20-40)



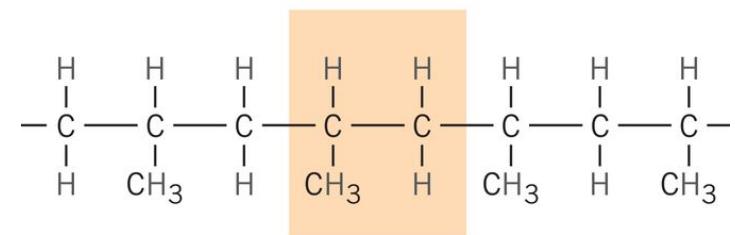
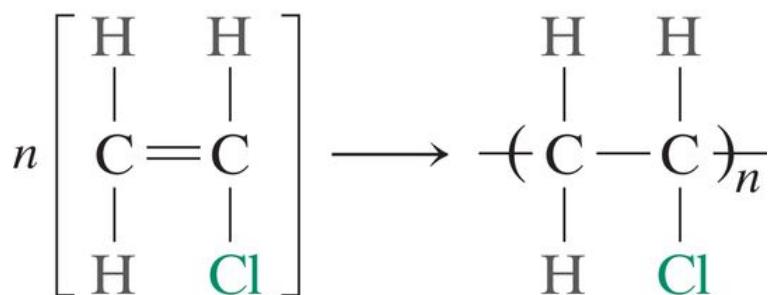
## Polytetrafluoroethylene (PTFE)



Repeat unit  
(a)



Repeat unit  
(b)



Repeat unit  
(c)

Y

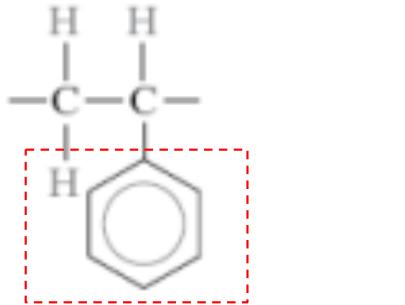
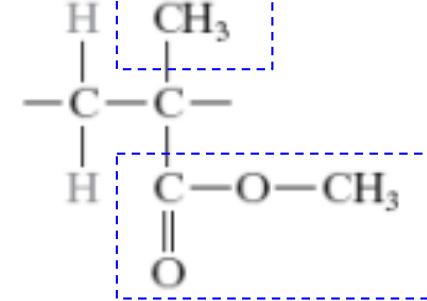
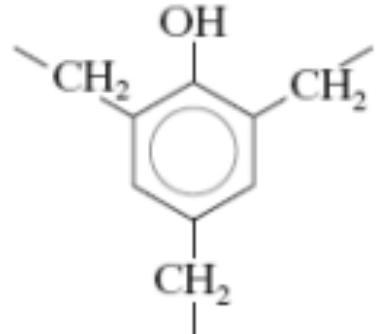
# Bulk or Commodity Polymers

**Table 14.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials**

Polymer	Repeat Unit
	$\begin{array}{c} \text{H} & \text{H} \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{H} \end{array}$
Polyethylene (PE) 聚乙烯	
	$\begin{array}{c} \text{H} & \text{H} \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{Cl} \end{array}$
Poly(vinyl chloride) (PVC) 聚氯乙烯	
	$\begin{array}{c} \text{F} & \text{F} \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{F} & \text{F} \end{array}$
Polytetrafluoroethylene (PTFE) 聚四氟乙烯	
	$\begin{array}{c} \text{H} & \text{H} \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{CH}_3 \end{array}$
Polypropylene (PP) 聚丙烯	

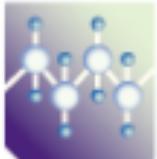
# Bulk or Commodity Polymers

**Table 4.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials**

Polymer	Repeat Unit
 Polystyrene (PS) 聚苯乙烯	 $\text{--C}(\text{H})\text{--C}(\text{H})\text{--}\text{C}_6\text{H}_4\text{--}$ The structure shows a central benzene ring connected to two ethylene groups. The first ethylene group has two methyl groups, and the second has a methacrylate group ( $\text{CH}_3\text{COOCH}_3$ ). The entire repeating unit is enclosed in a dashed red box.
 Poly(methyl methacrylate) (PMMA) 聚甲基丙烯酸甲酯	 $\text{--C}(\text{H})\text{--C}(\text{H})\text{--C}(=\text{O})\text{OCH}_3\text{--}$ The structure shows a central carbonyl group ( $=\text{O}$ ) connected to two methyl groups and an ethylene group. The entire repeating unit is enclosed in a dashed blue box.
 Phenol-formaldehyde (Bakelite) 苯酚-甲醛	 $\text{--CH}_2\text{C}_6\text{H}_3(\text{OH})\text{CH}_2\text{--}$ The structure shows a central benzene ring with three substituents: a hydroxyl group ( $\text{OH}$ ) at the top position and two methylene groups ( $\text{CH}_2$ ) at the 2 and 6 positions.

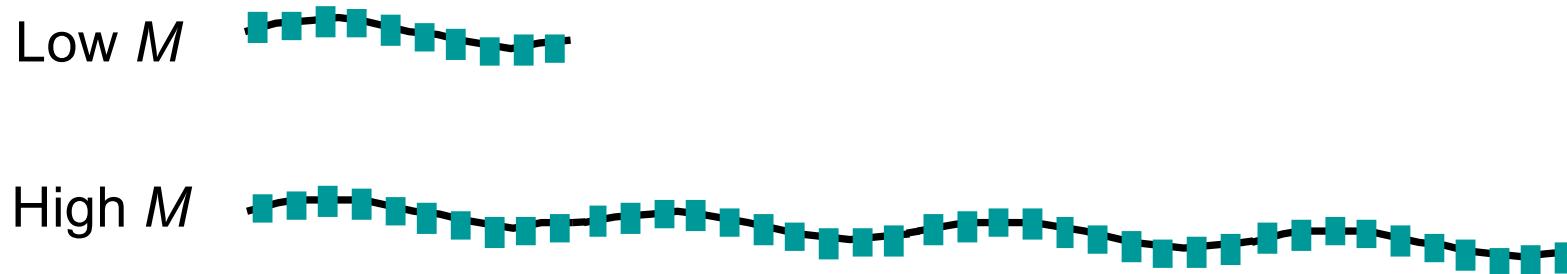
# Bulk or Commodity Polymers

**Table 4.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials**

Polymer	Repeat Unit
	$-\text{N}(\text{H})-\left[\begin{array}{c} \text{H} \\   \\ -\text{C}- \\   \\ \text{H} \end{array}\right]_6-\text{N}(\text{H})-\overset{\text{O}}{\parallel}\text{C}-\left[\begin{array}{c} \text{H} \\   \\ -\text{C}- \\   \\ \text{H} \end{array}\right]_4-\overset{\text{O}}{\parallel}\text{C}-$
	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{C}_6\text{H}_4-\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{O}- \end{array} \quad \begin{array}{c} \text{H} & \text{H} \\   &   \\ -\text{C}-\text{C}- \\   &   \\ \text{H} & \text{H} \end{array} \quad \text{O}-$
	$-\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{O}-\overset{\text{O}}{\parallel}\text{C}-$

# MOLECULAR WEIGHT

- Molecular weight,  $M$ : Mass of a mole of chains.



Not all chains in a polymer are of the same length

— i.e., there is a distribution of molecular weights

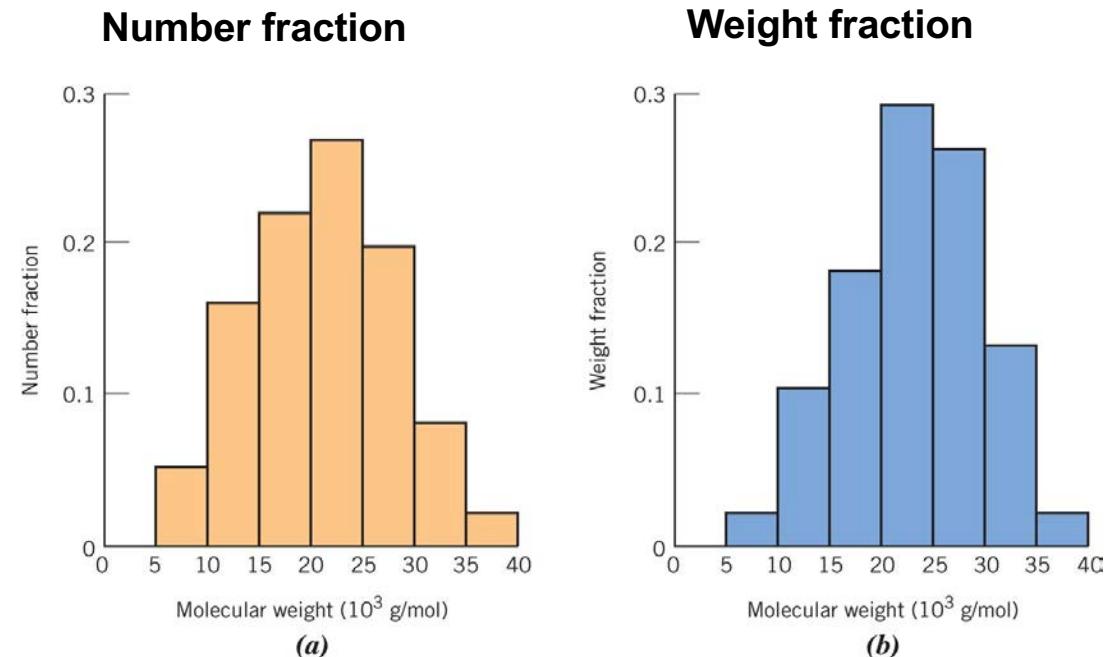
# Molecular Weight Distribution

$$\overline{M}_n = \frac{\text{total wt of polymer}}{\text{total # of molecules}}$$

$$\overline{M}_n = \sum x_i M_i$$

$$\overline{M}_w = \sum w_i M_i$$

**M<sub>n</sub>:** Number-average molecular weight  
數目平均分子量

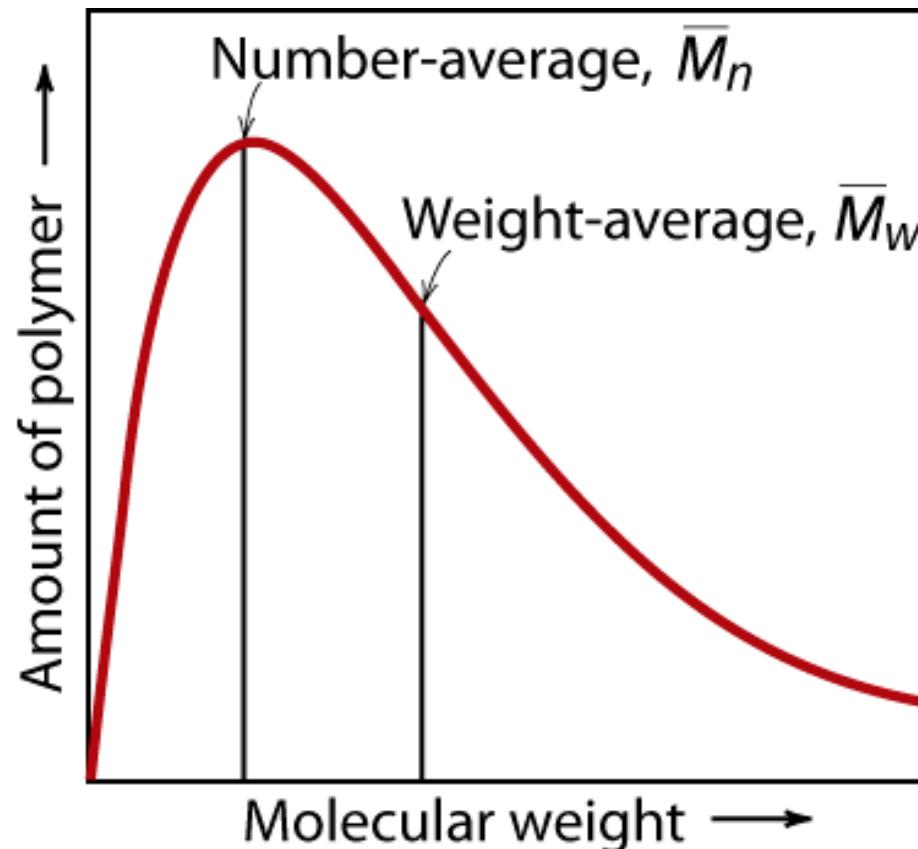


$M_i$  = mean (middle) molecular weight of size range  $i$

$x_i$  = number fraction of chains in size range  $i$

$w_i$  = weight fraction of chains in size range  $i$

# Molecular Weight Distribution



Adapted from Fig. 4.4, Callister & Rethwisch 5e.

$$\text{Degree of polymerization} = \frac{\bar{M}_n}{m}$$

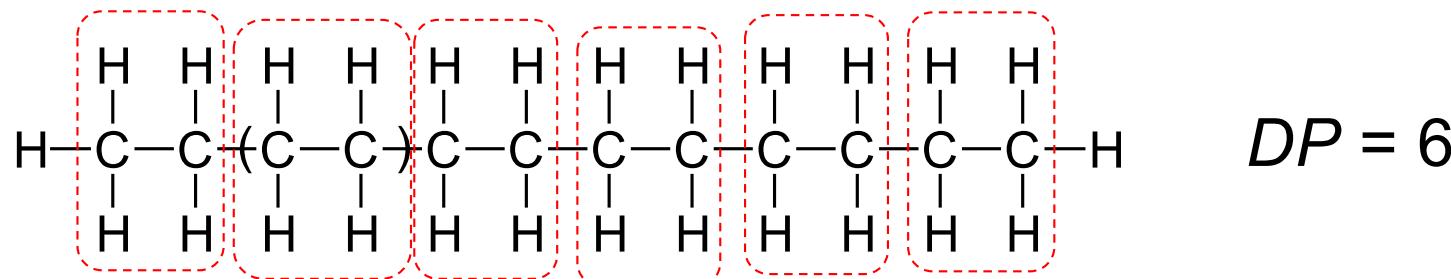
聚合度

$\bar{M}_n$ : Number-average molecular weight

m: repeat unit molecular weight

# Degree of Polymerization, $DP$

$DP$  = average number of repeat units per chain



$$DP = \frac{\bar{M}_n}{\bar{m}}$$

where  $\bar{m}$  = average molecular weight of repeat unit  
for copolymers this is calculated as follows:

$$\bar{m} = \sum f_i m_i$$

Chain fraction

mol. wt of repeat unit  $i$

# Molecular Weight Calculation

Example: Average mass of a class

Student	Weight mass (lb)
1	104
2	116
3	140
4	143
5	180
6	182
7	191
8	220
9	225
10	380

What is the average weight of the students in this class:

- a) Based on the **number fraction** of students in each mass range?
- b) Based on the **weight fraction** of students in each mass range?

# Molecular Weight Calculation

Solution: The first step is to sort the students into weight ranges.

Using 40 lb ranges gives the following table:

weight range mass (lb)	number of students $N_i$	mean weight mass (lb) $W_i$
81-120	2	110
121-160	2	142
161-200	3	184
201-240	2	223
241-280	0	-
281-320	0	-
321-360	0	-
361-400	1	380

$$\text{total number} \rightarrow \sum N_i = 10$$

$$\sum N_i W_i = 1881 \quad \text{total weight}$$

Calculate the number and weight fraction of students in each weight range as follows:

$$x_i = \frac{N_i}{\sum N_i} \quad w_i = \frac{N_i W_i}{\sum N_i W_i}$$

For example: for the 81-120 lb range

$$x_{81-120} = \frac{2}{10} = 0.2$$

$$w_{81-120} = \frac{2 \times 110}{1881} = 0.117$$

# Molecular Weight Calculation

weight range mass (lb)	mean weight $W_i$ mass (lb)	number fraction $x_i$	weight fraction $w_i$
81-120	110	0.2	0.117
121-160	142	0.2	0.150
161-200	184	0.3	0.294
201-240	223	0.2	0.237
241-280	-	0	0.000
281-320	-	0	0.000
321-360	-	0	0.000
361-400	380	0.1	0.202

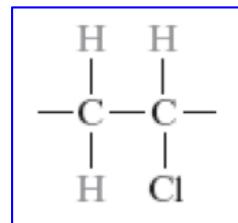
$$\bar{M}_n = \sum x_i M_i = (0.2 \times 110 + 0.2 \times 142 + 0.3 \times 184 + 0.2 \times 223 + 0.1 \times 380) = 188 \text{ lb}$$

$$\begin{aligned} \bar{M}_w = \sum w_i M_i &= (0.117 \times 110 + 0.150 \times 142 + 0.294 \times 184 \\ &\quad + 0.237 \times 223 + 0.202 \times 380) = 218 \text{ lb} \end{aligned}$$

$$\bar{M}_w = \sum w_i M_i = 218 \text{ lb}$$

# Molecular Weight Calculation (cont.)

polyvinyl chloride  
(PVC)



Compute

$$\bar{M}_n = \sum x_i M_i$$

- (a) the number-average molecular weight
- (b) the number-average degree of polymerization
- (c) the weight-average molecular weight.  $\bar{M}_w = \sum w_i M_i$

(a)  $M_n: 21,150$  g/mole

$$\begin{aligned} \bar{m} &= 2(12.01 \text{ g/mol}) + 3(1.01 \text{ g/mol}) + 35.45 \text{ g/mol} \\ &= 62.50 \text{ g/mol} \end{aligned}$$

$$(\text{DP}) \quad n_n = \frac{\bar{M}_n}{\bar{m}} = \frac{21,150 \text{ g/mol}}{62.50 \text{ g/mol}} = 338$$

**Table 4.4a** Data Used for Number-Average Molecular Weight Computations in Example Problem 4.1

Molecular Weight Range (g/mol)	Mean $M_i$ (g/mol)	$x_i$	$x_i M_i$
5,000–10,000	7,500	0.05	375
10,000–15,000	12,500	0.16	2000
15,000–20,000	17,500	0.22	3850
20,000–25,000	22,500	0.27	6075
25,000–30,000	27,500	0.20	5500
30,000–35,000	32,500	0.08	2600
35,000–40,000	37,500	0.02	750
			$\bar{M}_n = 21,150$

**Table 4.4b** Data Used for Weight-Average Molecular Weight Computations in Example Problem 4.1

Molecular Weight Range (g/mol)	Mean $M_i$ (g/mol)	$w_i$	$w_i M_i$
5,000–10,000	7,500	0.02	150
10,000–15,000	12,500	0.10	1250
15,000–20,000	17,500	0.18	3150
20,000–25,000	22,500	0.29	6525
25,000–30,000	27,500	0.26	7150
30,000–35,000	32,500	0.13	4225
35,000–40,000	37,500	0.02	750
			$\bar{M}_w = 23,200$

(c)  $M_w: 23,200$  g/mole

# Effect of Molecular Weight

- Mn range from 25 k to 50 k Da is suitable for condensation polymers
- Mn ~> 50 kDa are preferred for addition polymer

TABLE 2.6

## Relationship Between Molecular Weight of Poly(Lactic Acid) and Mechanical Properties

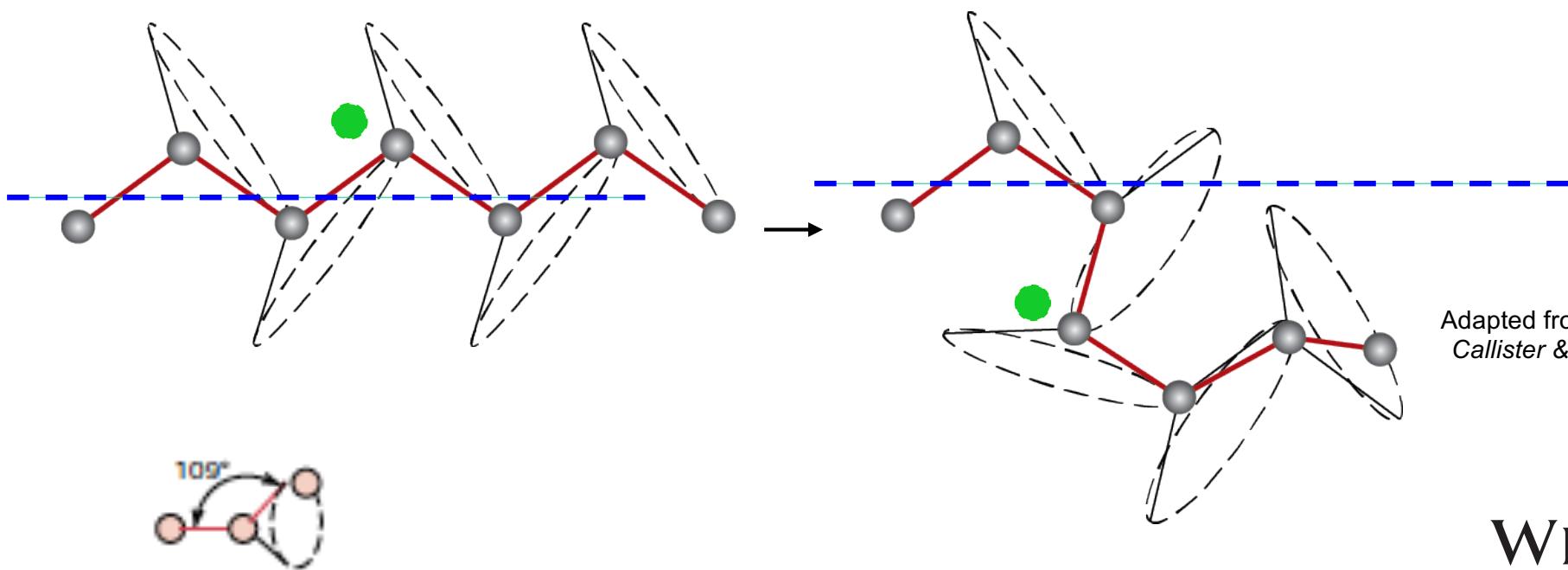
聚乳酸

Weight average molecular weight	Tensile modulus* (MPa)	Flexural modulus* (MPa)
50,000	1200	1400
100,000	2700	3000
300,000	3000	3250

# Polymers – Molecular Shape

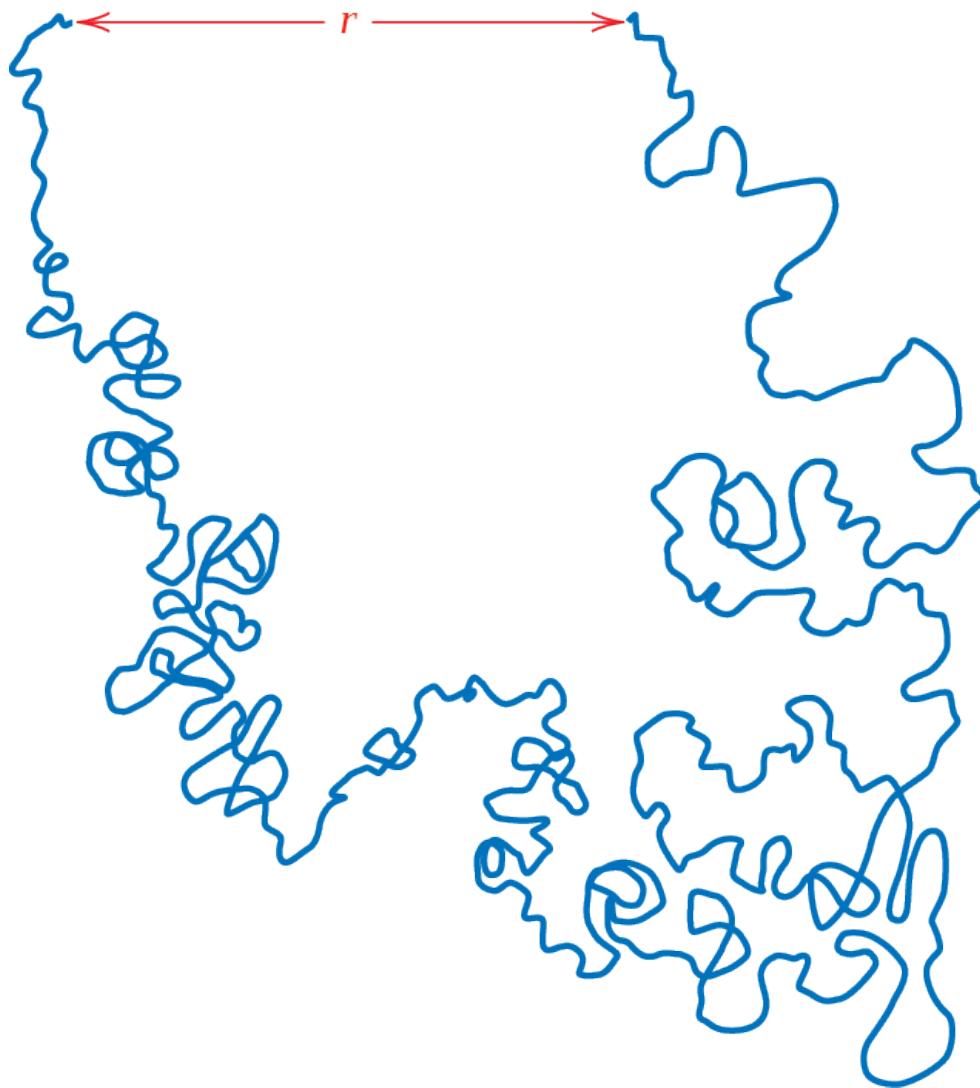
## Molecular **Shape** (or **Conformation**)

- chain bending and twisting are possible by rotation of carbon atoms around their chain bonds
  - note: *not necessary to break chain bonds to alter molecular shape*



Adapted from Fig. 4.5,  
Callister & Rethwisch  
5e.

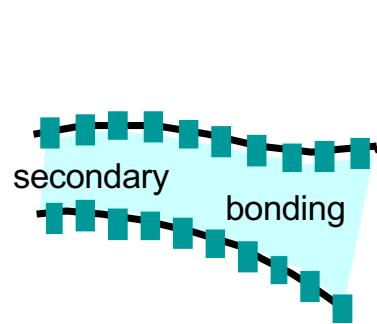
# Chain End-to-End Distance, $r$



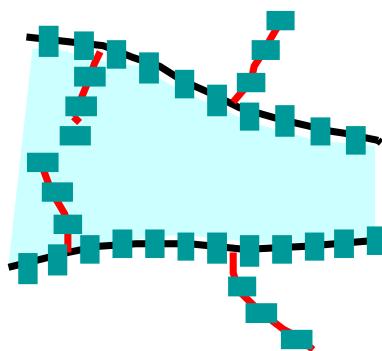
Adapted from Fig. 4.6,  
*Callister & Rethwisch*  
5e.

# Molecular Structures for Polymers

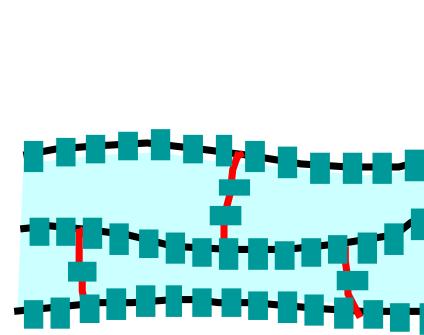
## 分子結構



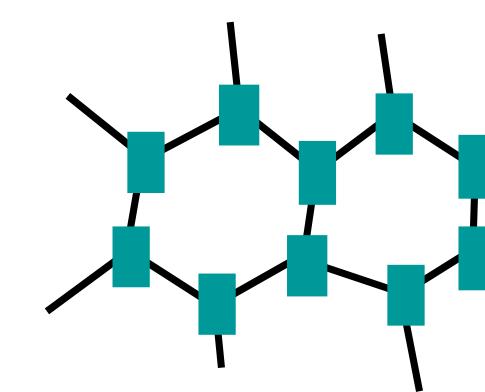
Linear  
線性



Branched  
支鏈



Cross-Linked  
交聯



Network  
網狀

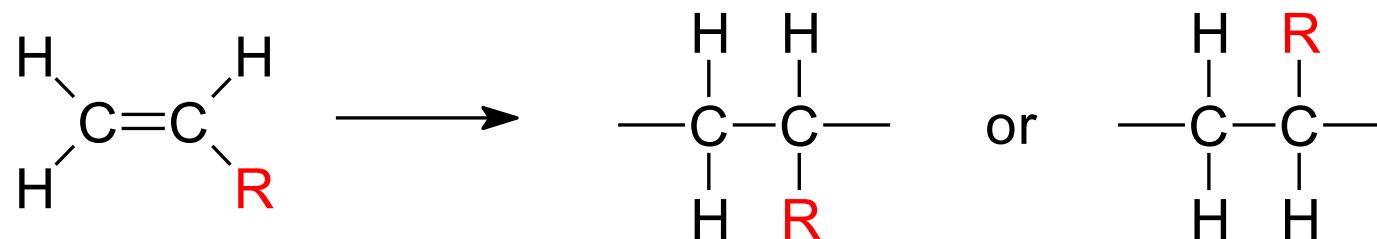
Adapted from Fig. 4.7, Callister & Rethwisch 5e.

# Molecular Configurations for Polymers

分子組態

**Configurations** – to change must break bonds

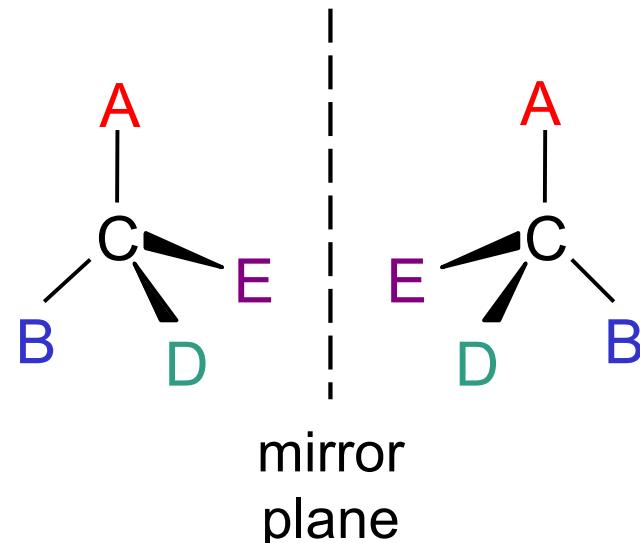
- **Stereoisomerism** (立體異構物)



Cl  
CH<sub>3</sub>

Stereoisomers are mirror images

- can't superimpose without breaking a bond

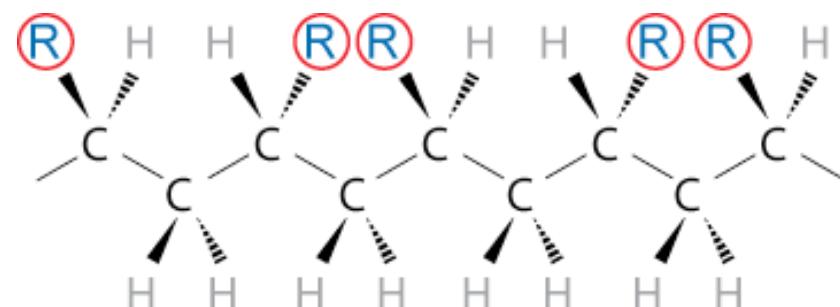
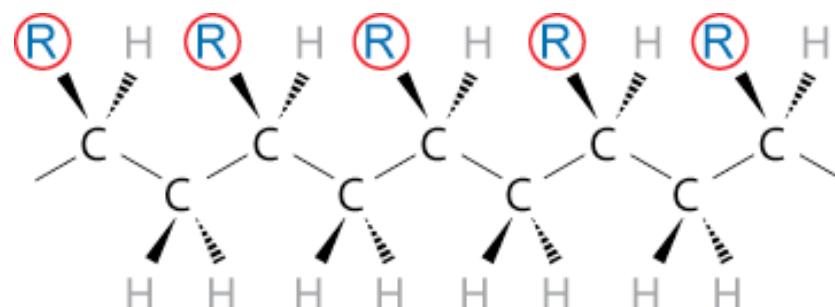
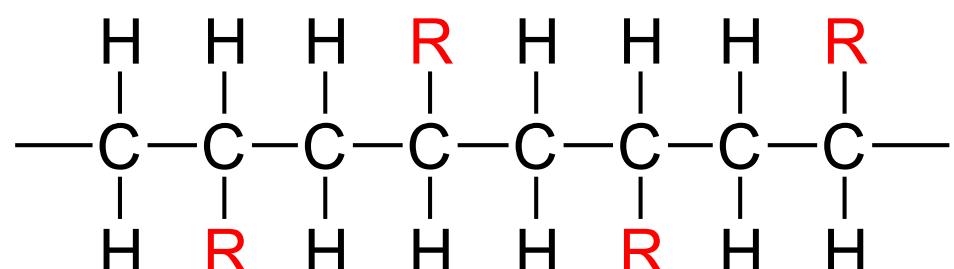
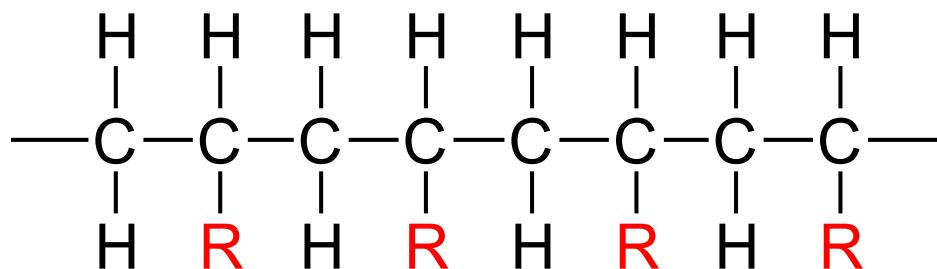


# Tacticity 構形規則度

**Tacticity** – stereoregularity or spatial arrangement of **R** units along chain

isotactic – all **R** groups  
同排              on **same side** of chain

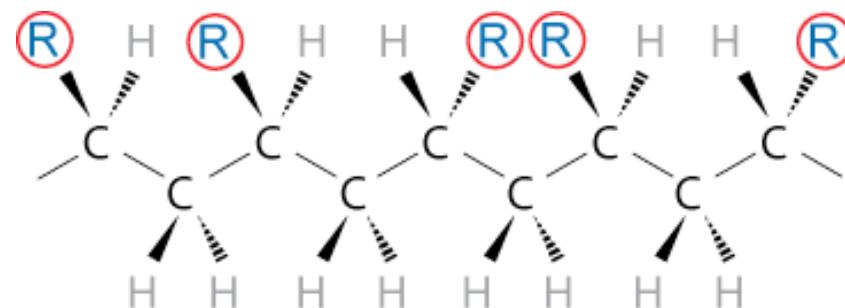
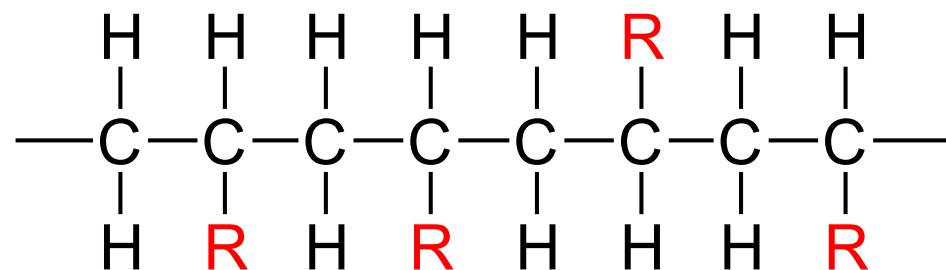
syndiotactic – **R** groups  
對排              alternate sides



# Tacticity (cont.)

atactic – R groups **randomly** positioned

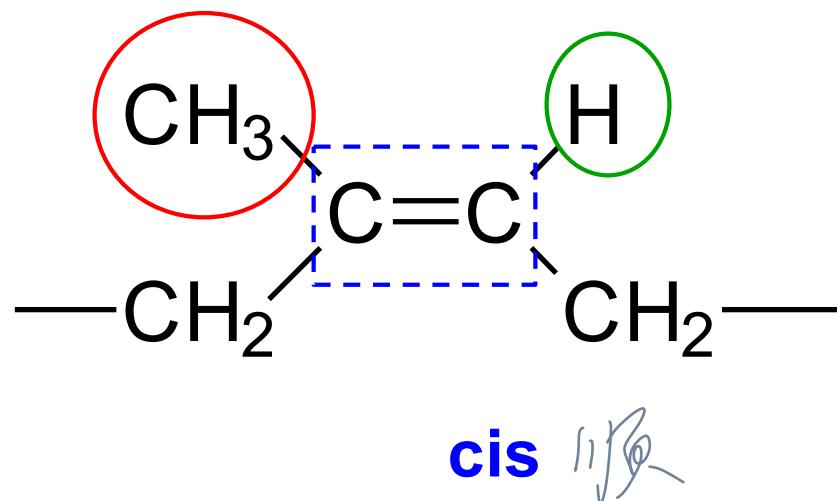
雜排



# cis/trans Isomerism

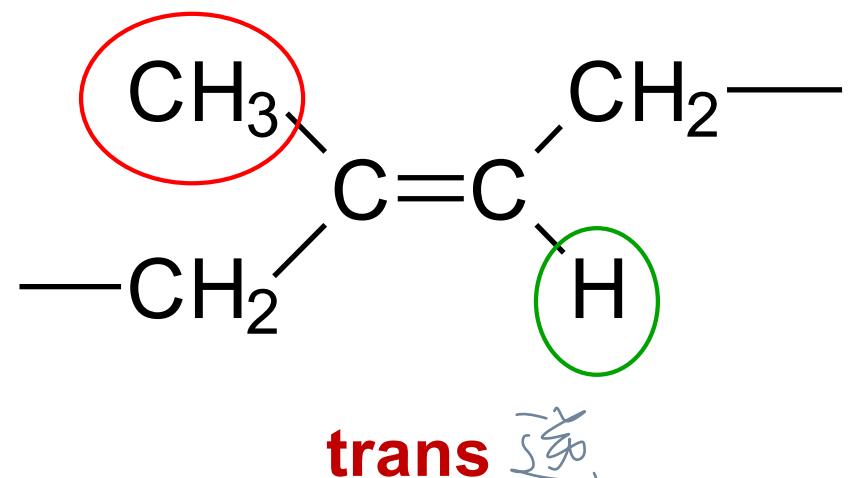
## Geometrical isomerism (幾何異構物)

- repeat unit having **a double bond** between chain



**cis-isoprene**  
(natural rubber)

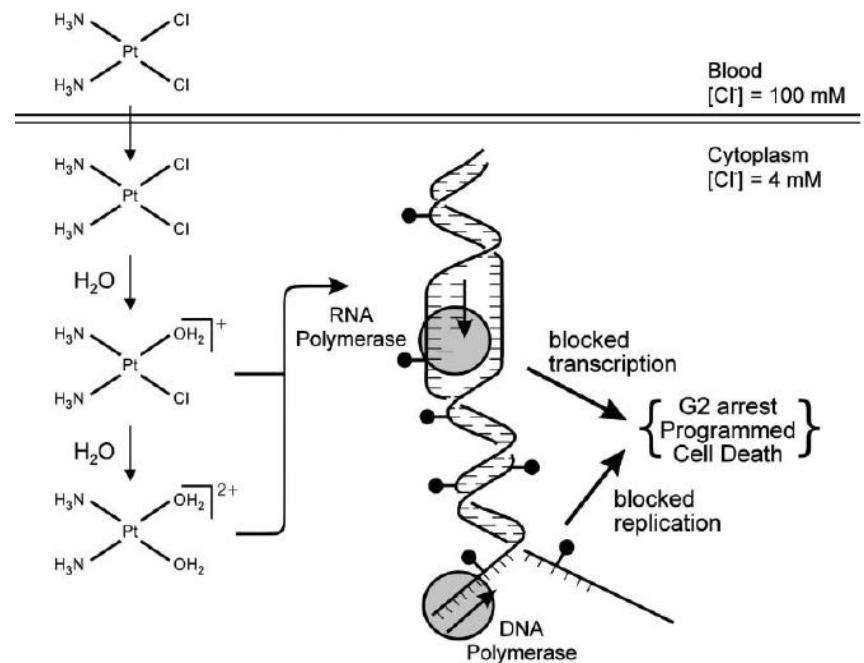
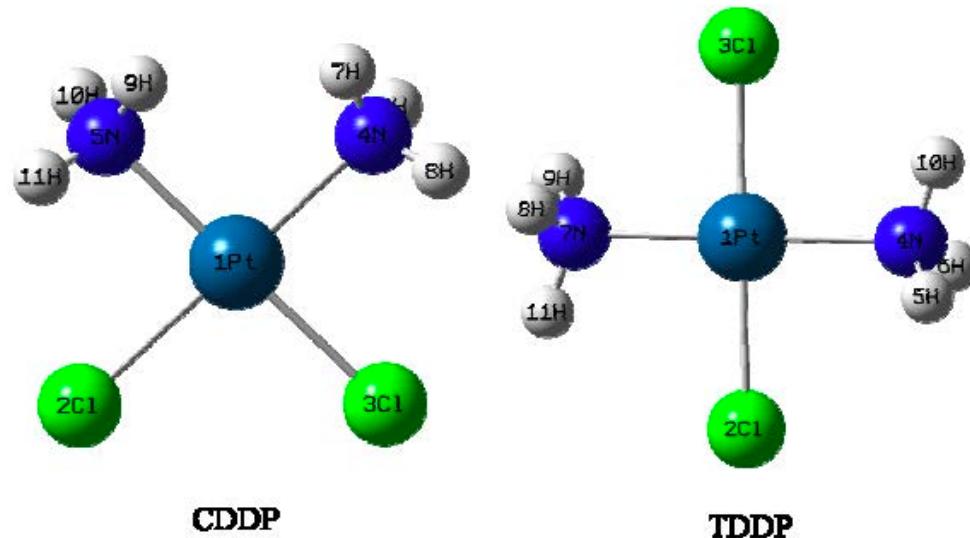
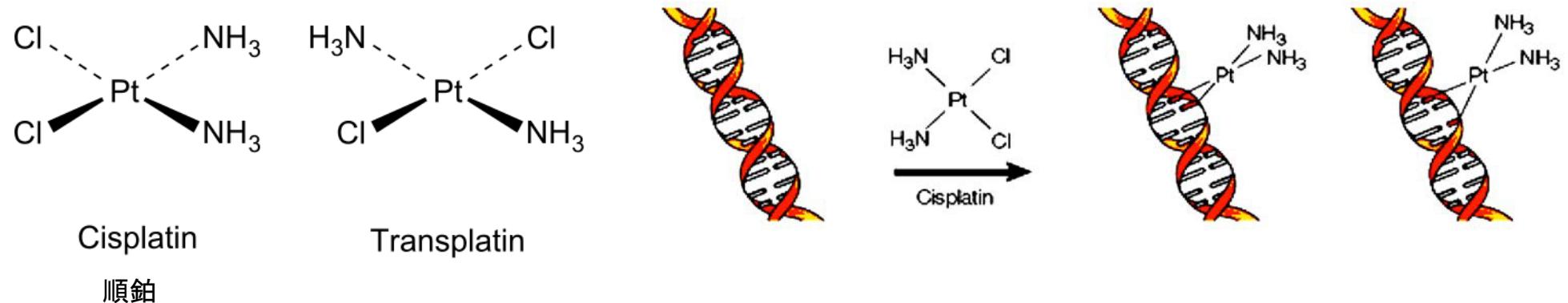
H atom and CH<sub>3</sub> group on  
**same** side of chain



**trans-isoprene**  
(gutta percha)

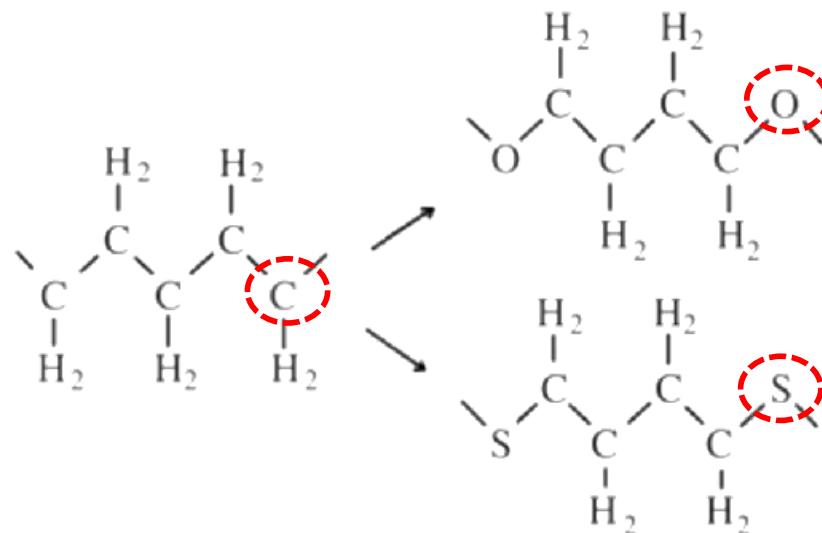
H atom and CH<sub>3</sub> group on  
**opposite** sides of chain

# cis/trans Isomerism

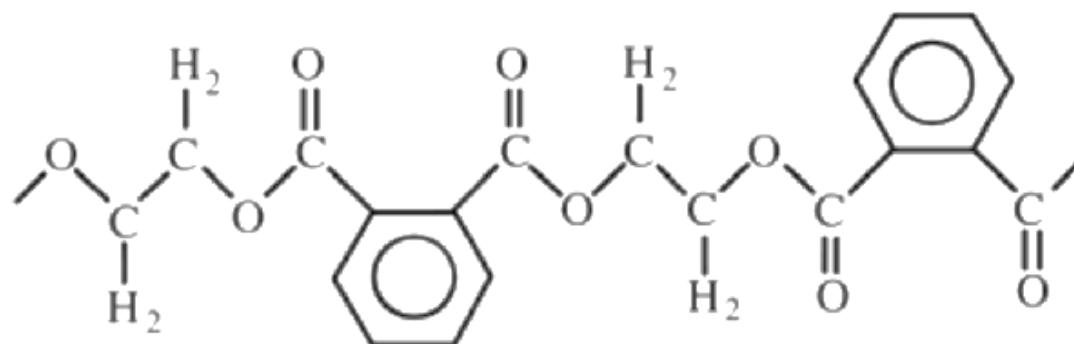


# Effect of Composition

Chemical composition of the backbone (the main molecular chain) or of side chains)



Flexible

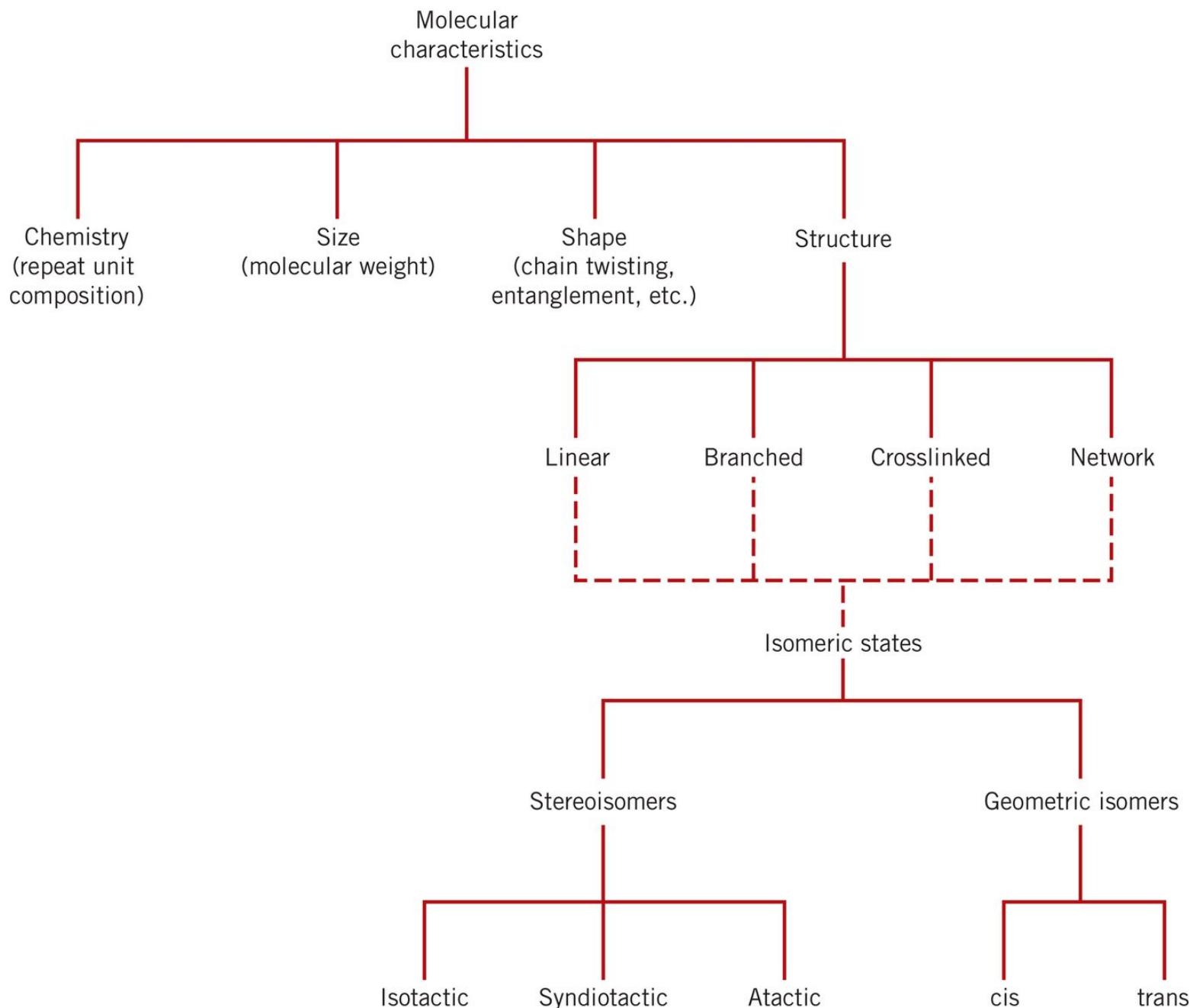


polyethylene terephthalate

(polyester, Dacron®)

stiffer

# Classification for the characteristics of polymer molecules



Adapted from Fig. 4.9, Callister & Rethwisch 5e.

# Copolymers (共聚物)

two or more monomers  
polymerized together

- **random** – A and B randomly positioned along chain
- **alternating** – A and B alternate in polymer chain
- **block** – large blocks of A units alternate with large blocks of B units
- **graft** – chains of B units grafted onto A backbone

A – ●

B – ●

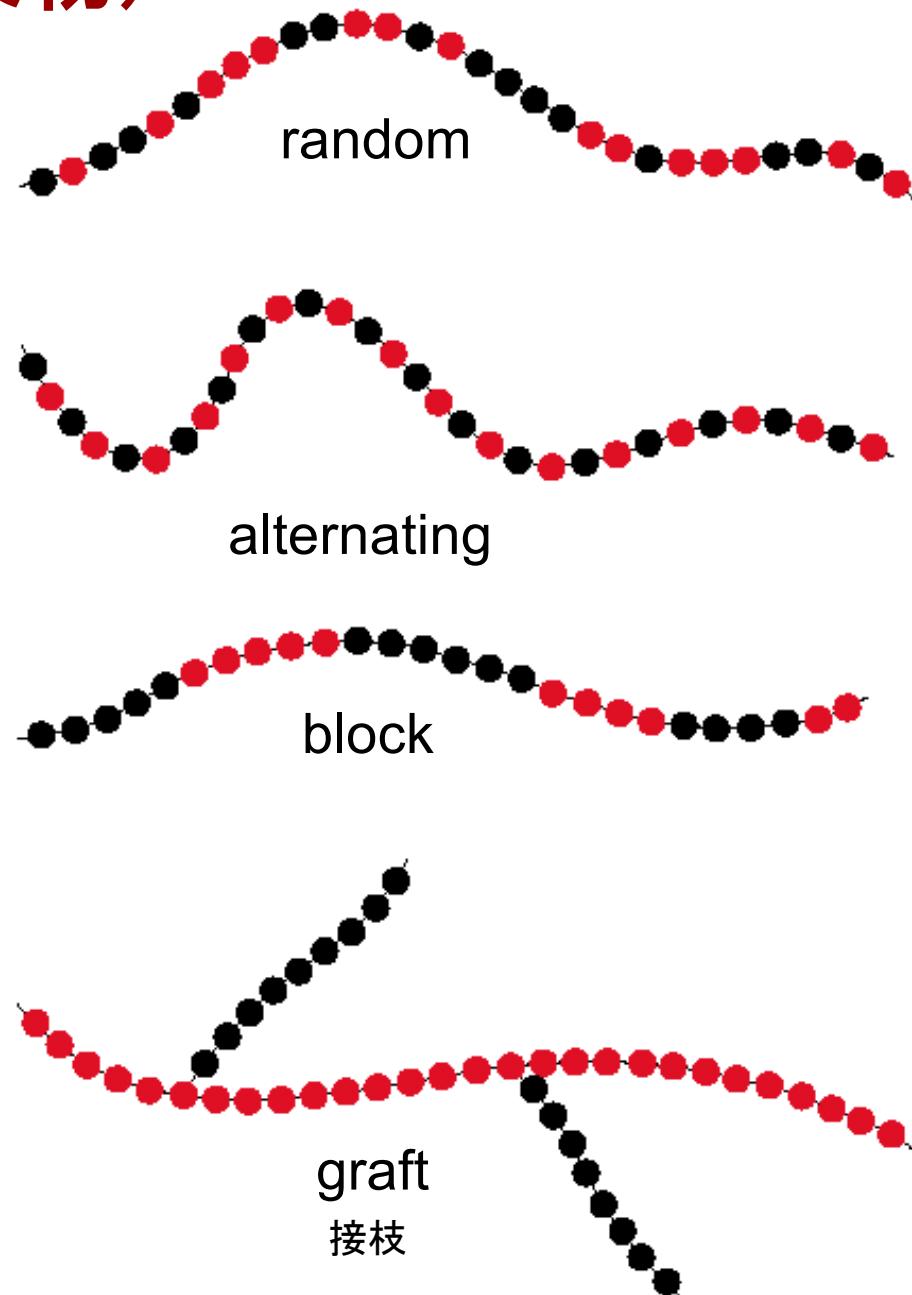
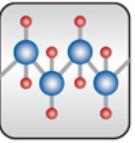
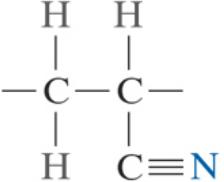
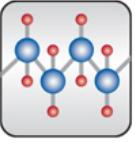
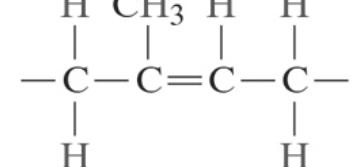
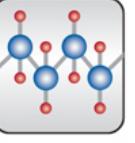
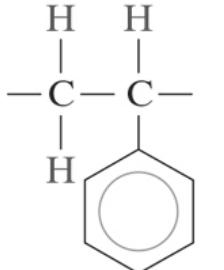
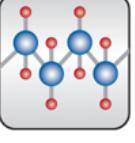
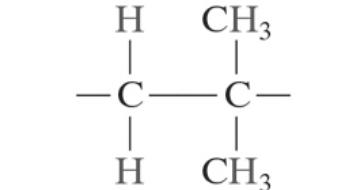
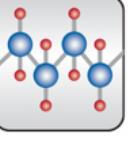
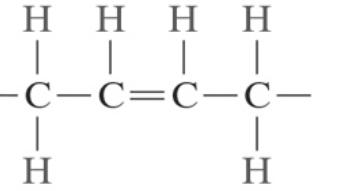
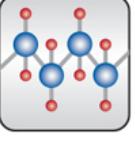
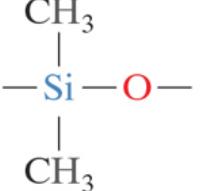
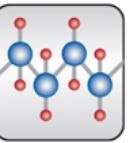
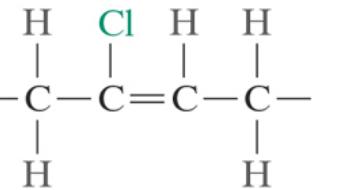
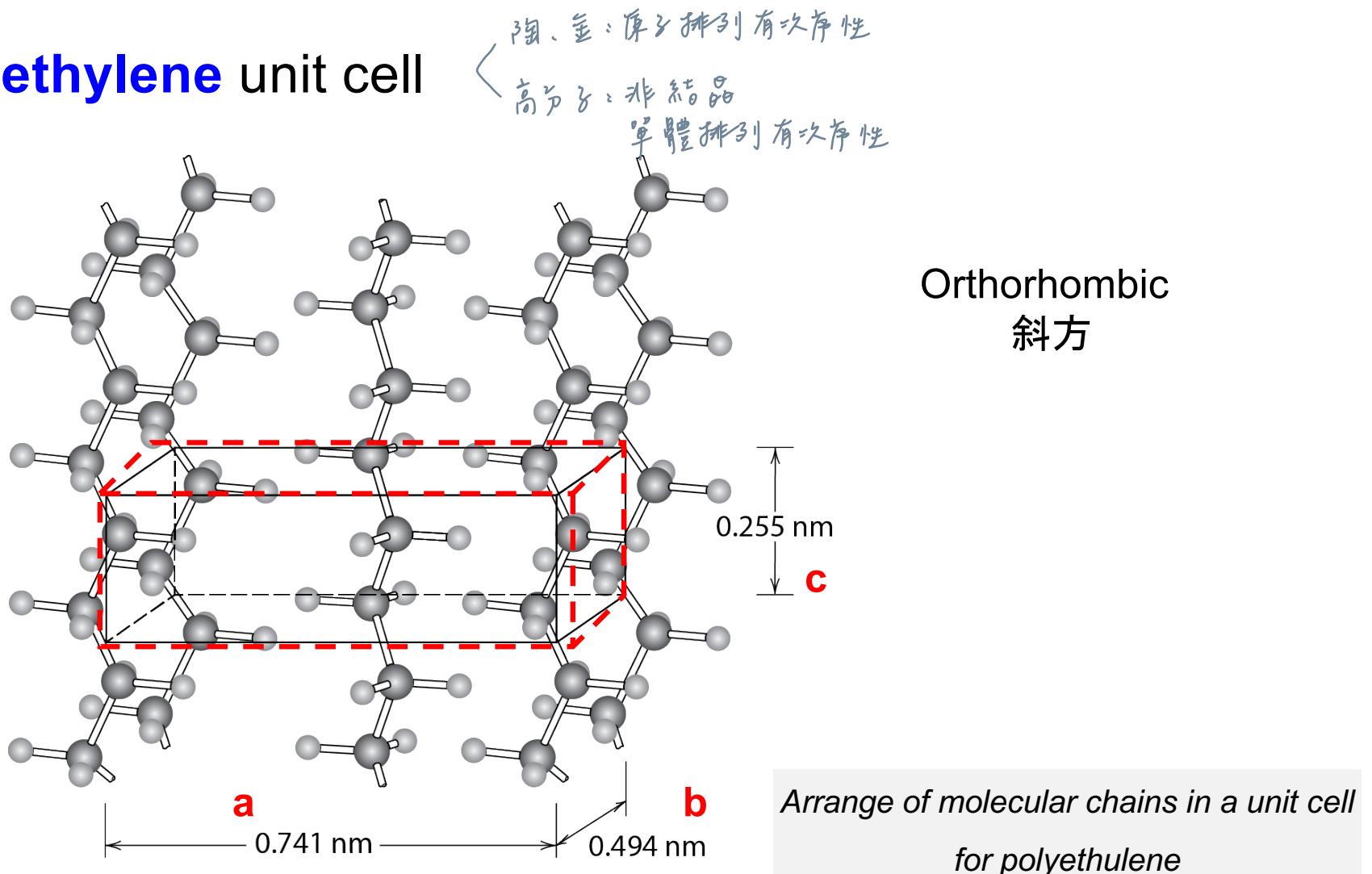


Table 4.5 Chemical Repeat Units - Copolymer Rubbers

<i>Repeat Unit Name</i>	<i>Repeat Unit Structure</i>	<i>Repeat Unit Name</i>	<i>Repeat Unit Structure</i>
 <b>VMSE</b> Repeat Units for Rubbers	Acrylonitrile  $\begin{array}{c} \text{H} & \text{H} \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{C}\equiv\text{N} \end{array}$	 Isoprene  $\begin{array}{c} \text{H} & \text{CH}_3 & \text{H} & \text{H} \\   &   &   &   \\ -\text{C} & -\text{C}=\text{C} & -\text{C}- & \text{C}- \\   & & &   \\ \text{H} & & & \text{H} \end{array}$	
 Styrene  $\begin{array}{c} \text{H} & \text{H} \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{C}_6\text{H}_5 \end{array}$		 Isobutylene  $\begin{array}{c} \text{H} & \text{CH}_3 \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{H} & \text{CH}_3 \end{array}$	
 Butadiene  $\begin{array}{c} \text{H} & \text{H} & \text{H} & \text{H} \\   &   &   &   \\ -\text{C} & -\text{C}=\text{C} & -\text{C} & -\text{C}- \\   & &   &   \\ \text{H} & & \text{H} & \text{H} \end{array}$		 Dimethylsiloxane  $\begin{array}{c} \text{CH}_3 \\   \\ -\text{Si} & -\text{O}- \\   \\ \text{CH}_3 \end{array}$	
 Chloroprene  $\begin{array}{c} \text{H} & \text{Cl} & \text{H} & \text{H} \\   &   &   &   \\ -\text{C} & -\text{C}=\text{C} & -\text{C} & -\text{C}- \\   & &   &   \\ \text{H} & & \text{H} & \text{H} \end{array}$			(P)DMS

# Crystallinity in Polymers

- Ordered atomic arrangements involving **molecular chains**
- Crystal structures in terms of unit cells
- **Polyethylene** unit cell



# Polymer Crystallinity (聚合物結晶度)

- Usually partial crystalline
- Chain disorder or misalignment will results in amorphous region could influence the degree of crystallinity.
- Twisting, kinking, coiling (prevent the strict ordering of every segment of every chain)
- The density of a crystalline polymer will be greater than an amorphous one (closely packed)

$$\% \text{ crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100 \quad (4.8)$$

$\rho_s$ : Specimen density to be determined

$\rho_c$ : density of the perfectly crystalline

$\rho_a$ : density of totally amorphous

Degree of crystalline

- Cooling rate 高速降低溫度
- Linear/branched
- Co-Polymer/irregular-random

# Computations of the Density and Percent Crystallinity of Polyethylene

## (a) Density of PE ( $C_2H_4$ )

n: 2

$$A = 2(A_c) + 4(A_H) = 28.05 \text{ g/mol}$$

$$\begin{aligned} V_c &= (0.741 \text{ nm})(0.494 \text{ nm})(0.225 \text{ nm}) \\ &= 9.33 \times 10^{-23} \text{ cm}^3/\text{unit cell} \end{aligned}$$

$$\rho = \frac{nA}{V_c N_A}$$

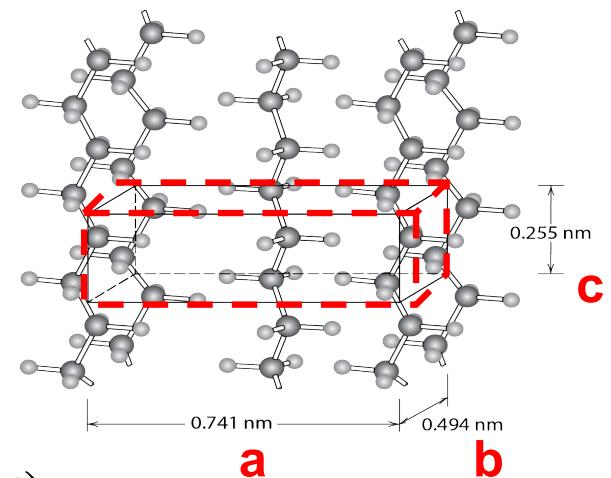
$$\rho = \frac{(2 \text{ rep u/u cell}) \times (28.05 \text{ g/mol})}{(9.33 \times 10^{-23} \text{ cm}^3/\text{unit cell})(6.022 \times 10^{23} \text{ rep u/mol})}$$

$$= 0.998 \text{ g/cm}^3$$

Number of formula units/unit cell

$$\rho = \frac{n'(\Sigma A_c + \Sigma A_A)}{V_c N_A}$$

Volume of unit cell



## Computations of the Density and Percent Crystallinity of Polyethylene

### (b) Calculate the % crystallinity of PE

(✓)  $\rho_c = 0.998 \text{ g/cm}^3$

(✗)  $\rho_a = 0.870 \text{ g/cm}^3$

$\rho_s = 0.925 \text{ g/cm}^3$

$$\% \text{ crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

$$\begin{aligned}\% \text{ Crystallinity} &= \frac{0.998 (0.925 - 0.870)}{0.925 (0.998 - 0.870)} \times 100 \\ &= 46.4\%\end{aligned}$$

# Effect of Side-Chain Substitution, Crosslinking, and Branching

- Increasing the size of side groups in linear polymers such as polyethylene will decrease the melting temperature due to the lesser perfection of molecular packing, i.e., decreased crystallinity.

自由移动性差

- Crosslinking of the main chains** lowers the melting temperature.

- This is due to the interference of crosslinking, which causes lesser mobility of the chains, resulting in further retardation of the crystallization rate.

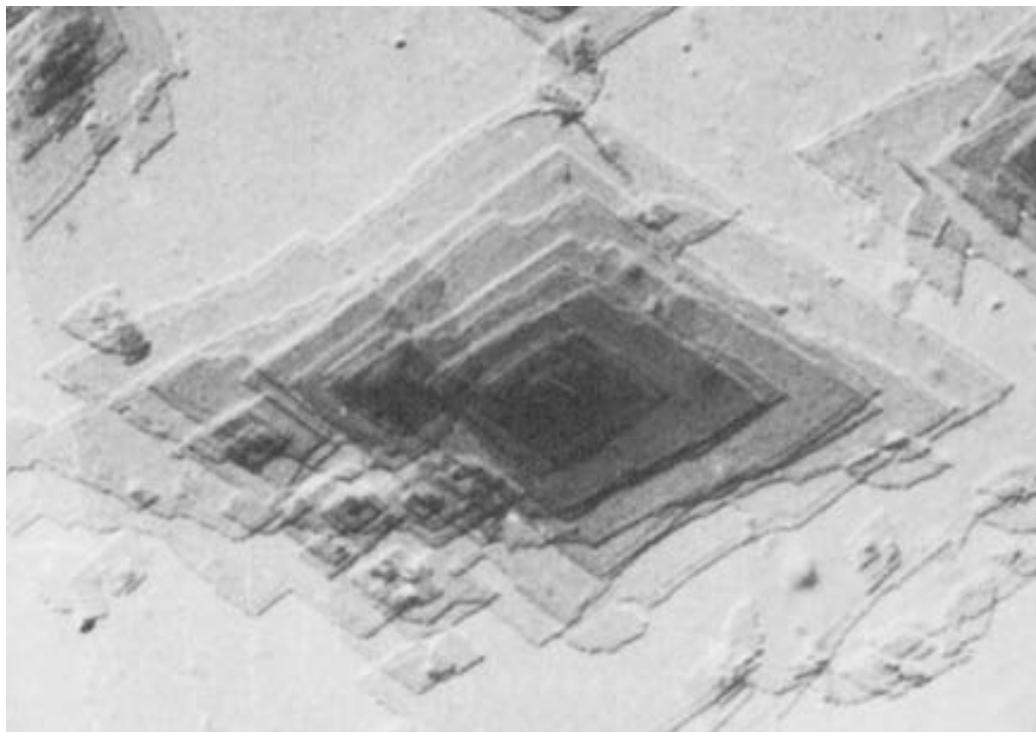
- When the **crosslinking density increases** for a rubber, the material becomes harder and the glass transition temperature also increases.

Table 7-4. Effect of Side Chain Substitution on Melting Temperature in Polyethylene

Side chain ↑, 熔点降低、结晶度 ↓	$T_m$ (°C)
-H	140
-CH <sub>3</sub>	165 melting temperature ↓
-CH <sub>2</sub> CH <sub>3</sub>	124
-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	75
-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	-55
-CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	196
CH <sub>3</sub>	
CH <sub>3</sub>	
-CH <sub>2</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -CH <sub>2</sub> CH <sub>3</sub>	350
CH <sub>3</sub>	

# Polymer Single Crystals

- Electron micrograph – multilayered single crystals (chain-folded layers) of polyethylene
- Single crystals – only for slow and carefully controlled growth rates



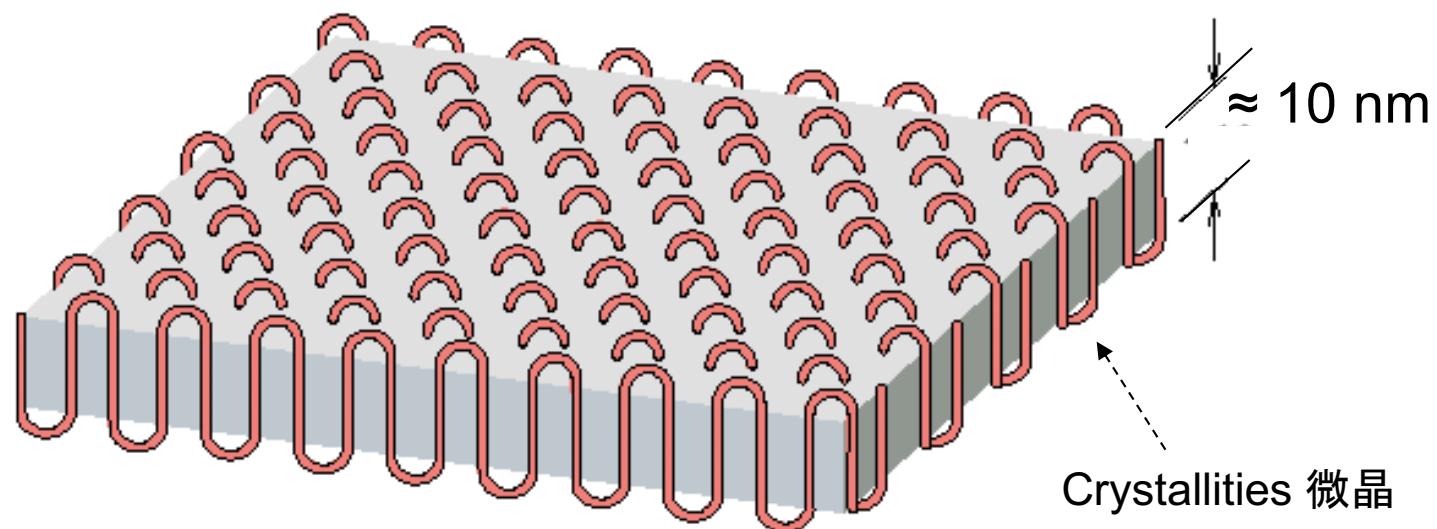
1 μm

Single crystal of a polyethylene  
acquired from electron micrograph

Crystallites

# Polymer Crystallinity (聚合物結晶度)

- Crystalline regions
  - thin platelets with chain folds at faces
  - Chain folded structure (鏈折疊結構)

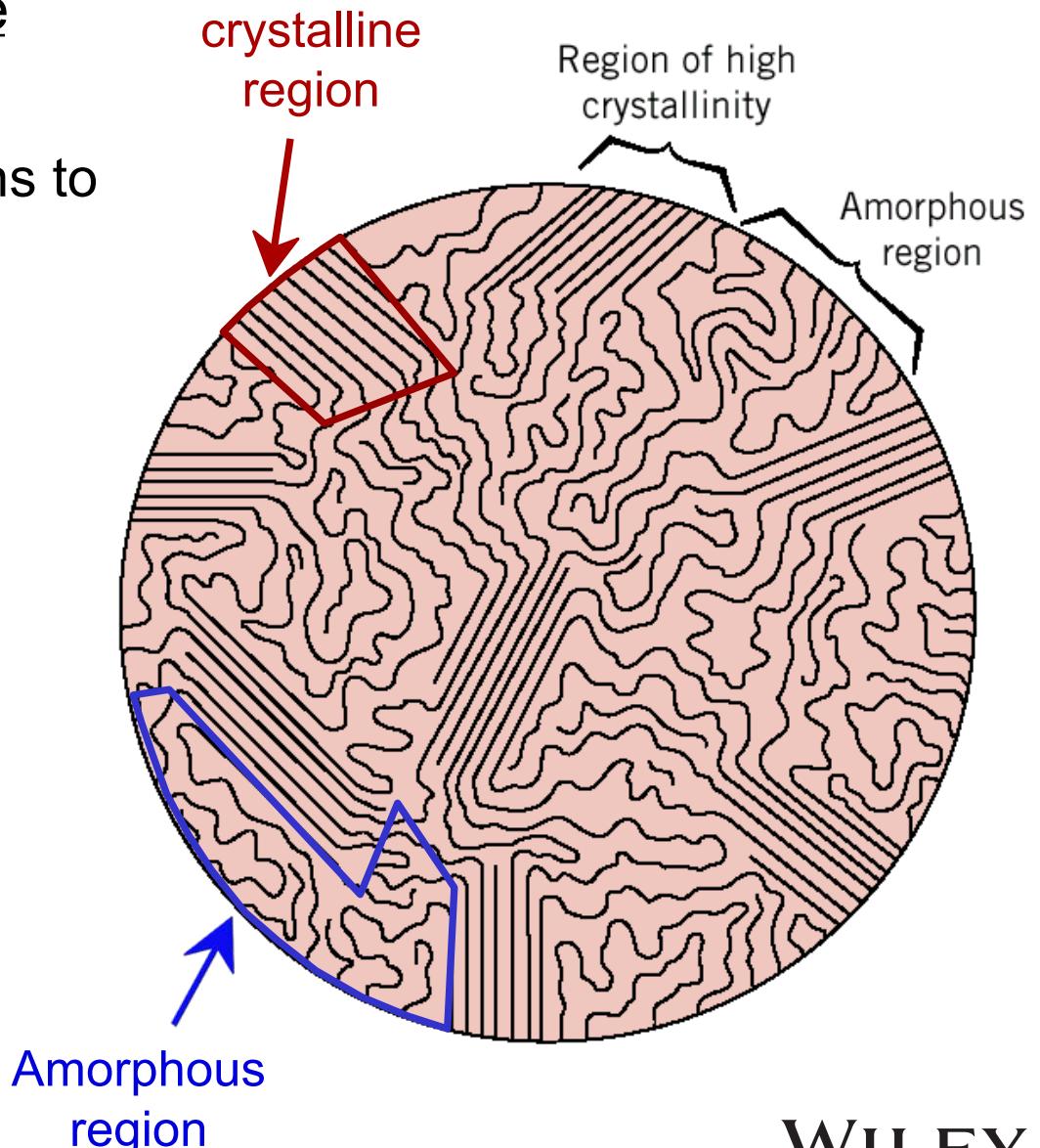


*The chain-folded structure for a plate-shaped polymer crystallite*

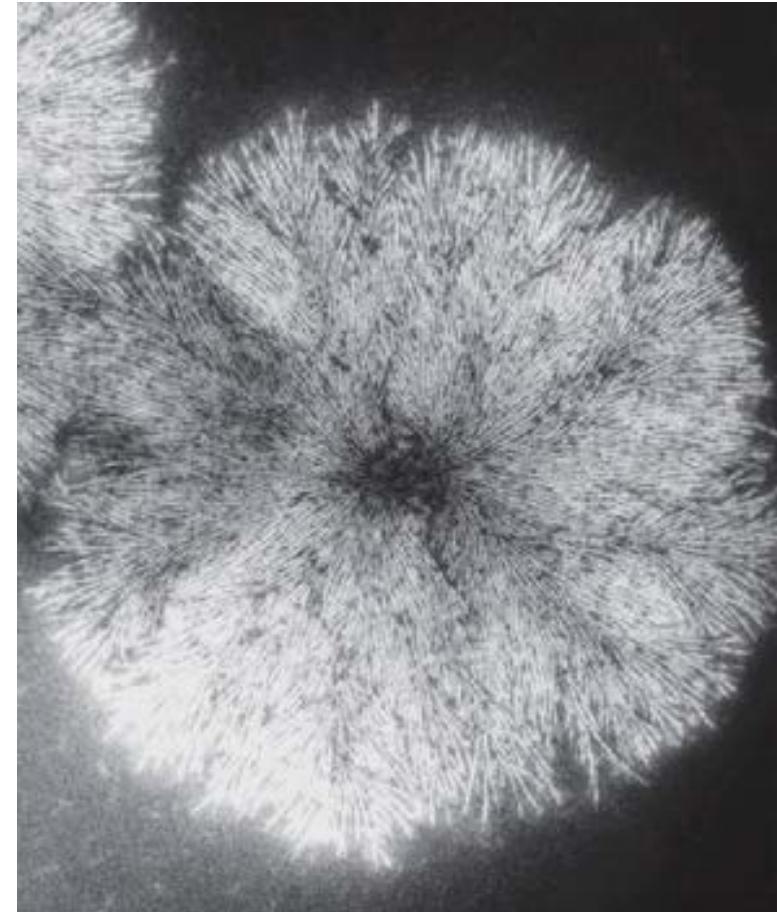
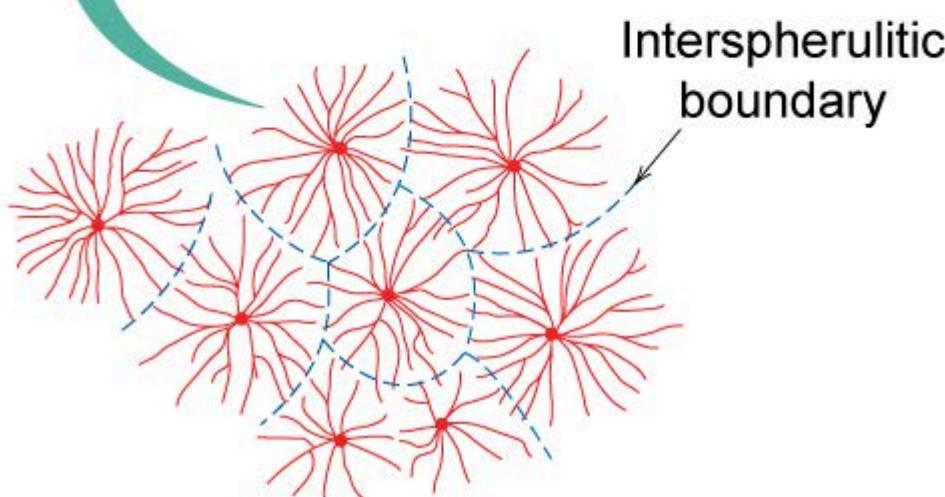
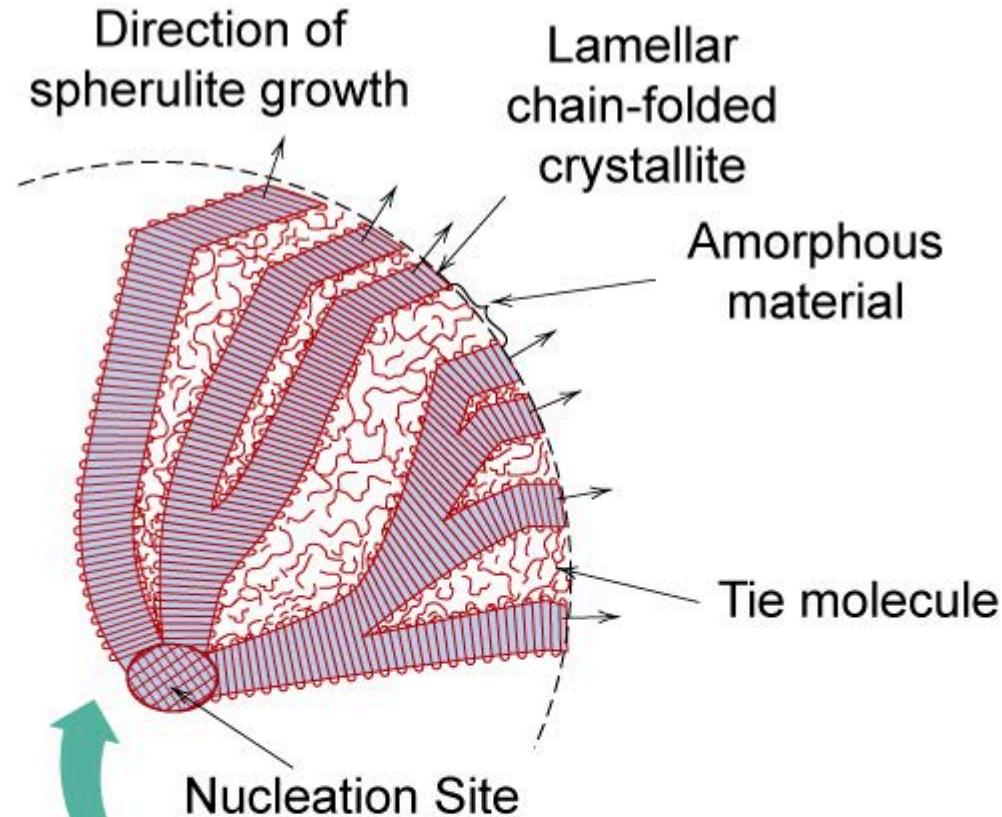
# Polymer Crystallinity

Polymers rarely 100% crystalline

- Difficult for all regions of all chains to become **aligned**
- **Degree of crystallinity**  
expressed as **% crystallinity**.
  - Some physical properties depend on % crystallinity.
  - Heat treating causes crystalline regions to grow and % crystallinity to increase.



# Semi-crystalline Polymers



TEM images of natural rubber specimen

- Some semi-crystalline polymers form **spherulite** (球晶) structures
- Alternating chain-folded crystallites and amorphous regions
- Spherulite structure for relatively rapid growth rates

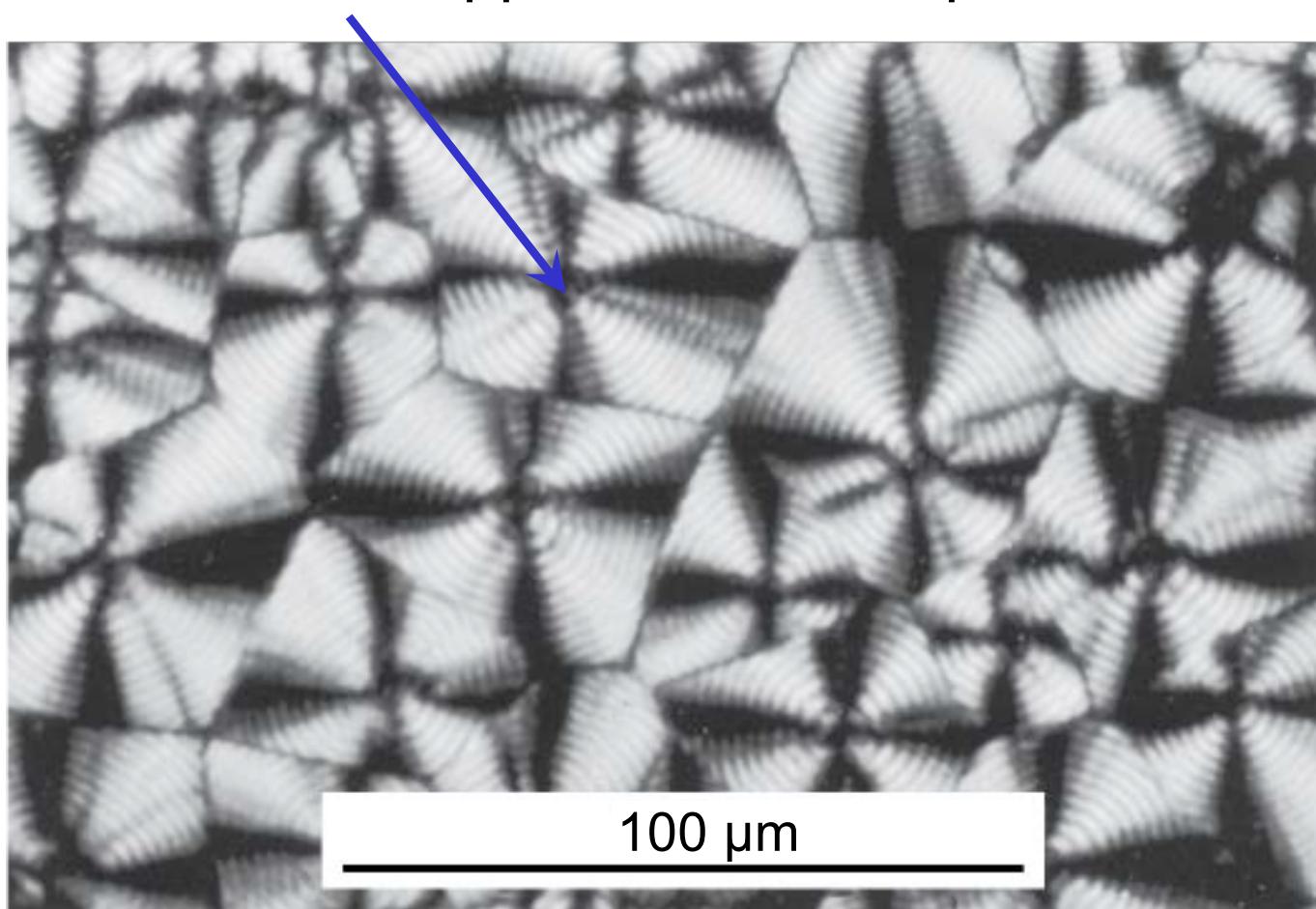
# Photomicrograph – Spherulites in Polyethylene

Cross-polarized light used

-- a maltese cross appears in each spherulite



[https://en.wikipedia.org/wiki/Maltese\\_cross#/media/File:Maltese\\_cross.svg](https://en.wikipedia.org/wiki/Maltese_cross#/media/File:Maltese_cross.svg)



Courtesy F. P. Price, General Electric Company

Fig. 4.14, Callister & Rethwisch 5e.

# Effect of Temperature on Polymer Properties

The Glassy state



T<sub>g</sub>  
玻璃界點

The Rubbery state



## The Rubbery state

- Amorphous
- Random coils have enough thermal energy for rotation to occur around single bonds.
- When melting, each random coil is continuously changing shape.
- Soft, flexible and extensible, due to the molecular motion available to the molecules.

## The Glassy state

- Temperature drops, the rate of rotation around main chain bonds becomes slower and the chain gets stiffer.
- At a low enough temperature, single bond rotation ceases and the interpenetrated random coils become frozen in space. (the glassy state)
- The temperature where single bond rotation ceases is called the glass transition temperature ( $T_g$ )
- $< T_g$ , hard, stiff and brittle.

# Effect of Temperature on Polymer Properties

## Glass transition temperature ( $T_g$ ) 玻璃轉化溫度

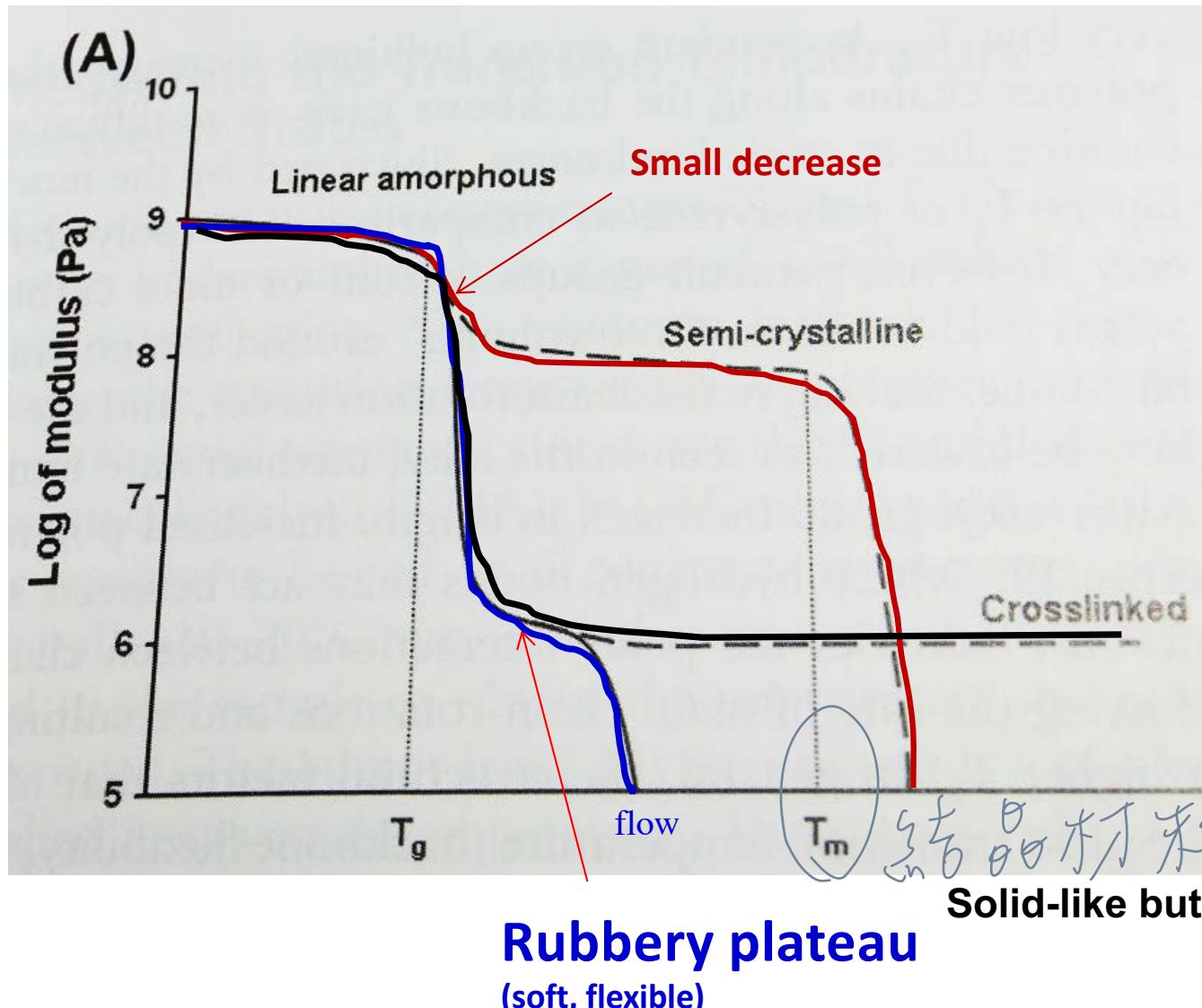
- In the liquid or melt state, a noncrystalline polymer possesses enough thermal energy for linking segments of each polymer to move randomly.
- As the melt is cooled, a temperature is eventually reached at which all long-range segmental motions cease.

## Crystalline melting temperature ( $T_m$ )

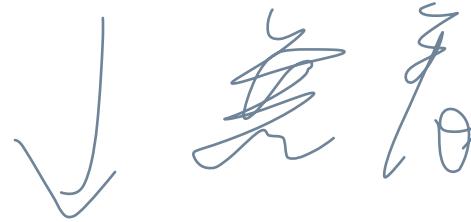
- Melting refers to the **loss of crystallinity**, begin to flow.

# Effect of Temperature on Polymer Properties

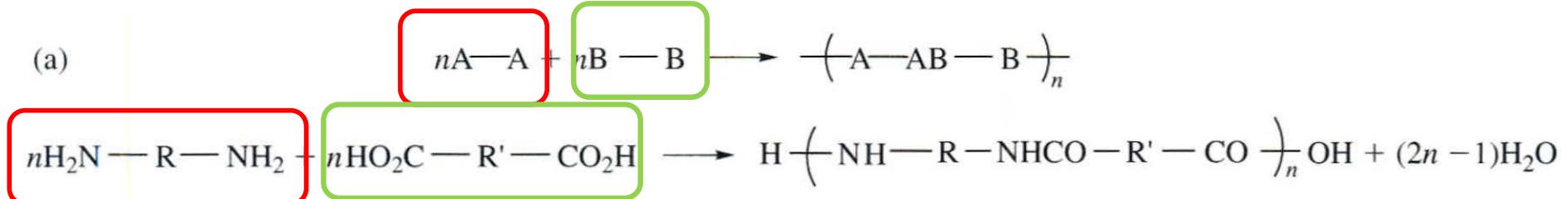
Conformation affects polymer modulus as a functional of temperature



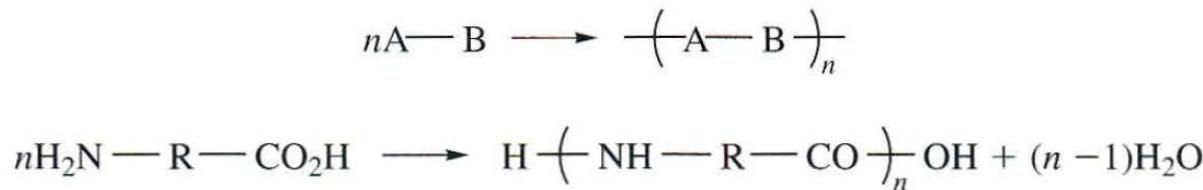
# Condensation



(a)



(b)



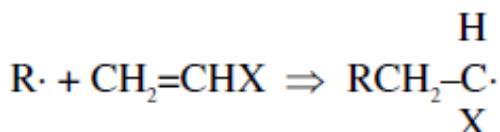
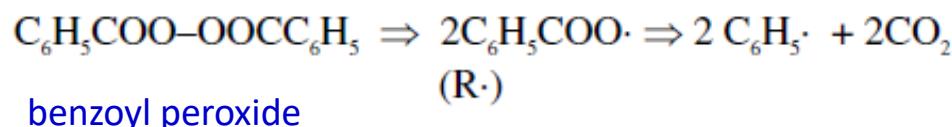
**Figure 2.29**

Condensation, or step reaction, polymerization mechanisms can be classified into two general groups, depending upon the types of monomers involved in the reaction. (a) The first group involves bifunctional or polyfunctional monomers, with each monomer possessing only one type of functional group. (b) The second group involves a single monomer species having both types of functional groups. In this figure, the general equation for each reaction mechanism (A and B are two different types of functional groups) is followed by an example reaction. (Adapted with permission from [10].)

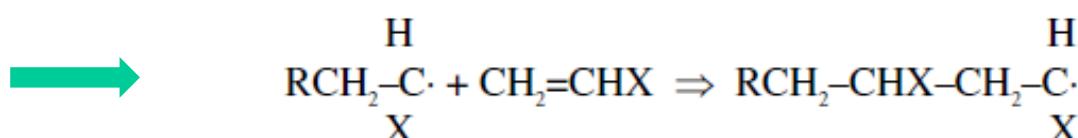
# Addition or Free Radical Polymerization

## (1) Initiation

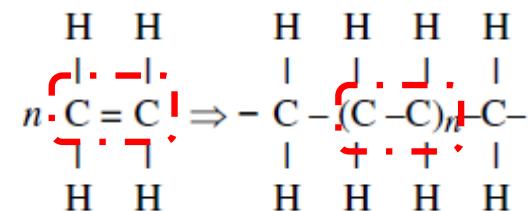
Free radical as initiator



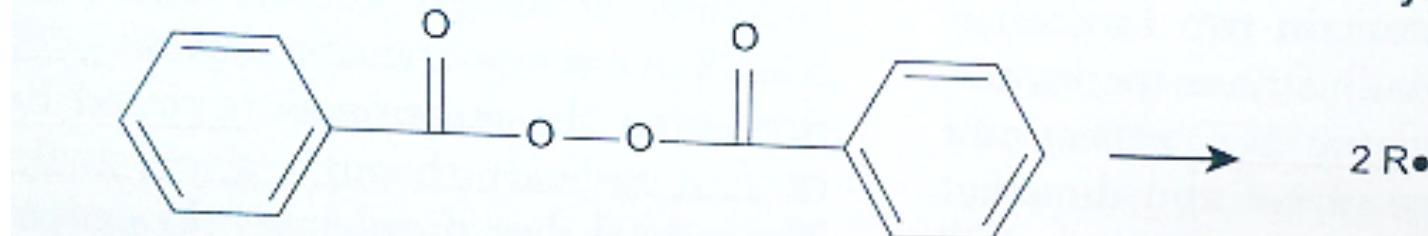
The breaking of a double bond can be made with an initiator



The free radicals (initiators) can react with monomers



Initiation - free radicals are generated through the decomposition of benzoyl peroxide.

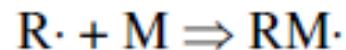


LEY

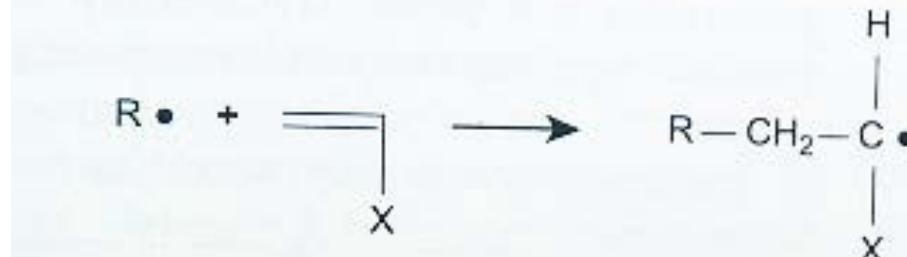
Chapter 4 -

# Addition or Free Radical Polymerization

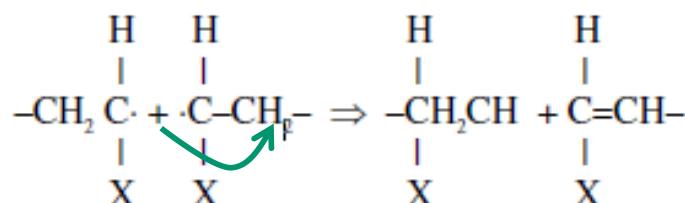
## (2) Propagation



Propagation - free radicals produce polymer chains through addition across carbon-carbon double bonds. X denotes a generic side group.

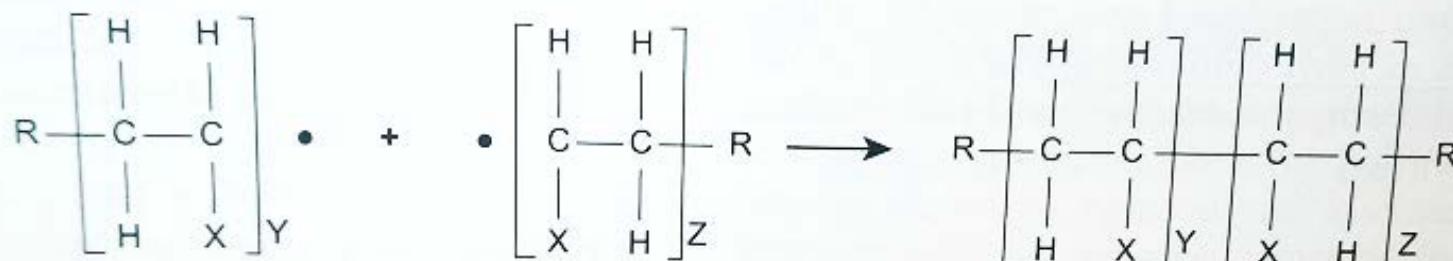


## (3) Termination



Disproportionate termination

Termination - two free radicals react to form a single bond through coupling to form one polymer chain.



Thank you for your attention