## Molecular forces

There are two types of forces within the molecules when they are came near each other's: **intramolecular** forces within the same molecule and **intermolecular** forces between the molecules. The all types of forces give the physical properties for the compounds like the physical phase (gas, liquid, solid), the melting and boiling point and the ability for forming fiber or sheets.

All these forces are called **Van der Waals forces,** type of these forces like permanent and induced dipole and hydrogen bonding. The summation of all these forces effect on the molecules and formed the **Cohesive energy**, whereby the attraction between one mole of molecules called molar cohesive energy (Ecoh) it was the energy needed to separate the molecules in the solid or liquid phase from their neighbor molecules.

Cohesive energy density (CED), it was the energy needed to separate 1 $cm^3$ of molecules at room temperature

$$CED = \frac{Ecoh\ (cal,)}{V\ (cm^3)}$$

V is the volume of one mole in $cm^3$.

The relation between the cohesive energy and the energy of vaporization is

$E = \Delta\ Hv - RT$

RT represents the loss work for convert the liquid molecules to vapor.

R is the gas constant = 1.97 cal\ mol.deg.

CED for polymers give information to the mechanical properties of the polymer. The high of CED mean that the polymer have good mechanical properties like fiber, on the other hand, the low value of CED mean that the polymer is brittle and soft.

Methods of CED determination:

The CED for small molecules is equal to $\Delta Hv$ divided by the volume of the vapour formed at boiling point.

In polymer, it is a different case, the polymer cannot vaporized . CED is the summation of CED for different moieties of the molecule

$$\mathrm{CED} = \frac{\rho\ \Sigma\mathrm{CED}}{M}$$

ρ= density

M= molecular weight of the repeating unit

Another term used in this meaning called( **solubility parameter** δ**)**

$$\boldsymbol{\delta} = \sqrt{\mathrm{CED}}$$

$$= \left( \frac{E}{V} \right)^{1\backslash 2}$$

In order to determine **δ** we can use all the attraction molar constant Ɛ for all the repeating units within the polymer chain

$$\boldsymbol{\delta} = \frac{\rho \Sigma n \mathcal{E}}{\mathrm{M}}$$

M= the molecular weight of the polymer

P = polymer density

n= degree of polymerization

to calculate **δ** for polypropylene with $10^4$ molecular weight and density of 0.906, the Ɛ for $=CH_2$, $-CH_3$ and $–CH$ is 303.259 and 269 respectively, so

$$\delta = \frac{0.906\ (303+259+269)283}{10.000}$$

= 17.5 $(J\backslash cm^2)^{1\backslash 2}mol^{-1}$

δ for solvent can also be calculated by the same way. In order to get some information about the solubility of the polymer in the solvent, the amount of

$\delta_{polymer} – \delta_{solvent}$ should be less than 4 $(J\backslash cm^2)^{1\backslash 2}$

# Flexibility of polymers

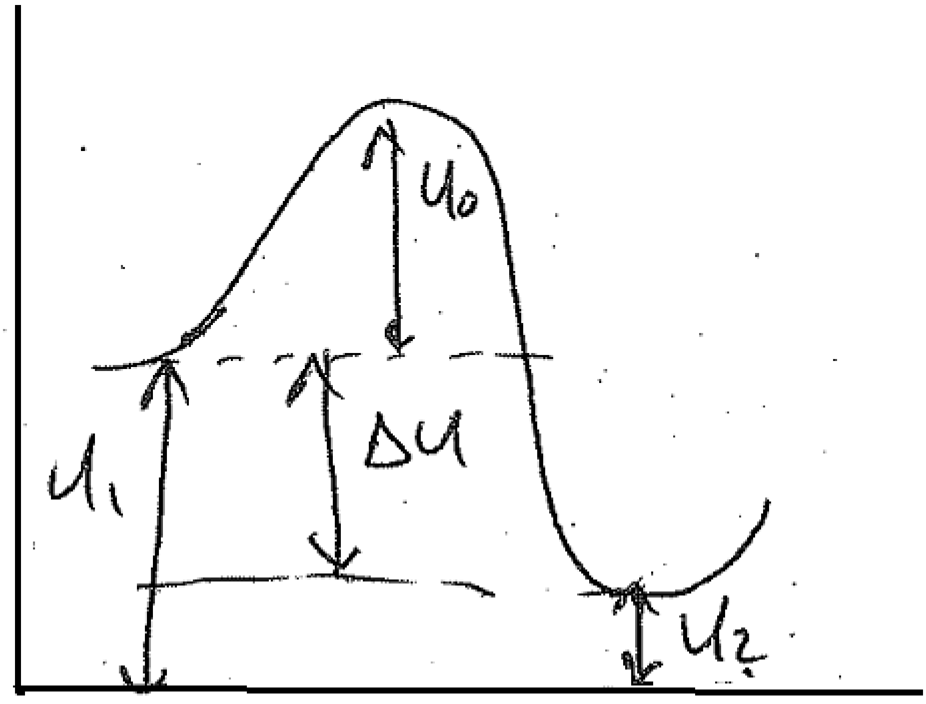
The flexibility of polymers is of two types

1-) thermodynamic flexibility

The energy needed to convert the polymers chains from state with potential energy $U_1$ to another state of potential energy $U_2$ is $\Delta U$

$\Delta U = U_2 - U_1$

$\Delta U$ represent the thermodynamic flexibility, it gives us idea to convert shape of the polymer chain



2-) Kinetic flexibility

The velocity of convert the chain from state to another state depends on the energy barrier $U_0$, as $U_O$ increase the rotation of the unit decrease and the flexibility decrease also.

**Factors effecting the polymer flexibility:**

1-) Rotation energy barrier:

It was the energy needed to rotate the atoms around the single bond complete cycle ($360^0$). If this energy is low, the chain have some flexibility ( PE, PP). if the chain have double bond , the energy is very low and the polymer have high flexibility as in rubber.

2-) The chemical structure of the chain

For example, the presence of polar group within the chain increase the association (inter and intra) and the flexibility will be decreased.

3-) The molecular weight

As the molecular weight increase, the number of conformations increase and the flexibility increase, whereby the chain can have more conformations (coiled, helical) with increasing the molecular weight.

4-) Cross- liking density

This will increase the bonds between the chains and effect their motion and decreased the flexibility

5-) The volume of the substituent

As the substituent volume increase, the rotation around the single bond will be hindered and the flexibility decreased, for example; polystyrene at room temperature is a solid matter because the chain have a bulk substituent (phenyl ) which will hindered the rotation, while the copolymer of styrene – butadiene have high flexibility where the phenyl groups are spread out.
PMMA is more rigid than the polyacrylate
Poly(α-methyl styrene) is more rigid than thane polystyrene

6-) temperature

As the temperature increased, the kinetic energy decreased and the velocity of rotation of the unit increase, the flexibility increased. The barrier energy did not increased with temperature elevation.

# Reactions of polymers

There are many types of reactions that the polymer chains can be undergoes.

## **1-)**Degradations:

It was the cleavage of the bonds of the chain. The cleavage may be physically or chemically.

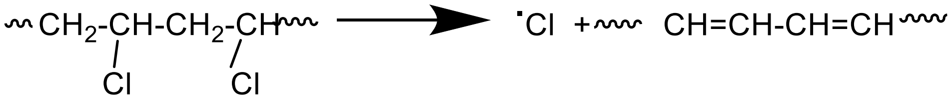
a-) thermal degradation: the polymer degrade by heating into smaller molecules with evolving of gases or liquids compounds. There are many types of these reactions as:

i-) degradation of the main chain (backbone): the cleavage of the bonds between the atoms within the backbone. The reaction cab be accomplished by many mechanisms:

$$CH_3CH_2 \wr CH_2CH_2CH_2 \sim\sim \longrightarrow CH_3CH_3 + CH_2CH{=}CH \sim\sim$$

b-) Regular degradation: In this type the polymer converts to the main monomer(depolymerization) as in PMMA or polystyrene.

ii-) Degradation without cleavage the backbone: As the degradation of PVC or polyvinylidine, when heated to elevated temperature PVC lose HCl molecule or formed crosslinked chains and the polymer converts to insoluble polymer



$$\sim CH_2\text{-}\underset{Cl}{CH}\text{-}CH_2\text{-}\underset{Cl}{CH} \sim\sim \longrightarrow {}^{\bullet}Cl + \sim\sim CH{=}CH\text{-}CH{=}CH \sim\sim$$

2-) Decomposition by light or by ionized rays:

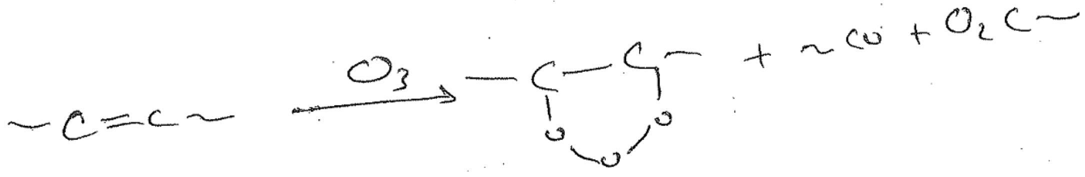
When the polymer exposed to light ray, it was decomposed by the same above mechanisms . The photolysis of polymers chains by UV and at elevated temperature depolymerized the polymer.

3-) Decomposition by mechanical – chemical factors:

Some mechanical process like grinding, crushing, pulping, mixing, extrusion can destroy the polymer chains.

4-) Oxidative decomposition

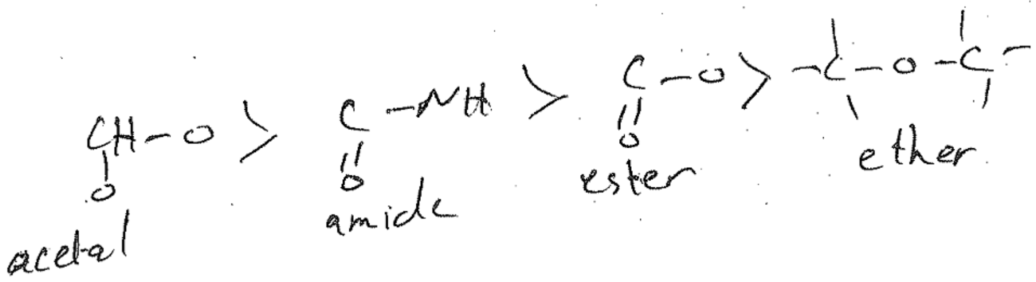
The polymer chains decomposed by the effect of oxygen or by oxidative agents, for example: the rubber oxidized by atmospheric ozone



5-) Decomposition by chemical reagent:

Many chemical reactions led to decompose the polymer chain by using different chemicals as:

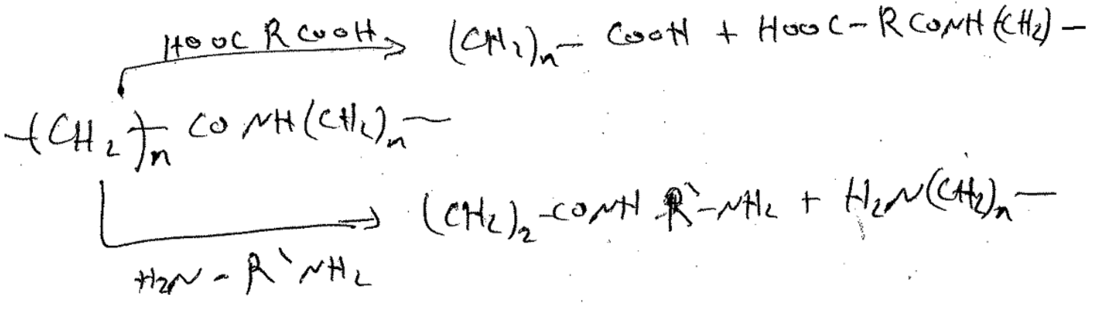
a-) hydrolysis : by using acidic , basic or salty aqueous solutions, where water molecule will be added to a site that the bond will be break down. The rate of decomposition depend on the type of the polymer as below



cellulose (acetal ) is decompose more raped than protein (amide) in aqueous solution.

b-) acidolysis and aminolysis :

this type is known as the hydrolysis by effecting of carboxylic acids or by effecting of some amines



## 2-) Grafting and Elongation reactions

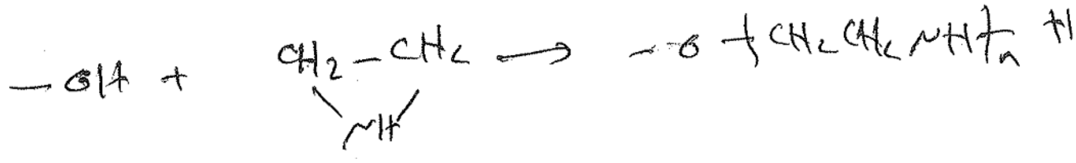
These reactions lead to increase the molecular weight of the polymer. The reactions depends on the type of copolymerization reaction as below

a-) Block copolymerization

in this reaction a block is added to the chain(the chain is of a live type), examp;e the preparation of styrene- butadiene copolymer.

b-) Graft reaction

the polymer chain contains functional group can initiate new reaction, for example the presence of OH group in cellulose can initiate the polymerization of ethylene imine

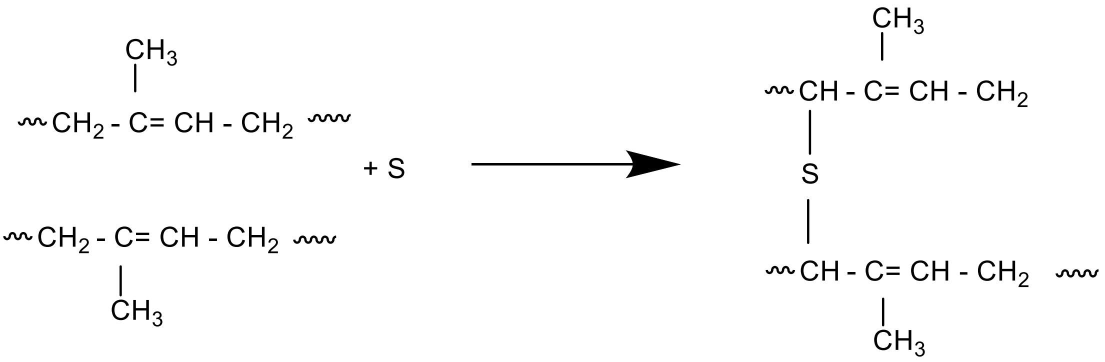


3-) Crosslinking reactions

These reactions led to linked chains with each other's by a side bond to form network structure . The product are insoluble and infusible polymers, for example curing reaction and vulcanization of rubber, the process known as hardening or curing in plastic technology and known as vulcanization in rubber industry.

a-) curing : These reactions are done by thermal treatment of low molecular weight compounds that produced from condensation reactions, for example : heating directly the phenol – formaldehyde polymers convert them to resol (30% crosslink) and resetol (60-70% crosslink) and to resetit (very hard polymer)

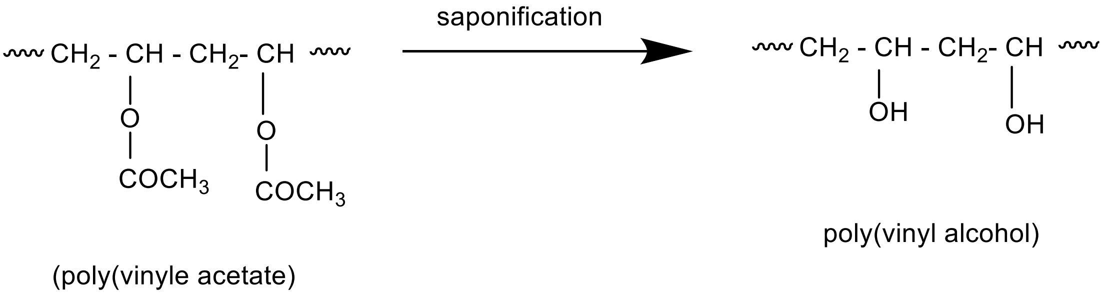
b-) vulcanization of rubber: the natural and synthetic rubbers are thermally unstable materials. Adding the sulfur as a vulcanizing matter make some network structures which make the rubber hard and thermal stable.



At 2-3% sulfur, the product is flexible. The flexibility decreased as sulfur increased. At 32% sulfur content the produced rubber is hard and known as (**Ebonite).**

**4- Functional groups reactions:**

By these reactions anew polymers are produced from another polymers. The new polymers cannot be obtained from their monomers because the monomers are unavailable or cannot be polymerized. e.g.

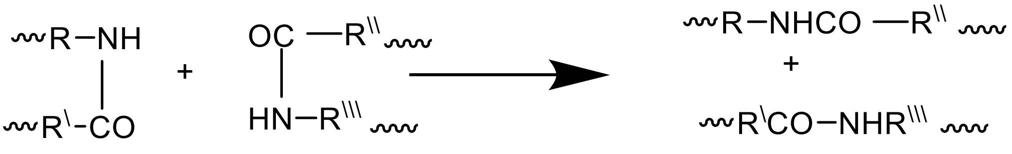


**5- Isomerization**

It was the reaction of changing the chemical structure of the molecule without changing the molecular weight. These reactions include exchange reactions, constituent transformation and configuration transformation.

a-) Exchange reactions

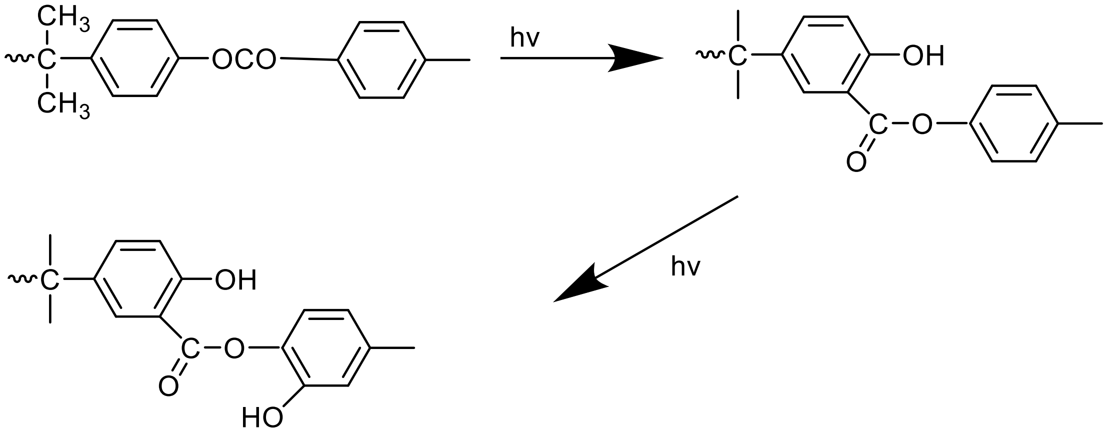
polymeric segments can be exchanged between two adjacent chains without changing the degree of polymerization



These reactions known normally as transamidation or transesterfication

**b-) Constitutional transformation:**

when the polymer exposed to external influential, it may change their constitutional , for example



c-) configuration transformation

Cis and trans isomers can be found in presence of double bond within the molecule. Diene polymers can be isomerized in presence of a radical as an the following mechanism, whereby the groups can rotate around the C-C single bond.