Chapter 9 **Polymers**

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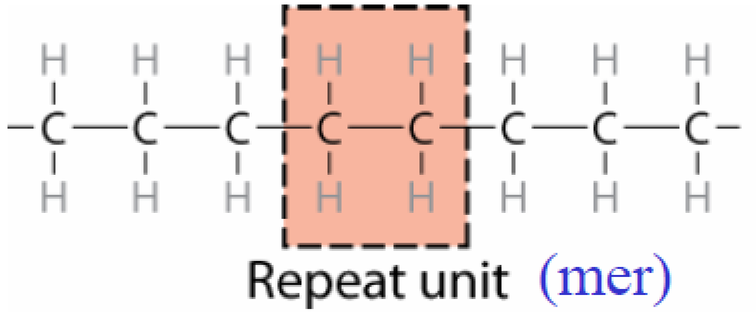
Introduction

- **Polymers – materials consisting of *polymer molecules*** that consist of repeated chemical units (`mers') joined together, like beads on a string. Some polymer molecules contain hundreds or thousands of monomers and are often called *macromolecules.*
- Polymers may be **natural, such as leather, rubber,** cellulose or DNA, or **synthetic, such as nylon or** polyethylene.

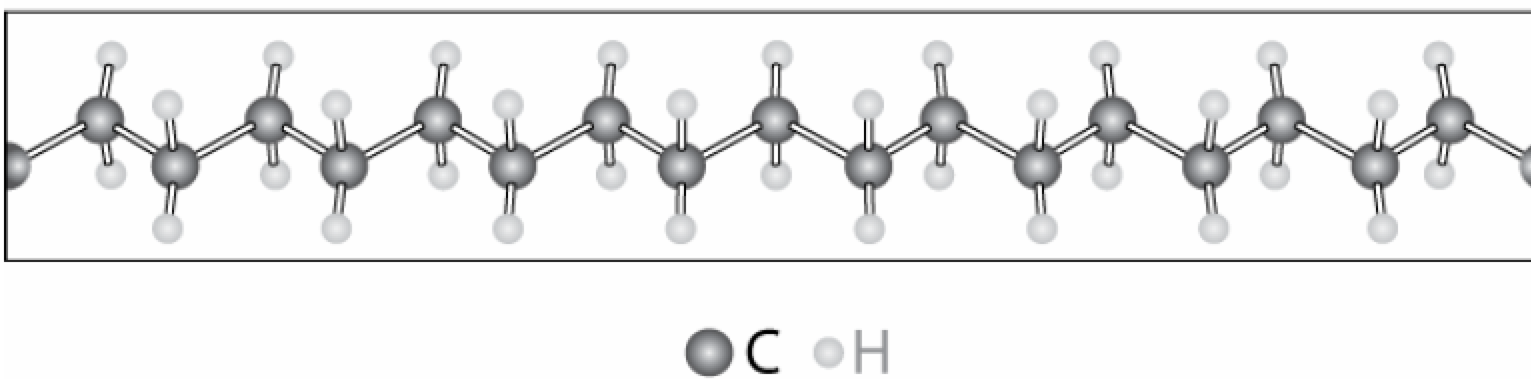
Many of important current research problems and technological applications involve polymers. Living organisms are mainly composed of polymerized amino acids (proteins) nucleic acids (RNA and DNA), and other *biopolymers. The most powerful* computers - our brains - are mostly just a complex polymer material soaking in salty water. We are just making first small steps towards understanding of biological systems.

Polymer molecules

- Polymer molecules can be very large (macromolecules)
- Most polymers consist of long and flexible chains with a string of C atoms as a backbone
- Side-bonding of C atoms to H atoms or radicals (an organic group of atoms that remains as a unit and maintains their identity during chemical reactions (e.g. CH_3, C_2H_5, C_6H_5))
- Double bonds are possible in both chain and side bonds
- Repeat unit in a polymer chain ("unit cell") is a **mer**
- Small molecules from which polymer is synthesized is **monomer. A single mer is sometimes also called a monomer.**



polyethylene (e.g. paraffin wax for candles)

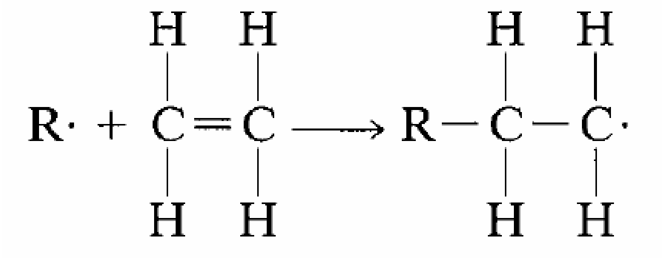


Chemistry of polymer molecules (I)

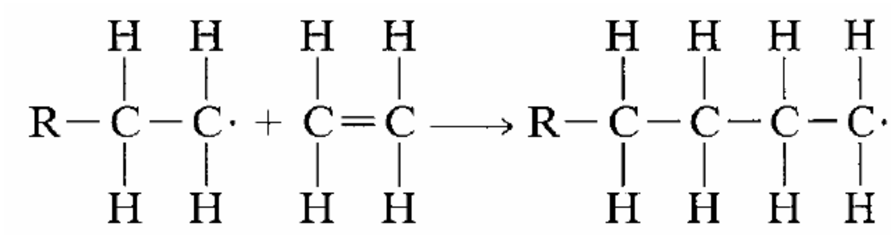
- Ethylene (C_2H_4) is a gas at room temp and pressure.
- Ethylene transform to polyethylene (solid) by forming active mer through reaction with initiator or catalytic radical (R**.)**
- (**.) denotes unpaired electron (active site)**

Polymerization

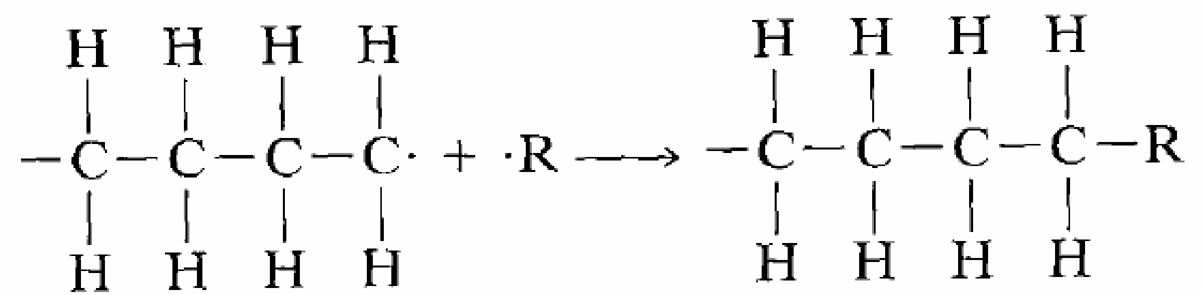
1. Initiation reaction:



2. Rapid propagation ~1000 mer units in 1-10 ms:

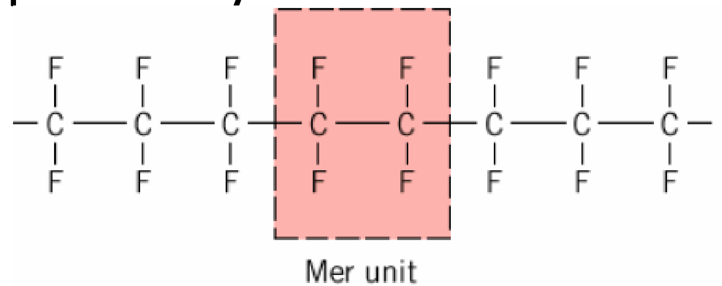


3. Termination when two active chain ends meet each other or active chain end meet with initiator or other species with single active bond:

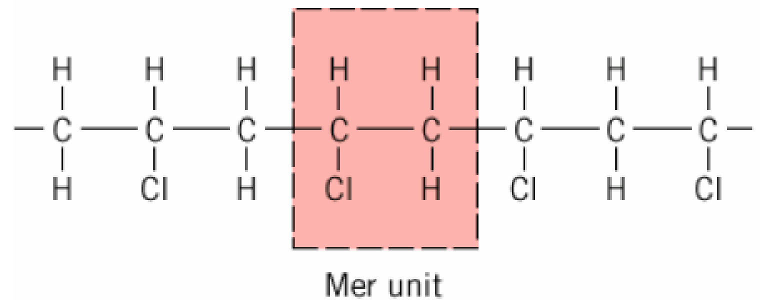


Chemistry of polymer molecules (II)

- hydrogen atoms in polyethylene are replaced by fluorine: polytetraflouroethylene PTFE – Teflon.

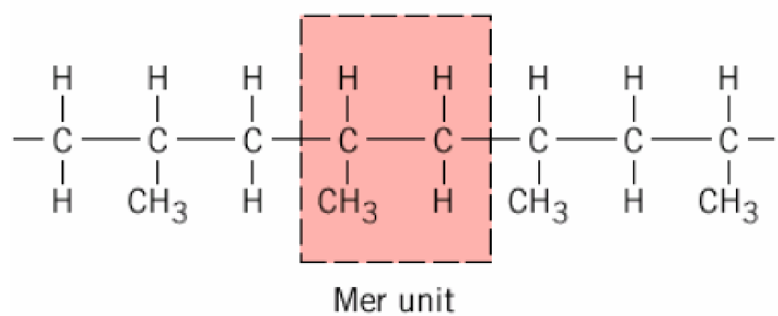


- every fourth hydrogen atom in polyethylene is replaced with chlorine: poly(vinyl chloride) PVC.



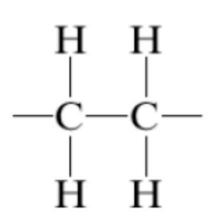
- every fourth hydrogen atom in polyethylene is replaced with methyl group (CH_3): polyproplylene PP

More examples on pp. 539-540 of the textbook



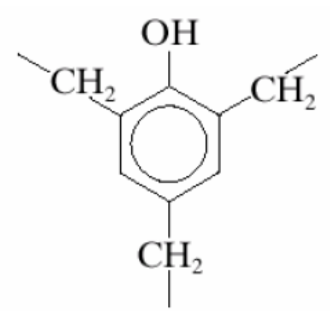
Chemistry of polymer molecules (III)

- When all mers are the same, the molecule is called a **homopolymer.**
- When there is more than one type of mer present, the molecule is a **copolymer.**
- Mer units that have 2 active bonds to connect with other mers are called **bifunctional.**
- Mer units that have 3 active bonds to connect with other mers are called **trifunctional. They form three-dimensional** molecular network structures



Polyethilene

(bifunctional)



Phenol-formaldehyde

(trifunctional)

Molecular weight

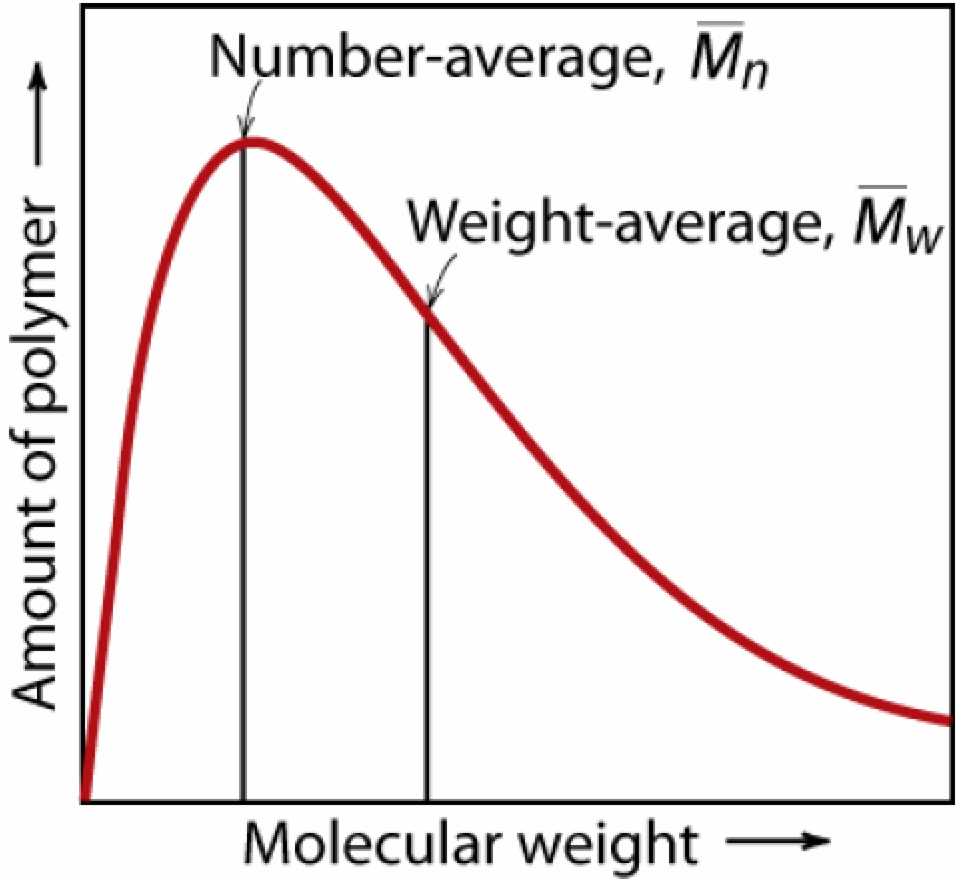
- The molecular weight (chain length) is controlled by the synthesis process: Relative rates of initiation, propagation, termination steps of polymerization.
- Formation of macromolecules during polymerization results in a distribution of chain lengths and molecular weights.
- The average molecular weight can be obtained by averaging the masses with the fraction of times they appear (**number average molecular weight) or with the mass fraction of the** molecules (**weight-average molecular weight).**

number-average:

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

weight-average:

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



w_i is weight fraction of chains of length *i*
x_i is number fraction of chains of length *i*

Molecular weight: Example illustrating the difference between number-average and weight-average

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 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?

Solution:

The first step is to sort the students into weight ranges (let's use 40 lb ranges).

weight range	# of students	mean weight	number fraction	weight fraction
	N_i	M_i	x_i	w_i
81-120	2	110	0.2	0.117
121-160	2	142	0.2	0.150
161-200	3	184	0.3	0.294
201-240	2	223	0.2	0.237
241-280	0	-	0	0.000
281-320	0	-	0	0.000
321-360	0	-	0	0.000
361-400	1	380	0.1	0.202

$$\sum N_i = 10 \quad \sum N_i M_i = 1881 \quad x_i = N_i \Big/ \sum N_i \quad w_i = N_i M_i \Big/ \sum N_i M_i$$

$$\overline{M}_n = \sum x_i M_i = 0.2\times110 + 0.2\times142 + 0.3\times184 + 0.2\times223 + 0.1\times380 = 188\ lb$$

$$\overline{M}_w = \sum w_i M_i = 0.117\times110 + 0.150\times142 + 0.294\times184 + 0.237\times223 + 0.202\times380 = 218\ lb$$

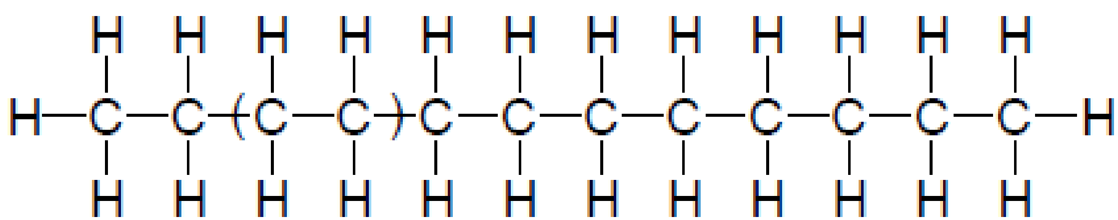
$$\overline{M}_w > \overline{M}_n$$

Degree of polymerization

- Alternative way to express average polymer chain size is **degree of polymerization - the average number of** mer units in a chain:

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

$\overline{m}$ is the average molecular weight of repeat unit
for copolymers it is calculated as $\overline{m}=\Sigma f_i m_i$
(f_i is fraction of mer i of molecular weight m_i)



$DP = 6$

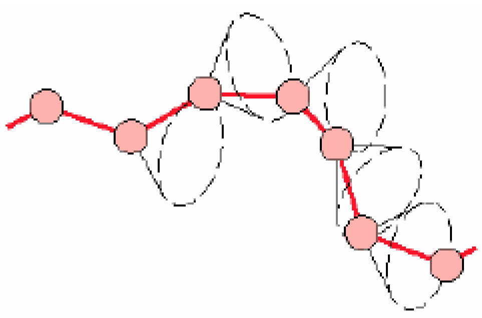
Properties of polymers depend on molecular weight

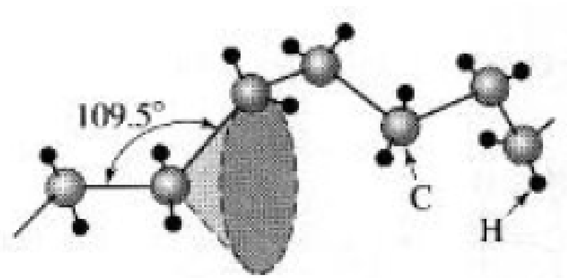
• Melting/softening temperatures increase with molecular weight (up to ~ 100,000 g/mol)

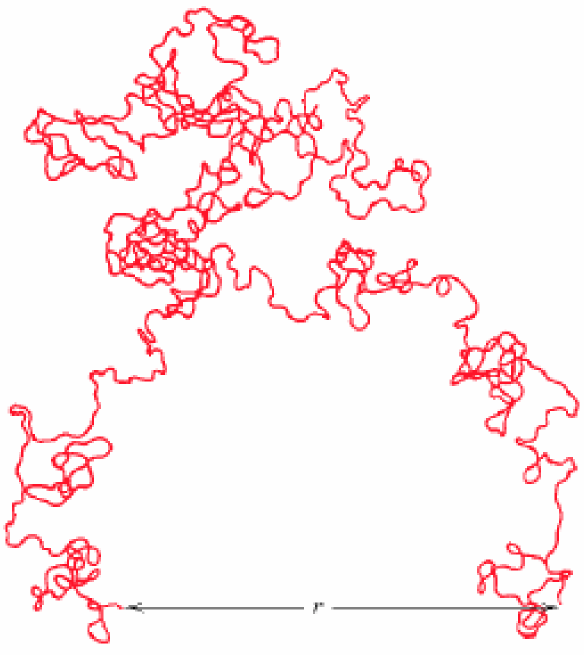
• At room temperature, short chain polymers (molar weight ~ 100 g/mol) are liquids or gases, intermediate length polymers (~ 1000 g/mol) are waxy solids, solid polymers (sometimes called *high polymers) have* molecular weights of 10^4 - 10^7 g/mol

Molecular shape (conformation)

- The angle between the singly bonded carbon atoms is ~109° – carbon atoms form a zigzag pattern in a polymer molecule.
- Moreover, while maintaining the 109° angle between bonds polymer chains can rotate around single C-C bonds (double and triple bonds are very rigid).
- Random kinks and coils lead to entanglement, like in the spaghetti structure:

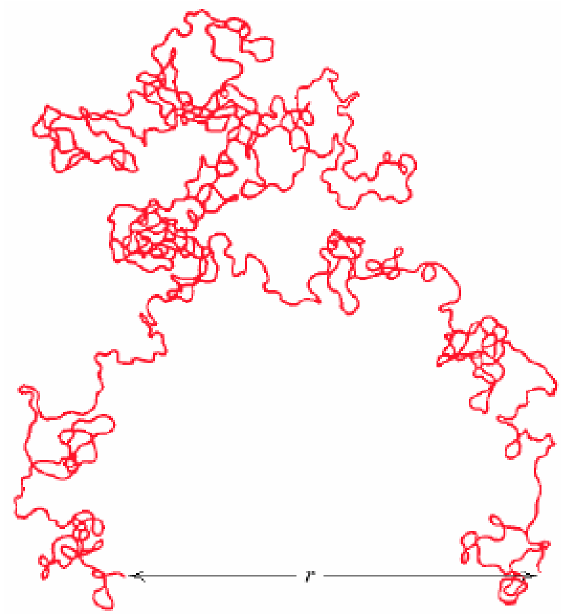






Molecular shape (conformation)

- Molecular chains may thus bend, coil and kink
- Neighboring chains may intertwine and entangle
- Large elastic extensions of rubbers correspond to unraveling of these coiled chains
- Mechanical / thermal characteristics depend on the ability of chain segments to rotate



chain end-to-end distance, r

Molecular structure (I)

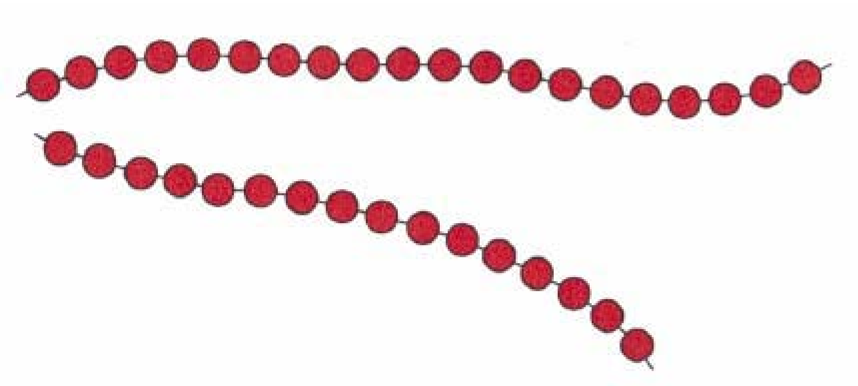
- The physical characteristics of polymer material depend not only on molecular weight and shape, but also on molecular structure:

1 Linear polymers: Van der Waals bonding between chains. Examples: polyethylene, nylon.

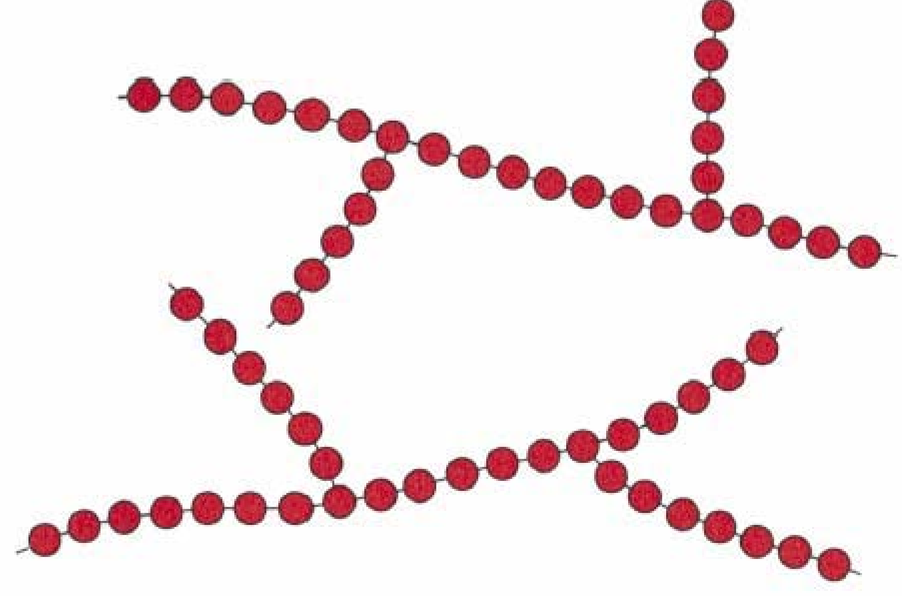
2 Branched polymers: Chain packing efficiency is reduced compared to linear polymers - lower density

3 Cross-linked polymers: Chains are connected by covalent bonds. Often achieved by adding atoms or molecules that form covalent links between chains. Many rubbers have this structure.

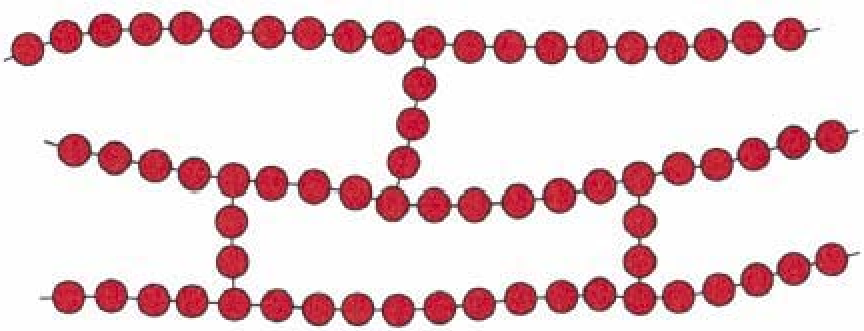
4 Network polymers: 3D networks made from trifunctional mers. Examples: epoxies, phenolformaldehyde



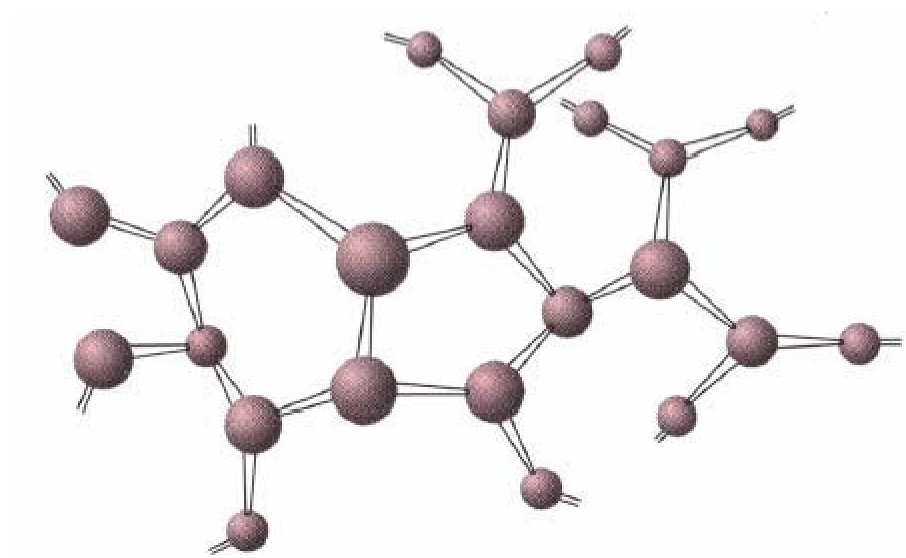
Linear polymers



Branched polymers



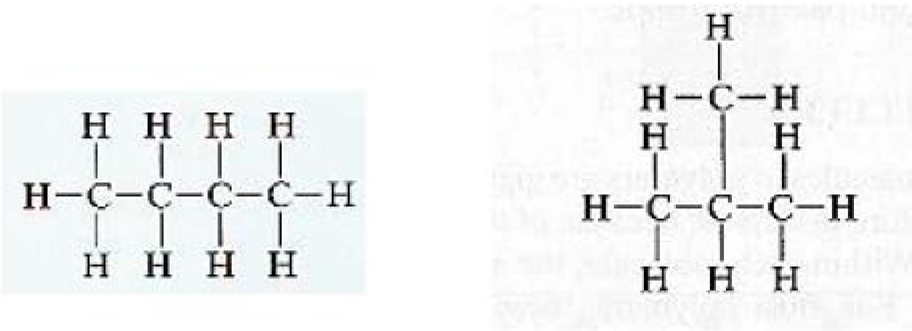
Cross-linked polymers



Network polymers

Isomerism

- **Isomerism: Hydrocarbon compounds with same** composition may have different atomic arrangements.
- Physical properties may depend on **isomeric state** (e.g. boiling temperature of normal butane is -0.5 ^{o}C, of isobutane -12.3 ^{o}C).

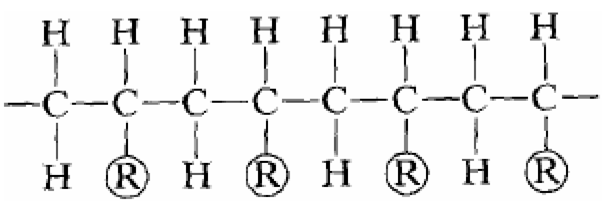


Butane → C_4H_{10} ← Isobutane

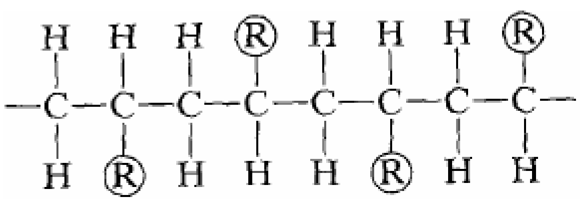
- **Two types of isomerism in polymers are possible:** stereoisomerism and geometrical isomerism

Stereoisomerism & Geometrical isomerism

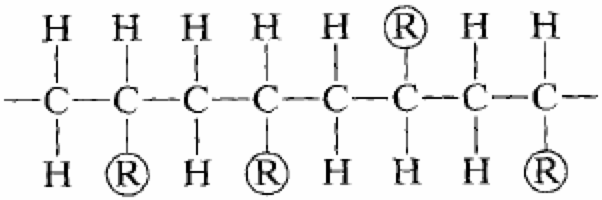
- **Stereoisomerism: atoms are linked together in the** same order, but can have different spatial arrangement.



1 Isotactic configuration

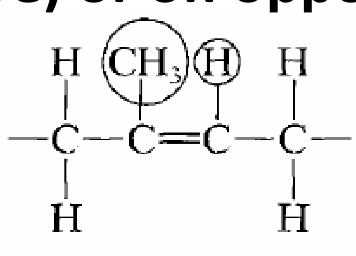


2 Syndiotactic configuration

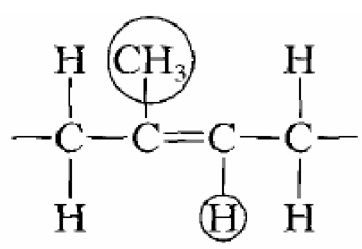


3 Atactic configuration

- **Geometrical isomerism: consider two carbon atoms** bonded by a double bond in a chain. H atom or radical R bonded to these two atoms can be on the same side of the chain (**cis structure) or on opposite sides of the chain (trans structure).**



Cis-polyisoprene



Trans-polyisoprene

Size – Shape – Structure classification