FKITMCMXIX

UNIVERSITY OF ZAGREB

FACULTY OF CHEMICAL ENGINEERING AND TECHNOLOGY

POLYMER SCIENCE AND TECHNOLOGY

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COPOLYMERIZATION

Reactivity of the monomer during propagation depends only on a monomer unit placed at the end of the polymer chain

- there are 4 possible propagation reactions: monomers M_1 and M_2 may be added to the growing polymer chain to the monomers M_1 or M_2:

$$M_1^\bullet + M_1 \xrightarrow{k_{11}} M_1^\bullet \qquad (1)$$

$$M_1^\bullet + M_2 \xrightarrow{k_{12}} M_2^\bullet \qquad (2)$$

$$M_2^\bullet + M_1 \xrightarrow{k_{21}} M_1^\bullet \qquad (3)$$

$$M_2^\bullet + M_2 \xrightarrow{k_{22}} M_2^\bullet \qquad (4)$$

- k_{11} constant of the speed of the reaction for the propagation chain, which ends with the monomer M_1 and the monomer M_1 is added to that chain
- k_{12} constant of the speed of the reaction for the propagation chain, which ends with the monomer M_1 and the monomer M_2 is added to that chain

- the similar principle is valid for the for the speed k_{21} and the speed k_{22}

- monomer M_1 disappears by the reactions (1) and (3), while monomer M_2 disappears by the reactions (2) i (4)
- the speeds of the disappearance of the monomers from the reaction mixtures are the speeds of their entrance to the copolymer:

$$\boxed{-\frac{d[M_1]}{dt} = k_{11}[M_1^\bullet][M_1]} \qquad \boxed{-\frac{d[M_1]}{dt} = k_{21}[M_2^\bullet][M_1]}$$

$$\boxed{-\frac{d[M_2]}{dt} = k_{12}[M_1^\bullet][M_2]} \qquad \boxed{-\frac{d[M_2]}{dt} = k_{22}[M_2^\bullet][M_2]}$$

The propagation which is going on by the adding of the same type of the monomer to the end of the polymer chain (M_1 to M_1 or M_2 to M_2) is called homopropagation.

The propagation which is going on by the adding of the different type of the monomer to the end of the polymer chain (M_1 to M_2 or M_2 to M_1) is called alternating (transitional) propagation.

$$r_1 = \frac{k_{11}}{k_{12}} \qquad r_2 = \frac{k_{22}}{k_{21}}$$

Mayo equation of copolymerization

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]\left(r_1[M_1]+[M_2]\right)}{[M_2]\left([M_1]+r_2[M_2]\right)}$$

r_1 and r_2 are the ratios of the copolimerization reactivity

Types of copolymerizations

Depending on the ratios of the copolimerization reactivity r_1 and r_2

$$r_1 = \frac{k_{11}}{k_{12}} \qquad r_2 = \frac{k_{22}}{k_{21}}$$

4 types of copolymerizations:

1. **Ideal copolymerization**
2. **Azeotropic copolymerization**
3. **Simetric copolymerization**
4. **Alternated copolymerization**

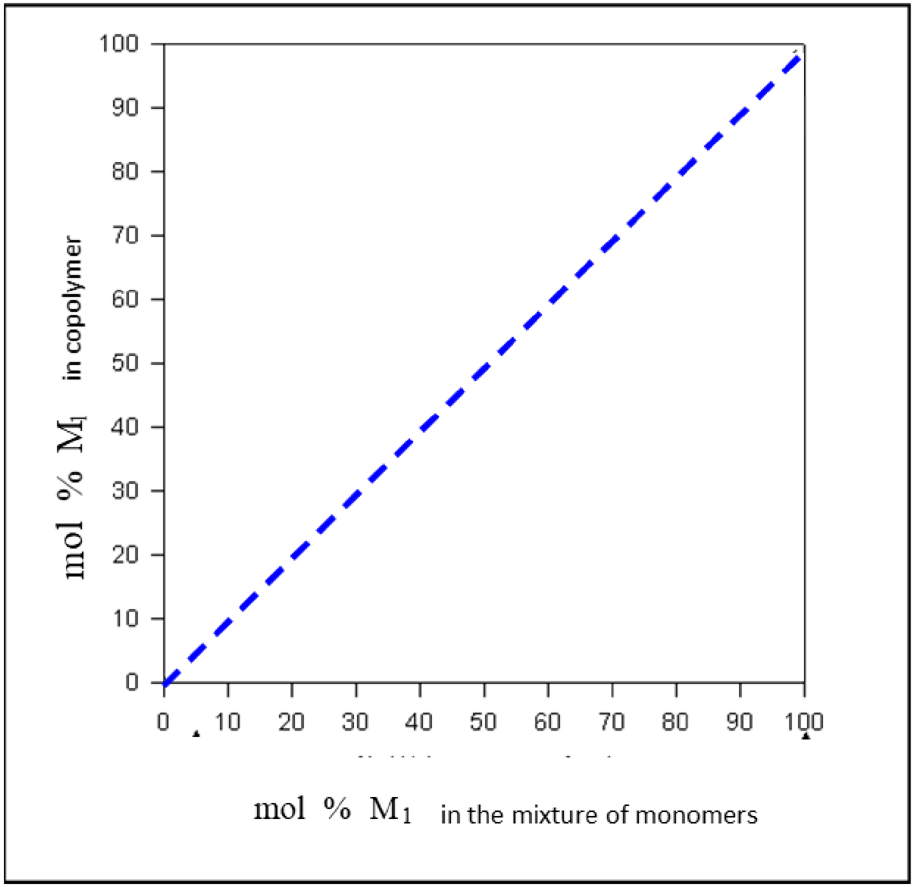
They are graphically presented as a dependence of copolymer composition on the composition of monomer mixture.

1. Ideal copolymerization

r_1 and r_2 = 1

- the propagation species M_1 i M_2 have the same affinity to be added to the first or to the second type of the monomer

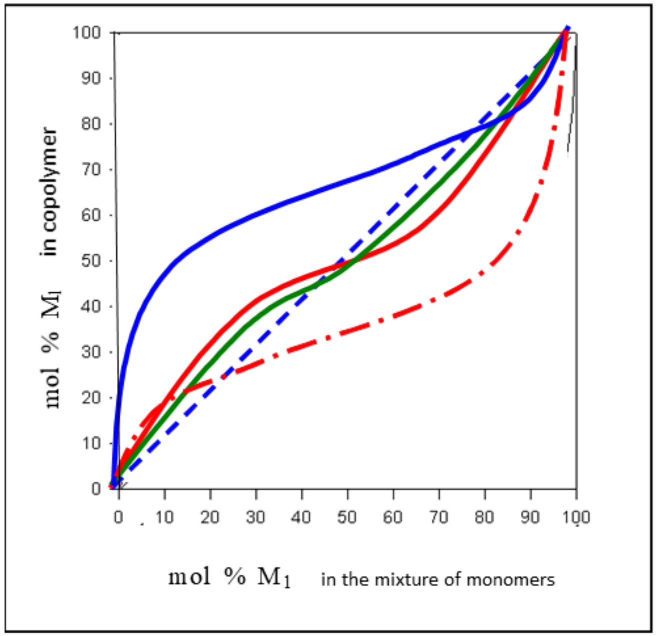
- the **copolymer with a statistic (random) distribution** of the monomer units is formed


100
90
80
70
60
50
40
30
20
10
0
mol % M_1 in copolymer
0
10
20
30
40
50
60
70
80
90
100
mol % M_1 in the mixture of monomers

- - - - - - - $r_1 = r_2 = 1$

2. Azeotropic copolymerization

$r_1 < 1$ i $r_2 < 1$



- - - - - - $r_1 = r_2 = 1$

——— $r_1 = 0{,}1$ $r_2 = 0{,}1$

——— $r_1 = 0{,}5$ $r_2 = 0{,}5$

——— $r_1 = 0{,}5$ $r_2 = 0{,}05$

—·—·—·· $r_1 = 0{,}05$ $r_2 = 0{,}5$

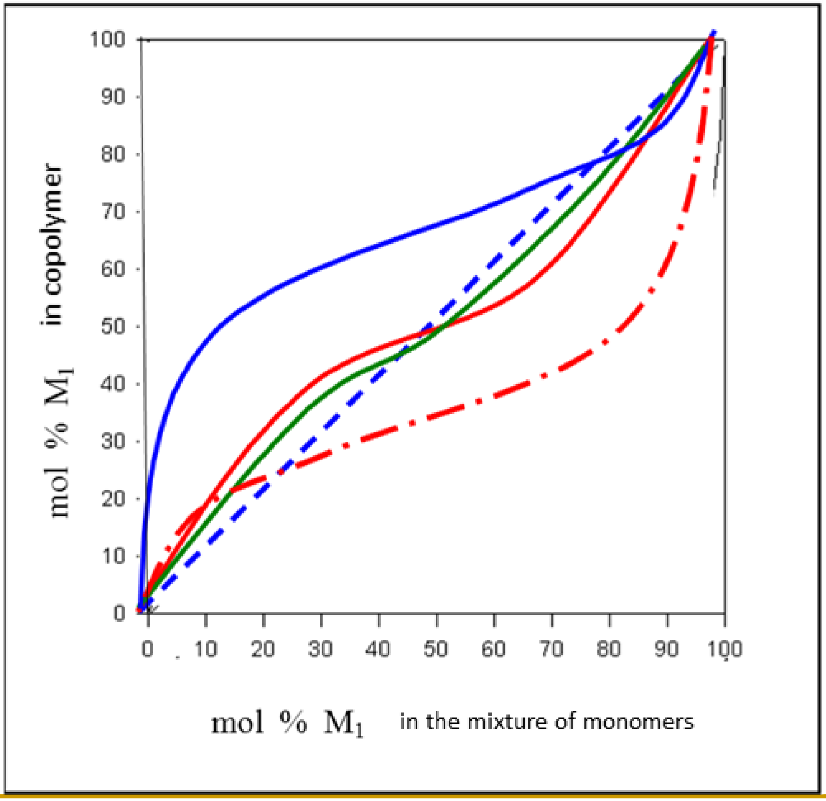
Azeotropic point:

The point at which the curve intersects the diagonal

ratio of M_1 *in the mixture of monomers =*

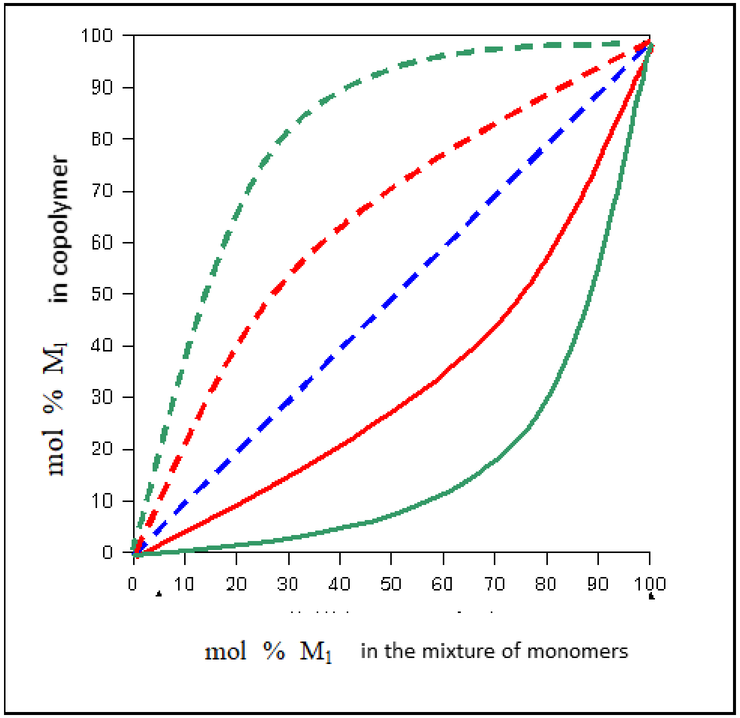
ratio of M_1 *in the copolymer*

There is a certain tendency of forming of alternated copolymer.



3. Simetric copolymerization

- **$r_1 > 1$ i $r_2 < 1$** one of the monomer is more reactive and it will have a higher ratio in a copolymer

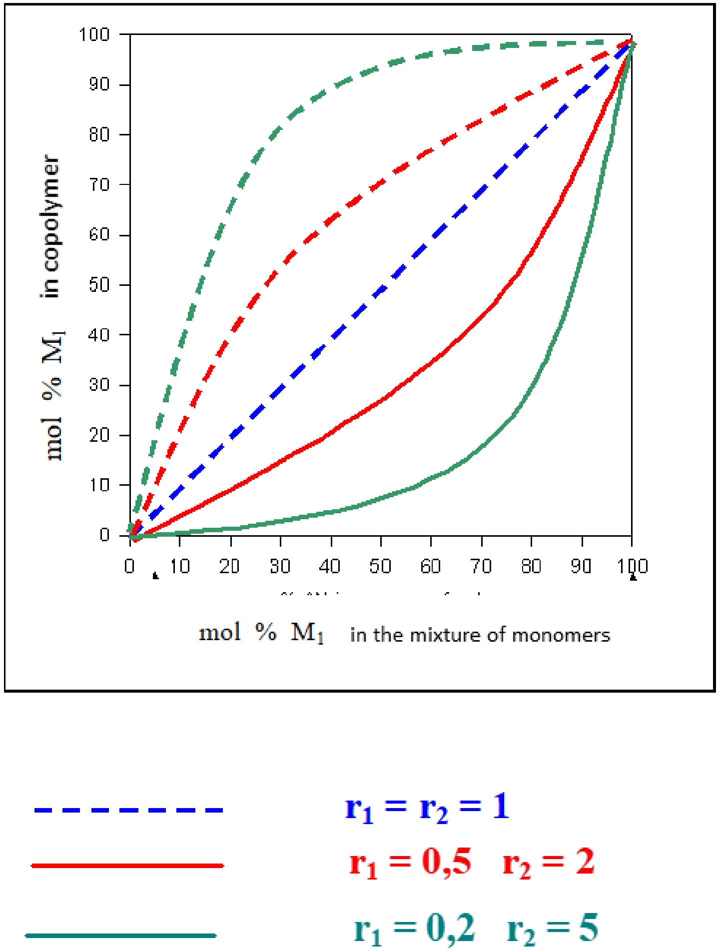


$r_1 = r_2 = 1$

$r_1 = 2$ **$r_2 = 0{,}5$**

$r_1 = 5$ **$r_2 = 0{,}2$**

or $r_1 < 1$ i $r_2 > 1$



Copolymer will contain higher quantity of the more reactive monomer

4. Alternated copolymerization

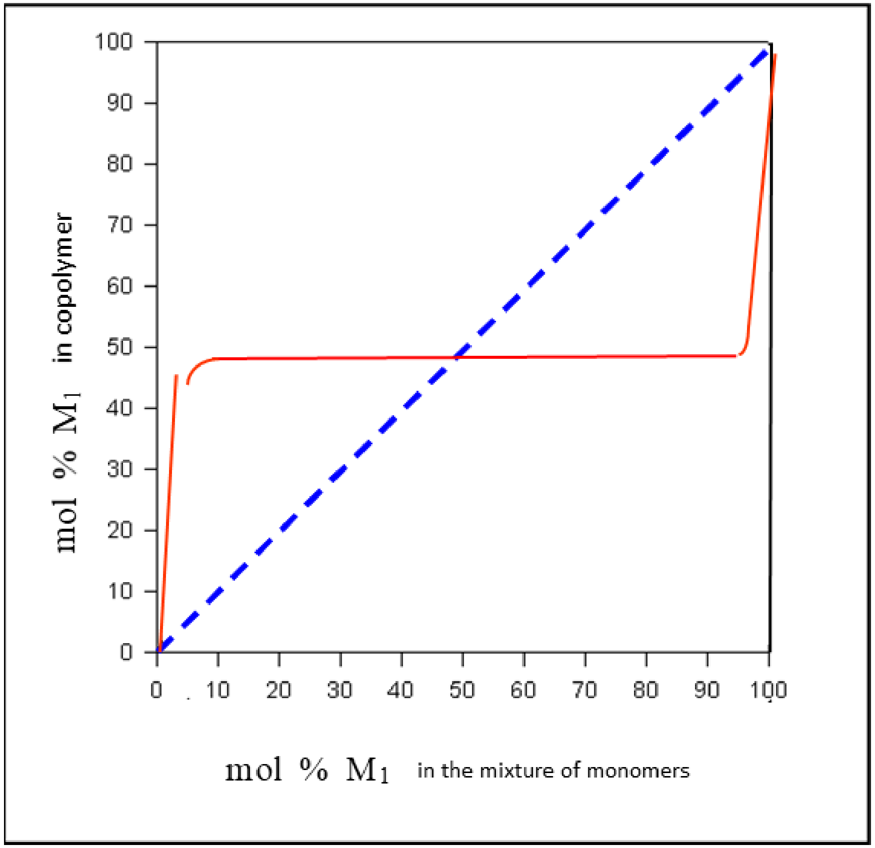
$r_1 = r_2 = 0$

- macroradical, which is at the exact moment present in a reaction mixture, has an affinity to react only with the other type of the monomer
- M_1 reacts only with M_2,
- M_2 reacts only with M_1

- the formed copolymer is consisted of the same quantity of each monomer!

- **The alternated copolymer is formed**

$M_1\ M_2\ M_1\ M_2\ M_1\ M_2\ M_1\ M_2\ M_1\ M_2\ M_1\ M_2$



- - - - - - - $r_1 = r_2 = 1$

—— $r_1 = 0{,}0095$ $r_2 \approx 0$

IONIC POLYMERIZATIONS

They are used to study the mechanism of polymerization reactions.

Some of the products may have intensive colour.

Such polymer products are not commercial.

Long lasting polimerizations, termination occurs only after the complete disappearance of monomer, terminations are rare.

„Living polymerizations"

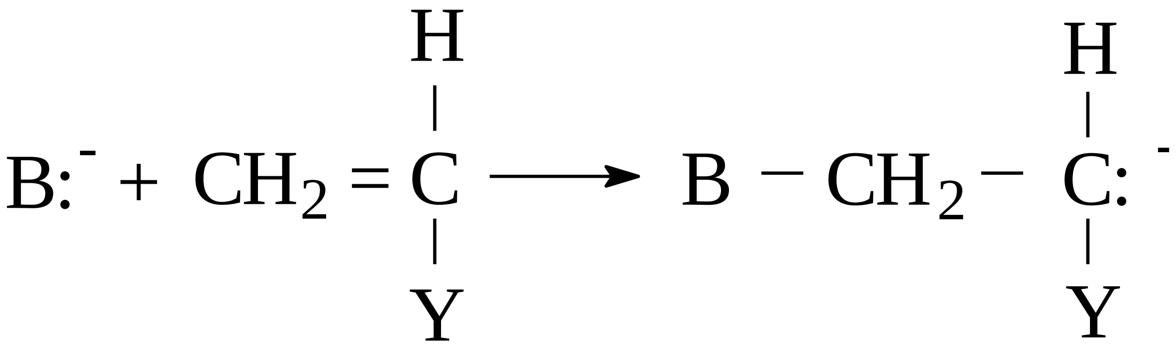
1. ANIONIC POLYMERIZATION

2. CATIONIC POLYMERIZATION

1. ANIONIC POLYMERIZATION

Initiators are covalent or ionic metal amides, alkyls or aryls.

Reaction of an initiator with a monomer = carbanion:



$$B:^{-} + CH_2 = \underset{\displaystyle Y}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}} \longrightarrow B - CH_2 - \underset{\displaystyle Y}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}:^{-}$$

carbanion

Initiation:

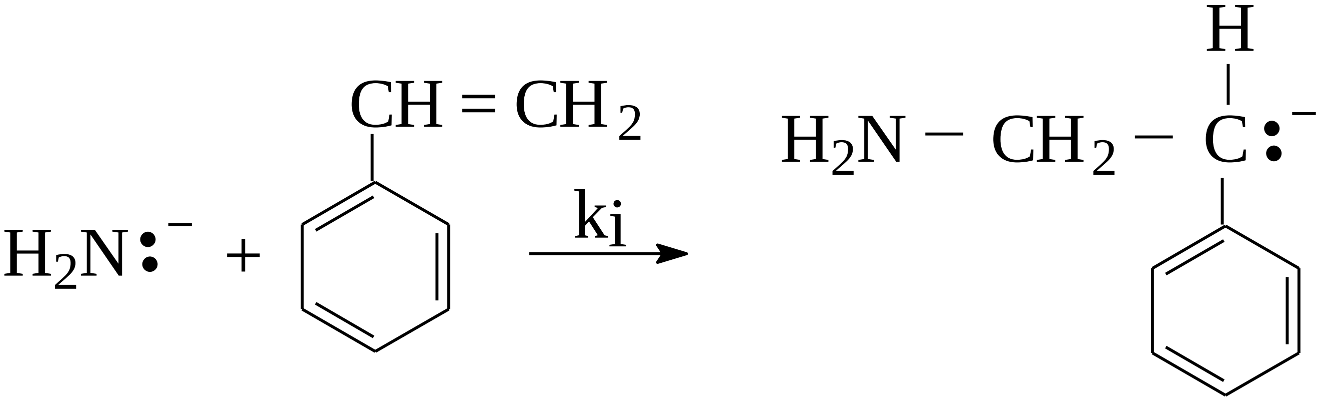
a) by metal amides
b) by electron transfer
c) by metal alkyls

a) by metal amides:

Polymerization of styrene with potassium amide in liquid ammonia at -33°C.

$$KNH_2 \overset{K}{\rightleftharpoons} K^+ + H_2N\!:^-$$

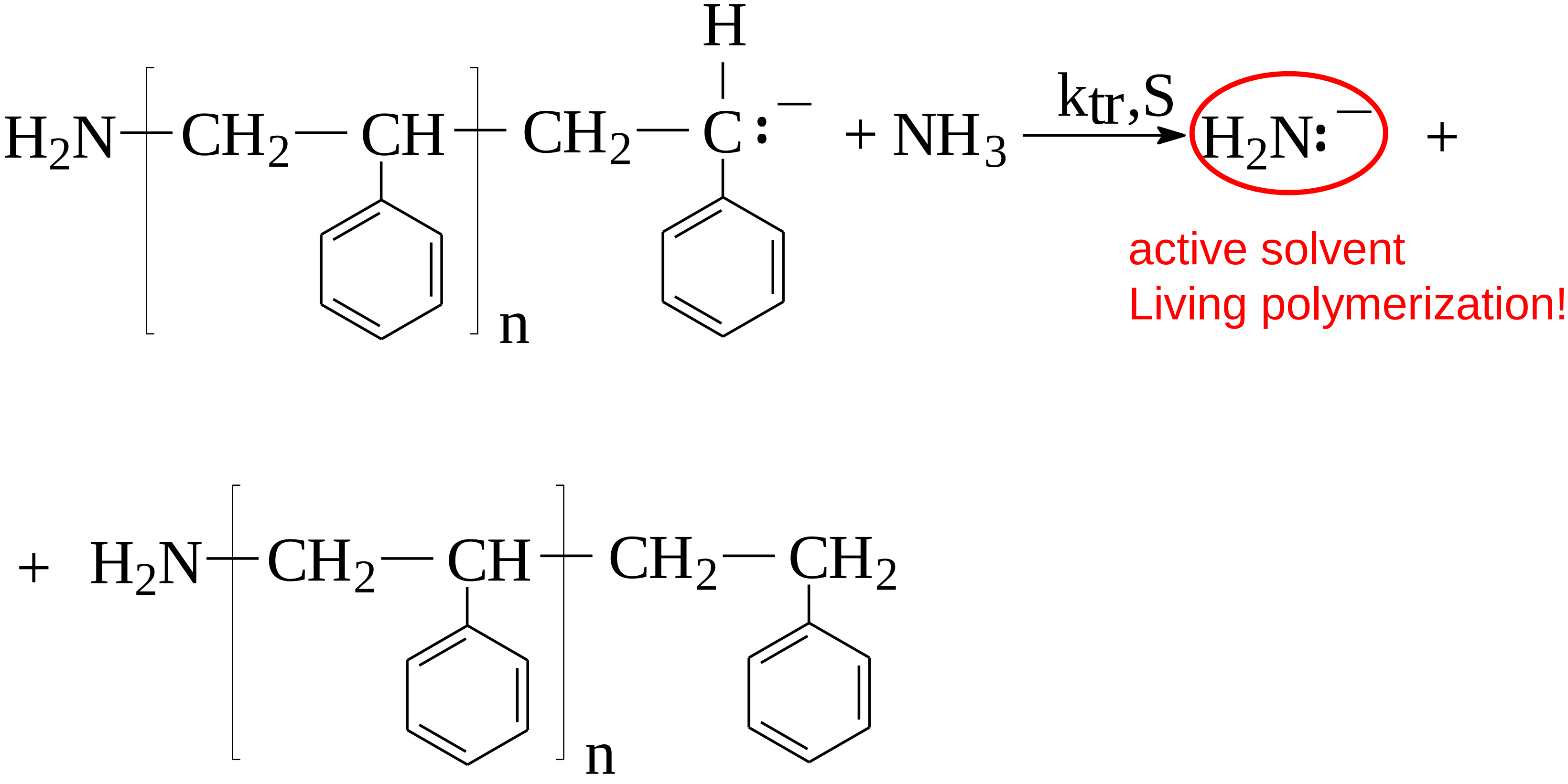
amide ion



propagating anionic center

$$R_i = k_i\left[H_2N:^-\right][M]$$

Chain-growth transfer termination to solvent:



active solvent

Living polymerization!

The final polymer product

2. CATIONIC POLYMERIZATION

Active end of the growing polymer molecule is a positive ion.

- Lewis acids and Friedel-Crafts catalyzators ($AlBr_3$, BF_3, $SnCl_4$, $ZnCl_2$, $TiBr_4$)

Example: cationic polymerization of isobutylene

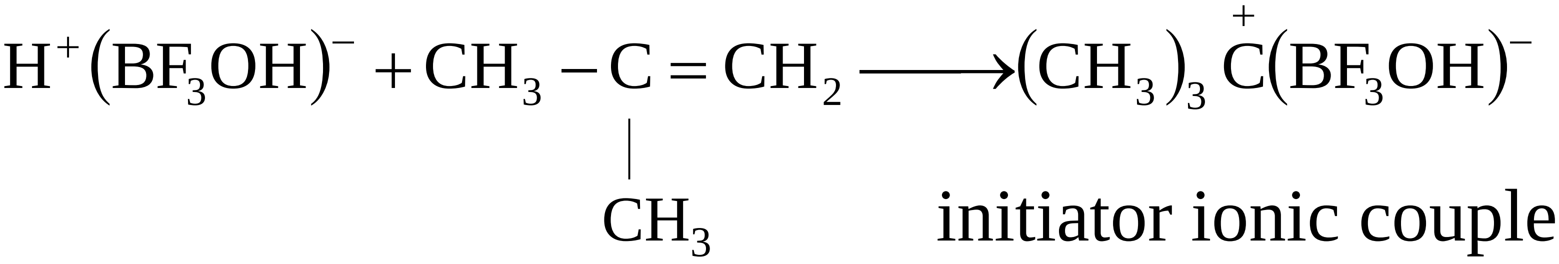
Isobutylene polymerizes with boron trifluoride (BF_3) and H_2O (at -100 ^{o}C)

BF_3 is catalyst, and H_2O is co-catalyst

$$\mathbf{BF_3 + H_2O \Leftrightarrow H^+(BF_3OH)^-}$$

co-catalyst/catalyst

Example: cationic polymerization of isobutylene



$$H^{+}(BF_3OH)^{-} + CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 \longrightarrow (CH_3)_3\overset{+}{C}(BF_3OH)^{-}$$

initiator ionic couple

Shematic view: $\mathbf{C + RH \Leftrightarrow H^{+}(CR)^{-}}$

$$\mathbf{H^{+}(CR)^{-} + M \xrightarrow{k_i} HM^{+}\,(CR)^{-}}$$

C = catalyst
RH = co-catalyst
M = monomer

PROPAGATION - ionic pair reacts with a monomer

$$\mathrm{H}\left[\mathrm{CH_2C(CH_3)_2}\right]_n^{+}\left(\mathrm{BF_3OH}\right)^{-}+\left(\mathrm{CH_3}\right)_2\mathrm{C}=\mathrm{CH_2}\longrightarrow$$

$$\mathrm{H}\left[\mathrm{CH_2C(CH_3)_2}\right]_n\ \mathrm{CH_2}\,\overset{+}{\mathrm{C}}\left(\mathrm{CH_3}\right)_2\left(\mathrm{BF_3OH}\right)^{-}$$

or schematically

$$\mathrm{H}\,\overset{+}{\mathrm{M}}\mathrm{n}\left(\mathrm{CR}\right)^{-}+\mathrm{M}\xrightarrow{\mathrm{kp}}\mathrm{HMn}\,\overset{+}{\mathrm{M}}\left(\mathrm{CR}\right)^{-}$$

TERMINATION

a) most common reactions are chain-growth transfer to monomer with formation of unsaturated polymer molecule

$$H\left[CH_2C(CH_3)_2\right]_n CH_2\overset{+}{C}(CH_3)_2(BF_3OH)^- +$$

$$CH_2=C(CH_3)_2 \longrightarrow$$

active monomer

$$(CH_3)_3\overset{+}{C}(BF_3OH)^- +$$

$$H\left[CH_2C(CH_3)_2\right]_n CH_2C(CH_3)=CH_2$$

unsaturated polymer molecule

b) reaction of a chain-growth transfer to monomer with elimination of hydrogen from monomer

$$H\left[CH_2C(CH_3)_2\right]_n CH_2\overset{+}{C}(CH_3)_2(BF_3OH)^- +$$

$$CH_2=C(CH_3)_2 \longrightarrow$$

active monomer

$$CH_2=C(CH_3)-\overset{+}{C}H_2(BF_3OH)^- +$$

$$H\left[CH_2C(CH_3)_2\right]_n CH_2CH(CH_3)_2$$

polymer

c) rearrangement of a propagating ion pair

⇨Spontaneous termination:

$$H\left[CH_2C(CH_3)_2\right]_n CH_2\overset{+}{C}(CH_3)_2(BF_3OH)^- \longrightarrow$$

$$\boxed{H^+}(BF_3OH)^- + H\left[CH_2C(CH_3)_2\right]_n CH_2\ C(CH_3)=\boxed{CH_2}$$

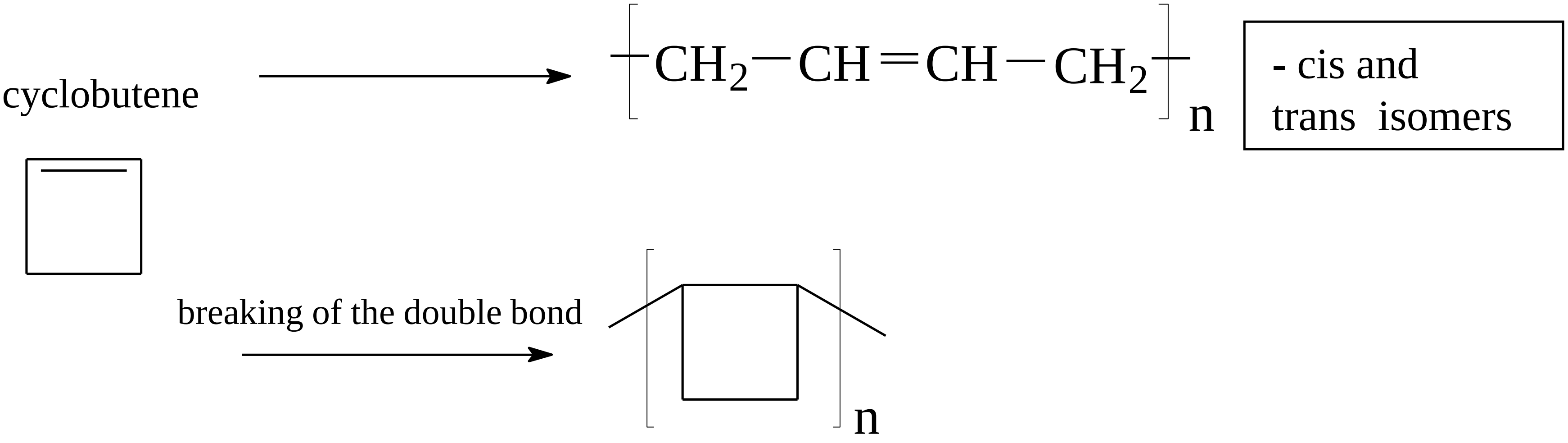
Active again!
Living polymerization!

RING-OPENING POLYMERIZATION

Monomers - **cyclic monomers:**

cyclobutene, cyclopentene, polycaprolactone,

Cyclobutene



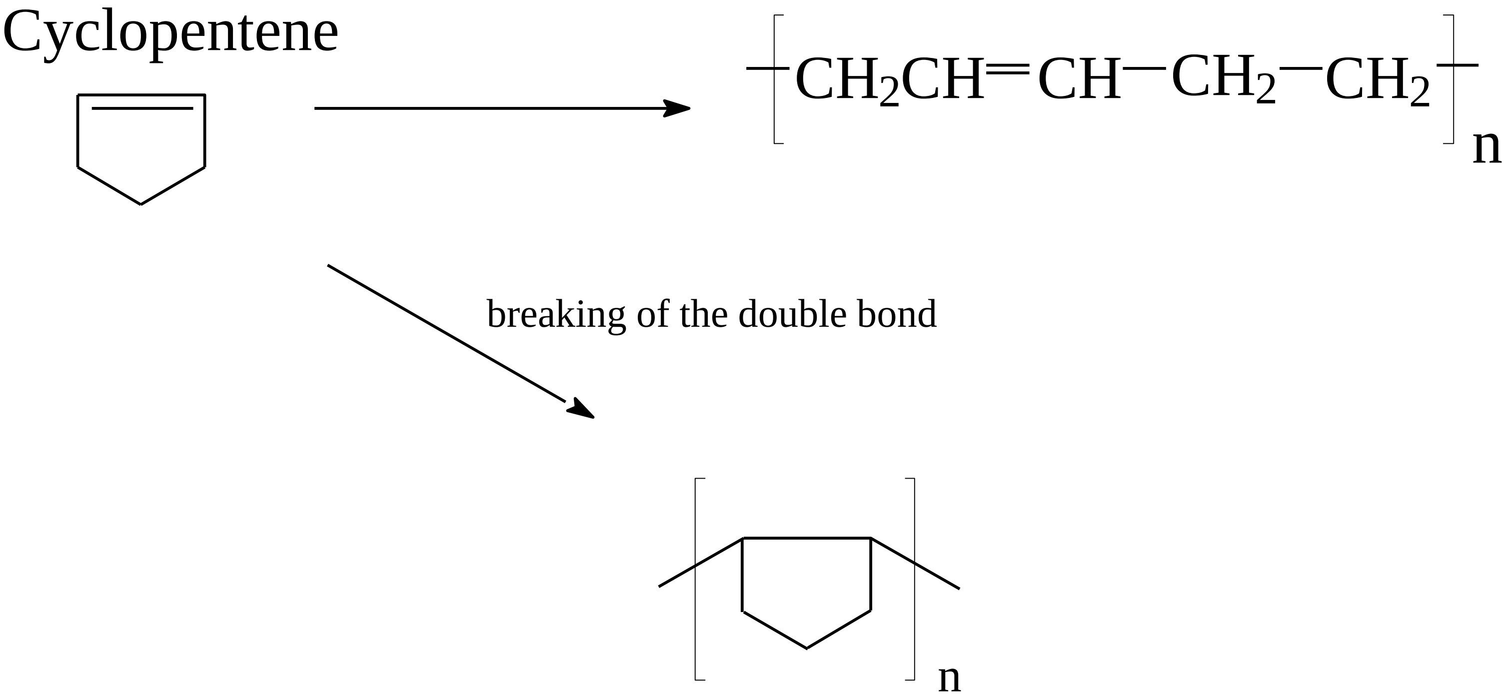
cyclobutene

$$\left[CH_2 - CH = CH - CH_2 \right]_n$$

- cis and
trans isomers

breaking of the double bond

Cyclopentene

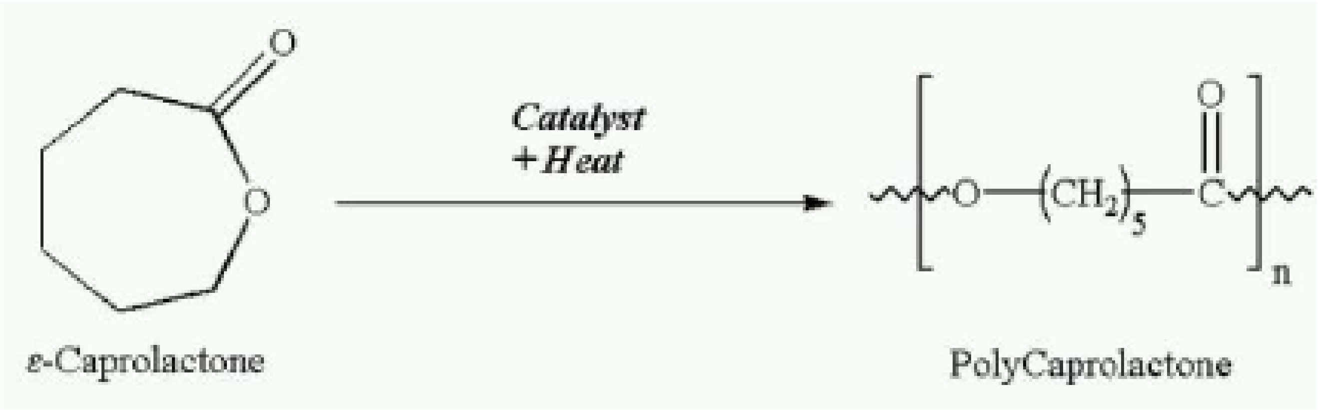


Cyclopentene

$$\left[-CH_2CH{=}CH-CH_2-CH_2-\right]_n$$

breaking of the double bond

Polycaprolactone (PCL)



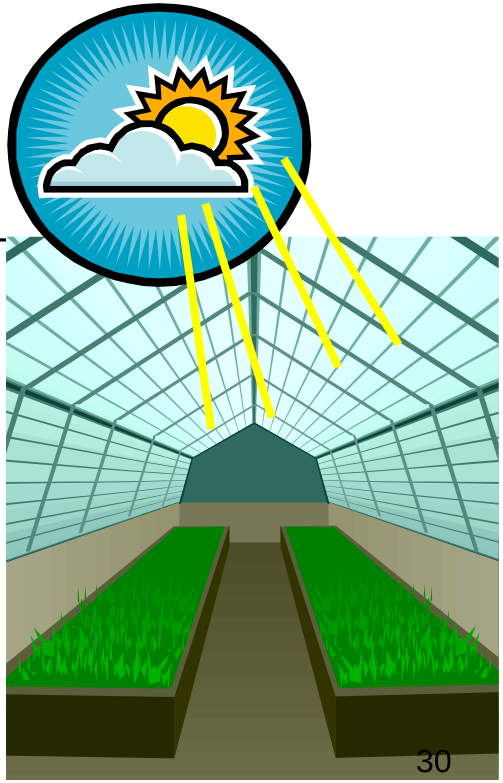
DEGRADATION OF POLYMERS

Degradation of polymers is each process where polymers lose their properties.

- changes in molecular and supramolecular structure due to the chemical and physical influences
- chemical process which changes the configuration of molecule

Types of degradation

Reason	**Degradation**
Heat	Thermal degradation
Oxygene	Oxidative degradation
Ozone	Ozone degradation
Electromagnetic radiation	Photochemical degradation
Radioactive radiation	Ionization degradation
Chemical effects	Chemical degradation
Mechanical strains	Mechanical degradation
Atmosphere activity	Ageing
Biological activity	Biodegradation



The harmful influences on polymers

Polymer materials and products are during their life always in interaction with environnment and may progressively degrade.

The processes of degradation proceed during
production, manufacturing, use, recycling and disposal of polymer materials
- degradation is specific for every polymer and the conditions of its usage

During the manufacturing polymers are exposed to:
temperature, oxygene and mechanical strains

During their use in nature they are exposed to
light, oxygene, moisture, ozone, mechanical strains

The consequences of degradation

- hardening, increase of brittleness and fading of colour
- diminishing of mechanical, electrical, reological and other properties.

(e.g the white colour of plastic boxes exposed to the light during a few years becomes yellow; cracking of a plastic vessel left in garden for a few years)

The most serious and expensive examples of degradation of polymers: some crashes of aeroplanes are caused by the degradation of polymer electric insulations.

Thermal degradation

For most polymers this process occurs at 200-300 °C and it is enough to break the bonds in polymer chains.
Thermal breaking of polymer molecules can proceed with different reaction mechanisms and the results are low molecular products, chains with unsaturated groups or even branched and crosslinked structures.

At pyrolysis, e.g. temperature over 400 °C, the rate of degradation of most polymers is very strong and proceeds during a few minutes.

The process of thermal decomposition at lower temperatures, typically below 200 °C, can be prevented by the addition of thermal stabilizers.

It is especially important to prevent degradation during processing of polymers (because the resulting degradation products accelerate the degradation of polymer during use under normal outdoor conditions).

- One of the most thermally unstable polymers is

  poly(vinyl-chloride) PVC

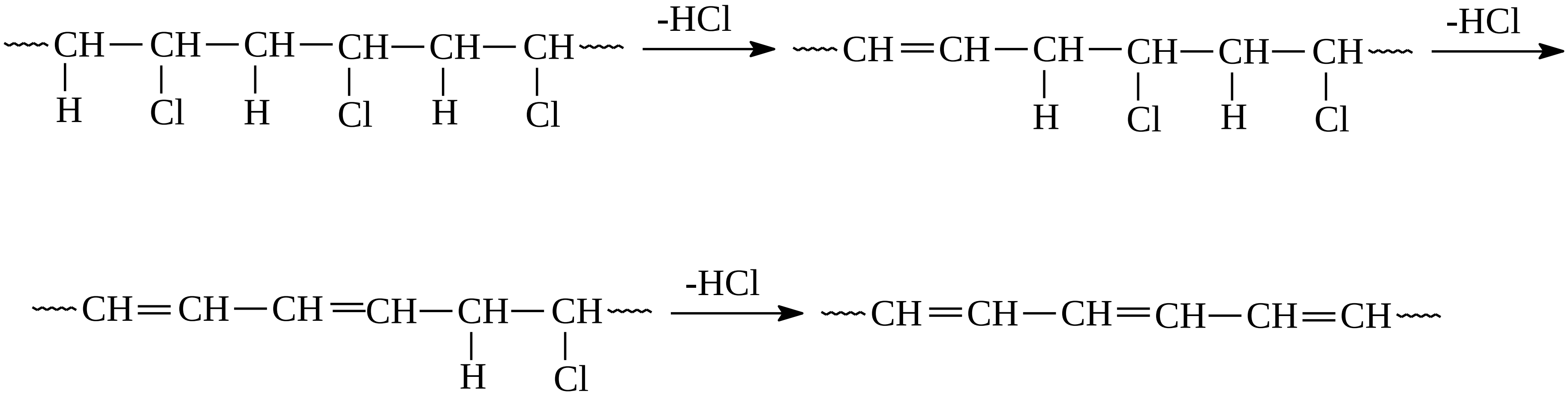
Its decomposition takes place with successive elimination of gaseous hydrogen chloride (HCl) through the ***intra-and inter-molecular dehydrochlorination*** without cleavage of the basic chain.

- Formed HCl has the function of an autocatalyst.

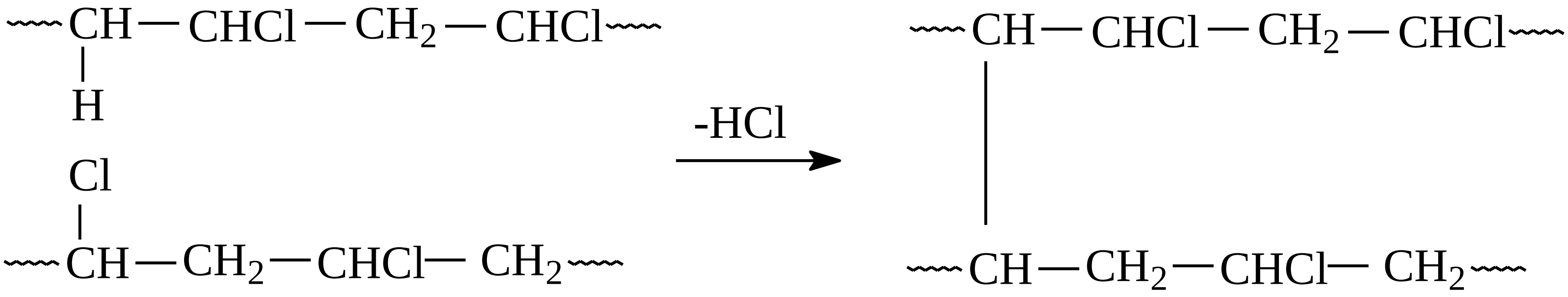
- Rapid reaction is almost complete at a temperature of 250 °C.

- Dehydrochlorinated chains can continue to interact with the formation of crosslinked and cyclic structures.

Intramolecular dehydrochloration of PVC macromolecules



Intermolecular dehydrochloration of PVC macromolecules



Thermally initiated process of degradation proceeds in the presence of oxygen with very fast oxygene degradation.

Process is called thermooxidative degradation and occurs at the temperatures lower than for thermal degradation.

Example: polypropylene is thermally stable polymer.
Its thermal degradation begins at 280-300 °C,
while its thermooxidative degradation begins at 120-130 °C.

Stabilizers

Stabilizers are added to the polymer materials to prolong their useful life:

thermal stabilizers
antioxidants
antiozonants
ultraviolet stabilizers

The choise of stabilizer depends on polymer type and the conditions during the use of polymer material.

CHEMISTRY AND TECHNOLOGY OF VULCANIZATION

- Charles Goodyear was first who vulcanized rubber just unexpectedly, in 1839 he heated natural caoutchouc cis-1,4-polyisoprene with small quantity of sulphur.

Vulcanization – a process by which uncrosslinked material (caoutchouc) becomes crosslinked (rubber).

Crosslinked material (rubber) can not be dissolved or melted.

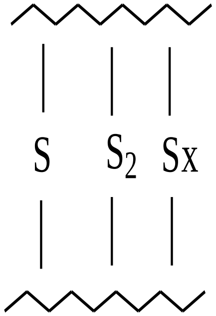
For reaction of vulcanization the components are:

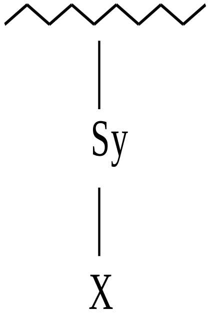
1. uncrosslinked material (caoutchouc)
2. agents for vulcanization (sulphur or other)
3. accelerators (merkaptanes)
4. ZnO – activator of accelerator
5. stearic acid and additives

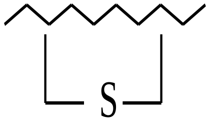
Sulphur vulcanization

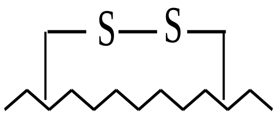
Sulphur is usually present in quantities of
2,5-3,0 phr (phr – parts per hundred)

Sulphur in vulcanization process may be present as:
monosulphide, disulphide, polysulphide
or cyclic monosulphide and cyclic disulphide:

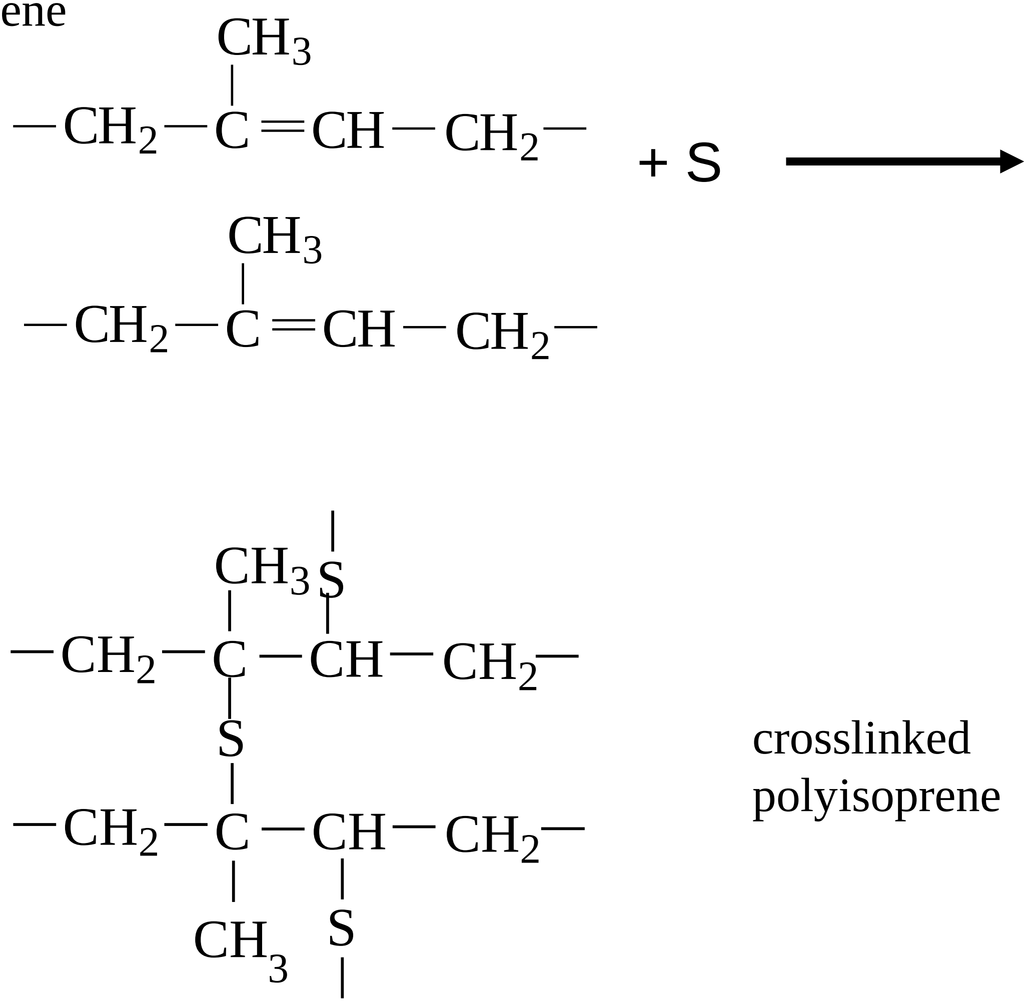








polyisoprene



$$\begin{array}{l}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2- \\ -CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-\end{array} + S \longrightarrow$$

$$\begin{array}{l}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle S}{|}}{C}}-\overset{\overset{\overset{|}{\displaystyle S}}{|}}{CH}-CH_2- \\ -CH_2-\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\underset{\underset{\underset{|}{\displaystyle S}}{|}}{CH}-CH_2-\end{array}$$

crosslinked
polyisoprene

Technological processes of vulcanization

- Vulcanization takes place in a large plants and factories for production of tires and other products.

1. Vulcanization in autoclaves
2. Continuous vulcanization
3. Vulcanization by pressing

1. <u>Vulcanization in autoclaves</u>

- the type of vulcanization with water vapour, which is carried out in cylindrical autoclaves, which can be vertical or horizontal, it is possible to use hot air vulcanization.

- advantage: uniform heating because there are no parts of cold surfaces.

- disadvantage: rubber is easily oxidized in the air, therefore, vulcanization is often carried out in autoclaves with steam.

Vulcanization in autoclaves

2. __Continuous vulcanization__

This process is usually connected to the extrusion or calendering (production of pipes, profiles, rubber insulated wires and cables).

a) Vulcanization in a tunnel with hot air – it is rarely performed because of low heat transfer and the possible deformation of extruded profiles and the product.

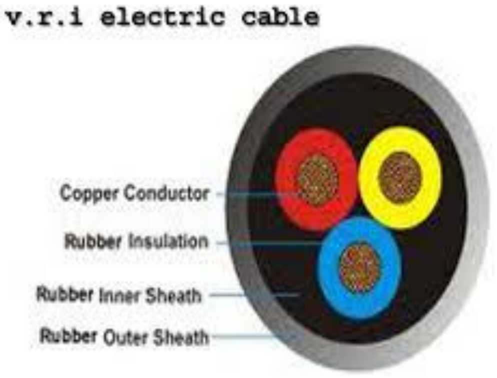
b) Vulcanization in the tunnels of hot steam – continuous vulcanization of cables and wires for insulation

c) Vulcanization in a bath of ethylene glycol - a simple procedure but with disadvantage because of the evaporation of the ethylene glycol from the bath and a product after vulcanization must be washed.

d) Vulcanization in the bath with the molten metal - not a suitable procedure for vulcanizing - the frequent deformation of products and harmful phenomena which metals cause to the surface of the product.

e) Fluid bed vulcanization - procedures in which the products pass through a heated bath stuffed with small glass pearls of diameter of ~ 0.2 mm; from the bottom of the bath the air, nitrogen or steam blows and the beads (pearls) behave as a liquid media.

- *advantage: fast vulcanization → heat transfer in a media is higher than in gas and deformations are minimized.*



3. <u>Vulcanization by pressing</u>

-molding product is molded by pressing while warming up, the procedure is carried out in strong hydraulic presses

-moulds in presses are heated with steam or by electricity for vulcanizing at higher temperatures

The first exam will be held

on Thursday, November 14th 2024

<u>from 10:15 to 11:15</u>

classroom: Vijećnica 2, Zagrepčanka