FKITMCMXIX

UNIVERSITY OF ZAGREB

FACULTY OF CHEMICAL ENGINEERING AND TECHNOLOGY

POLYMER SCIENCE AND TECHNOLOGY

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COPOLYMERIZATION

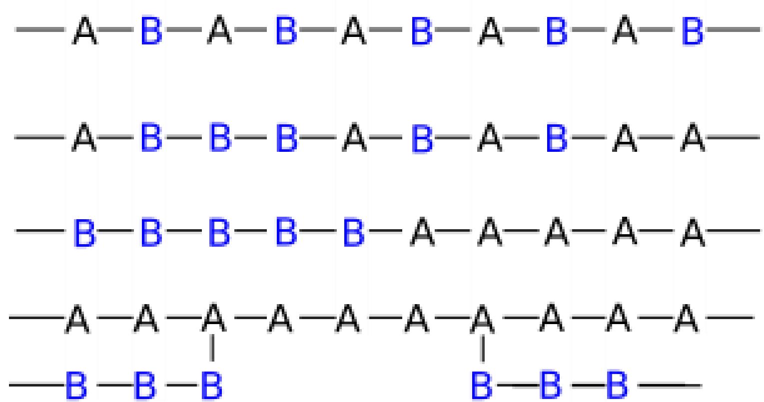
COPOLYMERIZATION

product: c**opolymer**

- the polymerization of two or more monomers at the same time in the same reaction mixture

<u>The mixture of 2 monomers</u>:

The polymer product with the two different structures in the polymer chain



$$M_1 + M_2 \rightarrow -M_1M_2M_2M_1M_2M_2M_2M_1M_1M_2M_2M_1M_1M_2-$$

- 2 monomers come into copolymer due to the their concentration and reactivity

terpolymerization - 3 monomers

multicomponent copolymerization – more than 3 monomers

The importance of the copolymerization:

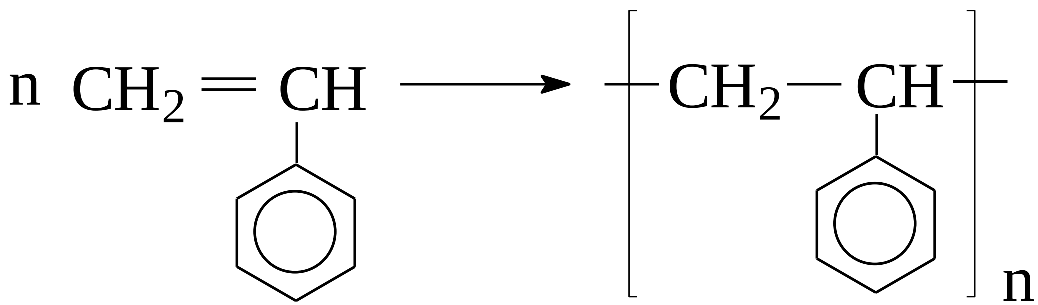
- The creation of the new types of polymer materials

- modification of the properties of the known polymers

- copolymerization allows a synthesis of many different polymer products

The example: **polystyrene**

- material with a poor tensile strength – it is a very breakable material



styrene **polystyrene**

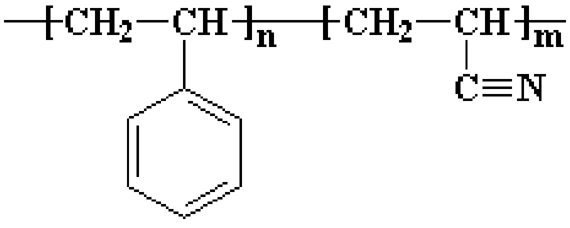
The copolymerization of a styrene with other types of monomers expands its application.

1. The copolymerization of **styrene** with **acrylonitrile** – the higher resistance to the solvents than in the case of the pure styrene

2. The copolymerization of **styrene** with **butadiene** – the higher elasticity of the material

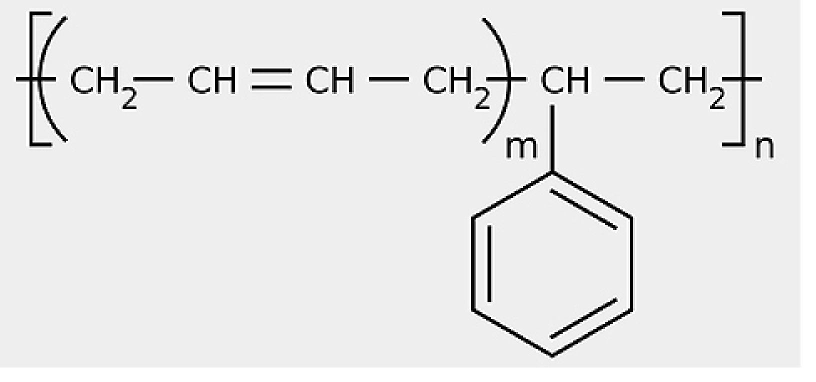
3. The terpolymerization of **styrene** with **acrylonitrile** and **butadiene** – many better properties than that of the pure polystyrene

styrene-acrylonitrile, SAN

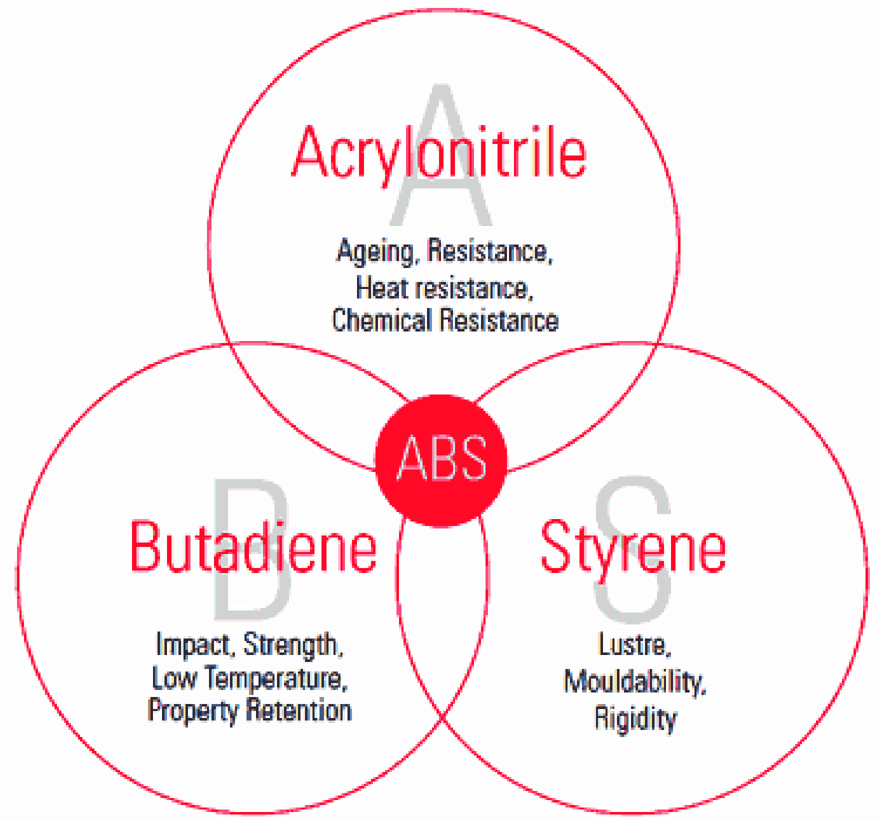


SAN

styrene-butadiene, SBR



acrylonitrile-butadiene-styrene, ABS



Types of copolymers

depending on to the distribution of the repeating units

1) **Statistic copolymer**
   - random structure!

-A-A-B-B-B-A-B-A-A-B-A-A-A-B-B-

2) **Alternated copolymer**
   - equal quantity of each monomer in the polymer structure

-A-B-A-B-A-B-A-B-A-B-A-B- A-

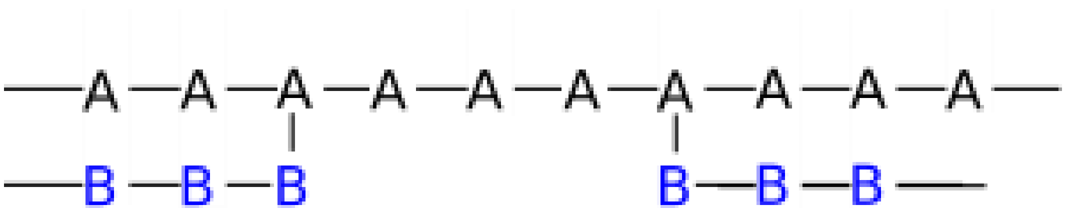
3) Block copolymer

- longer blocks of one monomer in the polymer chain

-A-A-A-B-B-B-B-B-A- A-A-A-A-B-B-B-

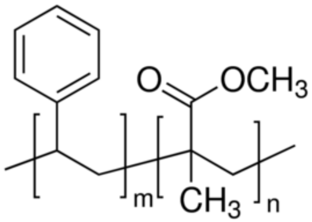
4) Graft copolymer

- branched copolymer- on the **main chain** of one monomer type **the branches** of the other monomer type are grafted



Nomenclature of copolymers

-**copolymer** of styrene and methyl-methacrylate:
poly(styrene-co-(methyl-methacrylate)) or
(***methyl-methacrylate)-styrene copolymer***



There is also a nomenclature depending on the distribution of monomer units:

-alt- -b- –g-
(alternated block graft)

-Grafted copolymer of styrene onto polybutadiene:
polibutadiene-g-polystyrene

- 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.

Mayo equation of copolymerization

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

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

r_1 and r_2 are the ratios of the copolymerization 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**

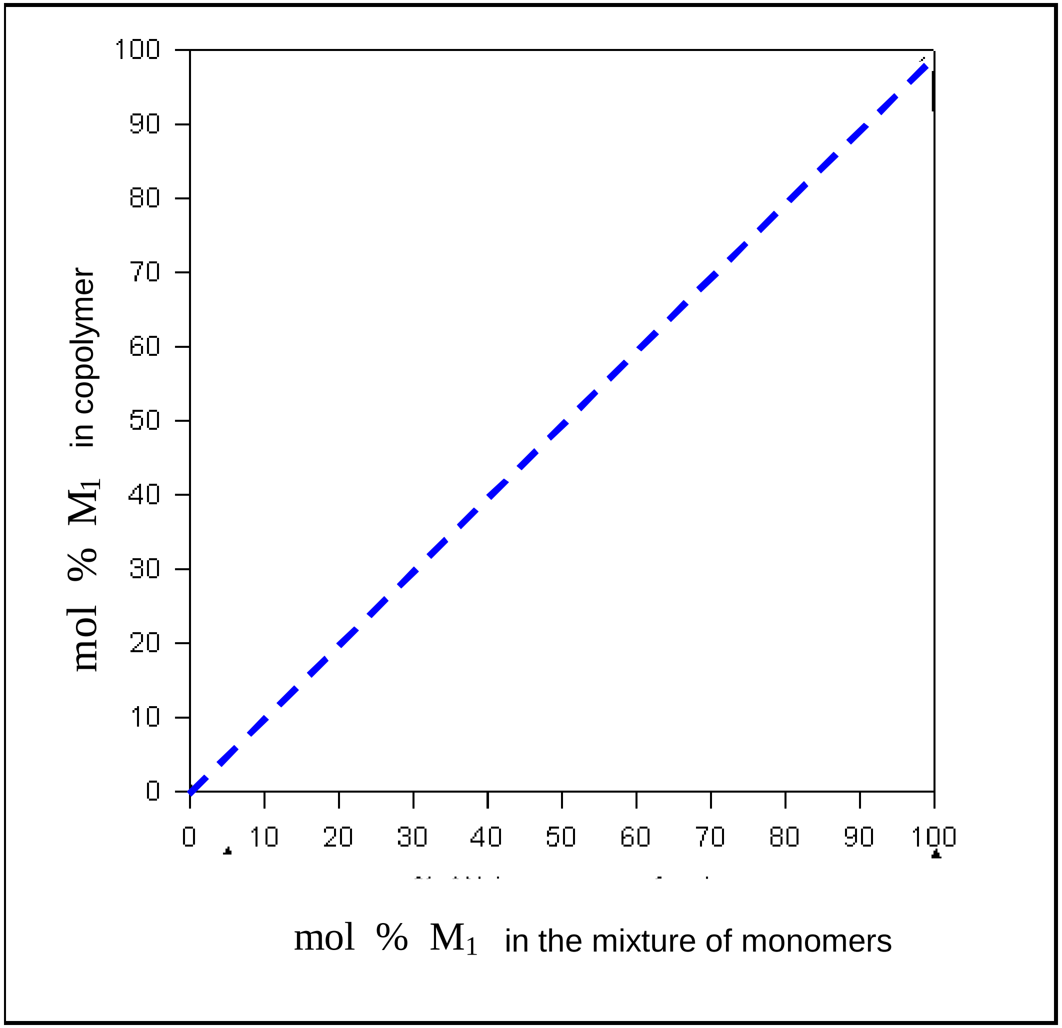
They are graphically presented as a dependence of copolymer composition on the composition of monomer mixture.

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

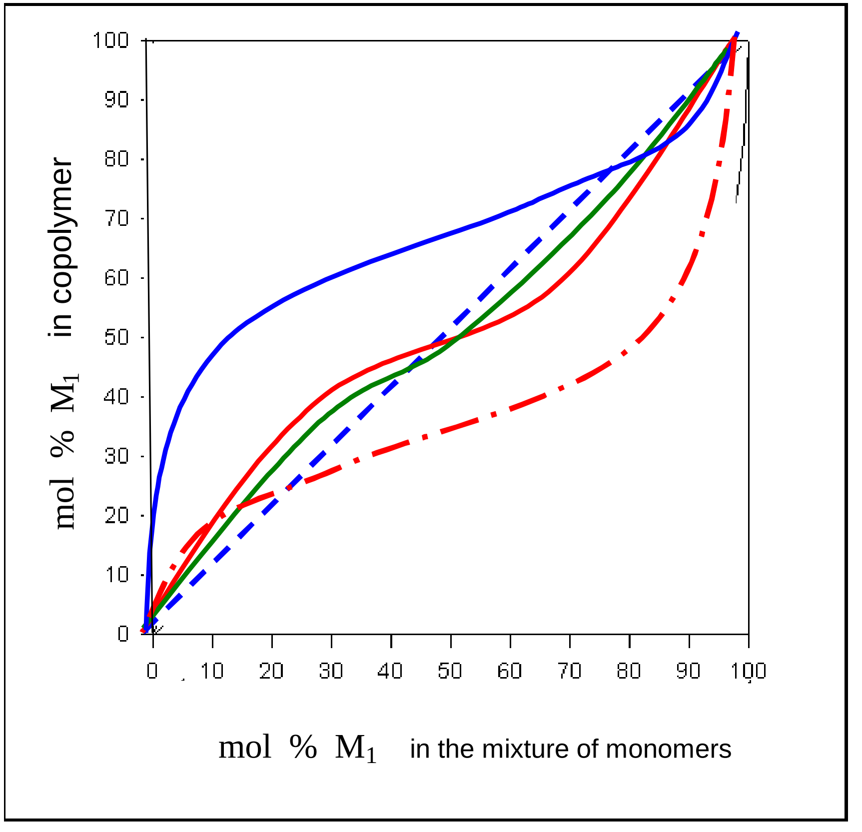


mol % M_1 in copolymer
100
90
80
70
60
50
40
30
20
10
0
0 10 20 30 40 50 60 70 80 90 100
mol % M_1 in the mixture of monomers

$r_1 = r_2 = 1$

2. Azeotropic copolymerization

$r_1 < 1$ i $r_2 < 1$



$r_1 = r_2 = 1$

$r_1 = 0{,}1$ $r_2 = 0{,}1$

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

$r_1 = 0{,}5$ $r_2 = 0{,}05$

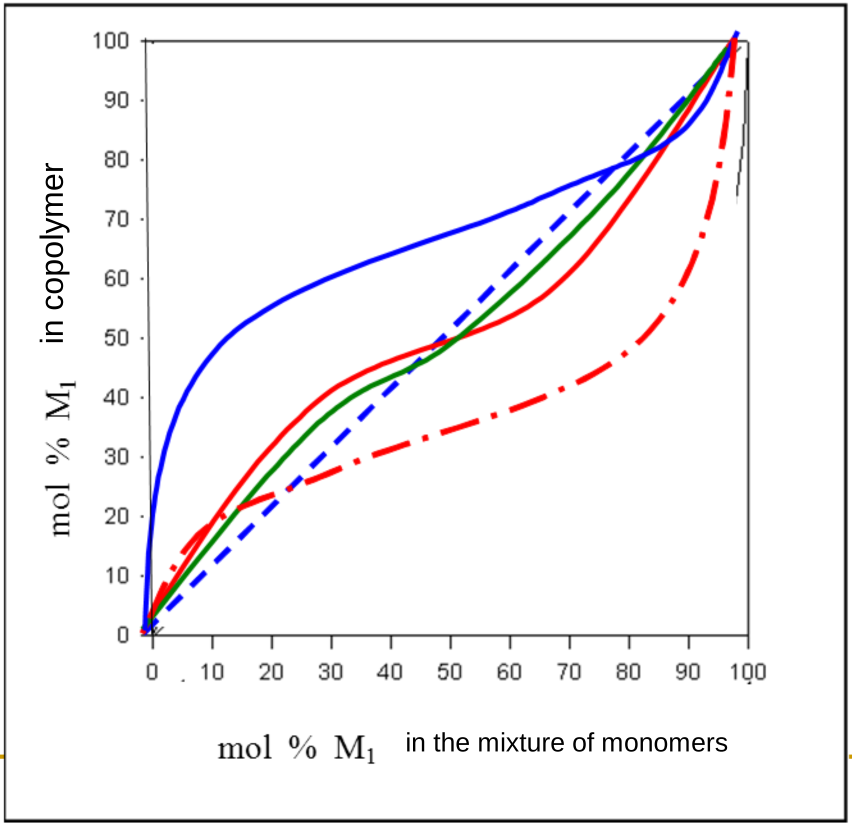
$r_1 = 0{,}05$ $r_2 = 0{,}5$

Azeotropic point:

The point at which the curve intersects the diagonal

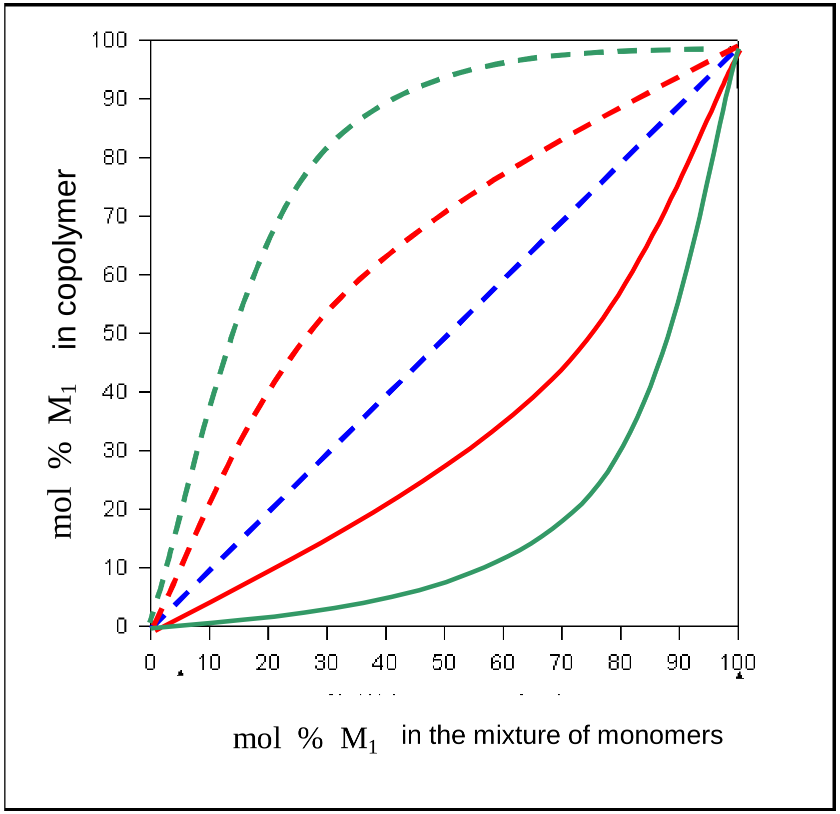
ratio of M_1 in the mixture of monomers =
ratio of M_1 in the copolymer

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

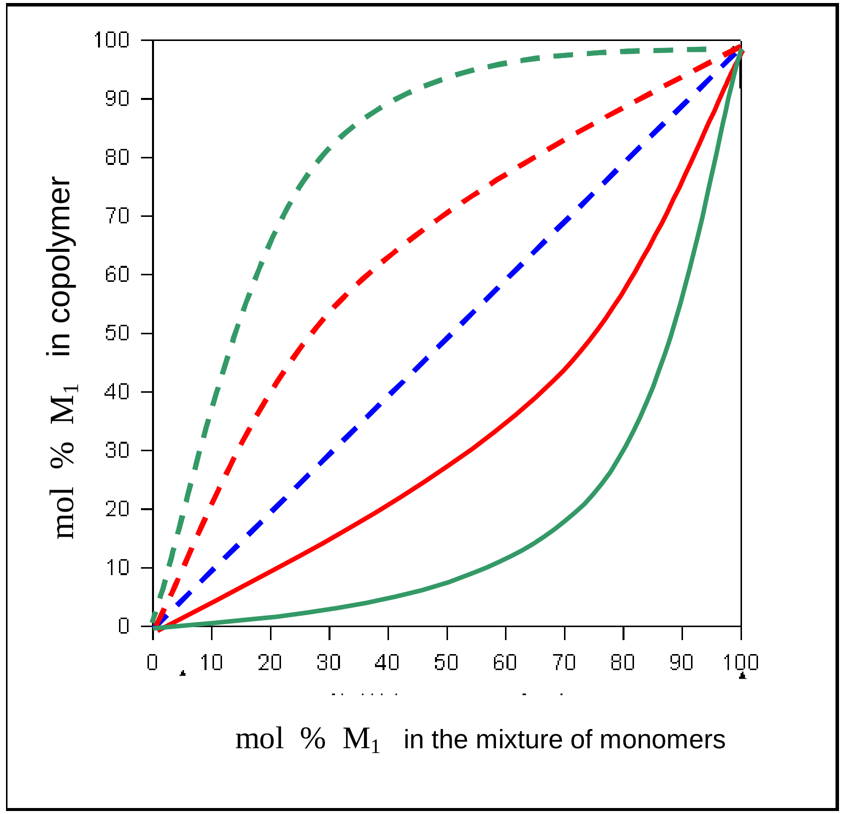


$r_1 = r_2 = 1$

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

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

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



$r_1 = r_2 = 1$

$r_1 = 0{,}5 \quad r_2 = 2$

$r_1 = 0{,}2 \quad r_2 = 5$

Copolymer will contain higher quantity of the more reactive monomer

4. Alternated copolymerization

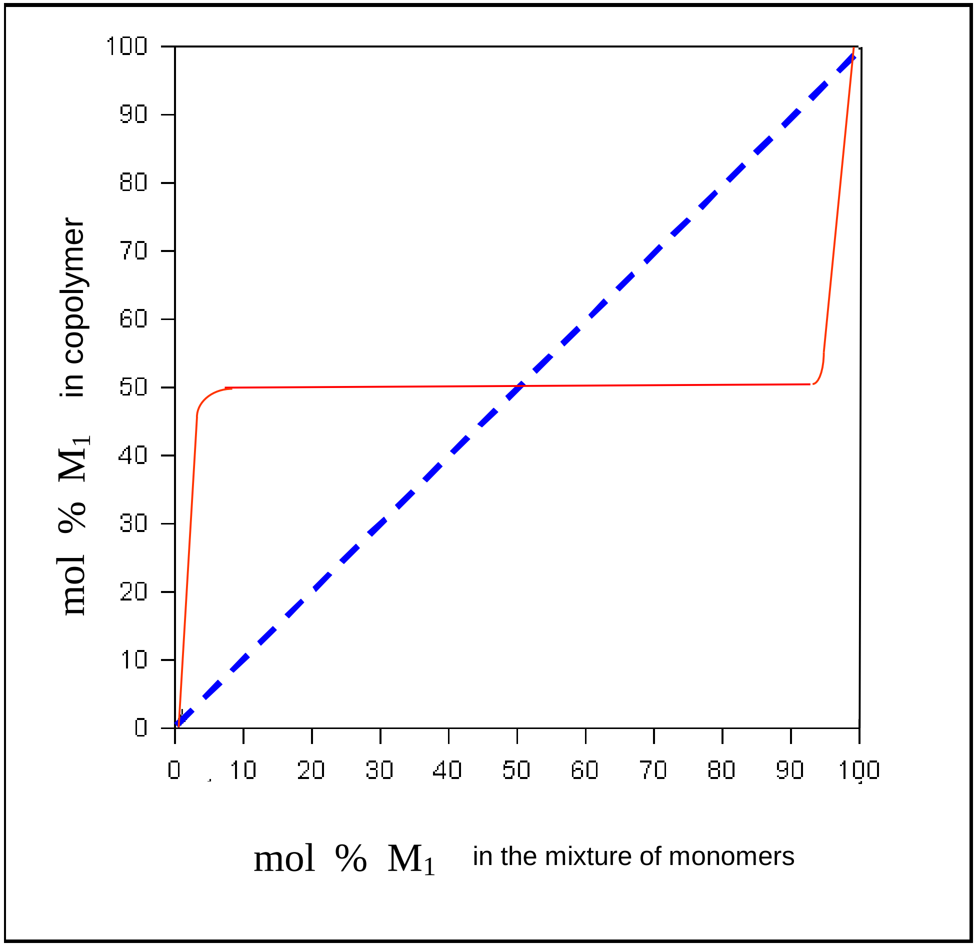
$r_1 = r_2 = 0$

- macroradical, which is at the exact moment present in a rection 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



$r_1 = r_2 = 1$

$r_1 = 0{,}0095$ $r_2 \approx 0$

RING-OPENING POLYMERIZATION

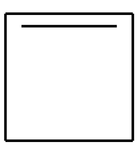
<u>Monomers</u> - cyclic monomers:

cyclobutene, cyclopentene, norbornene,

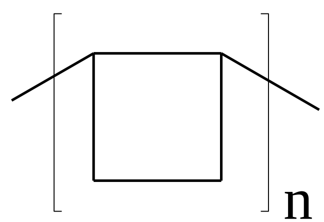
cyclobutene

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

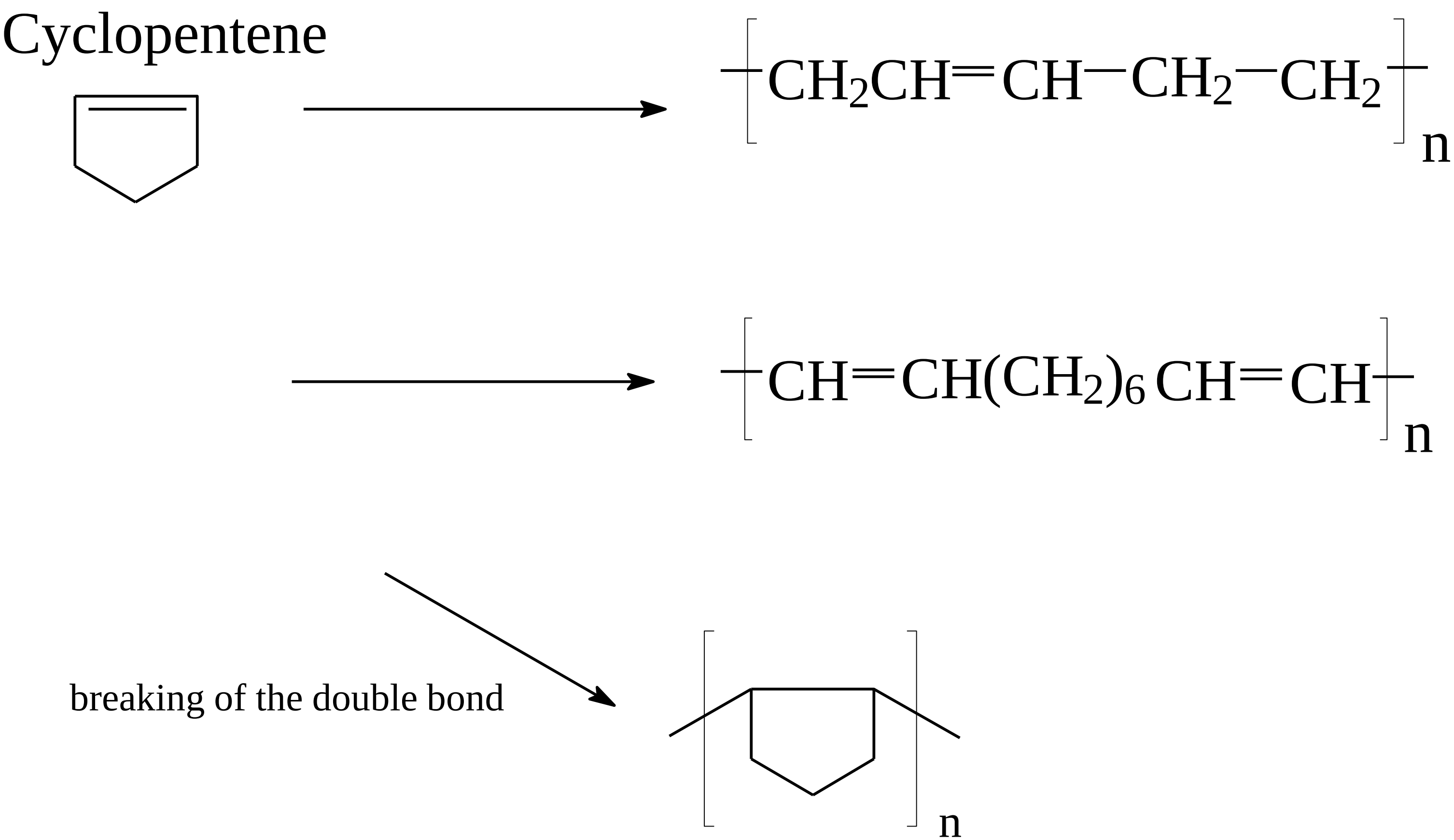
- cis and trans isomers



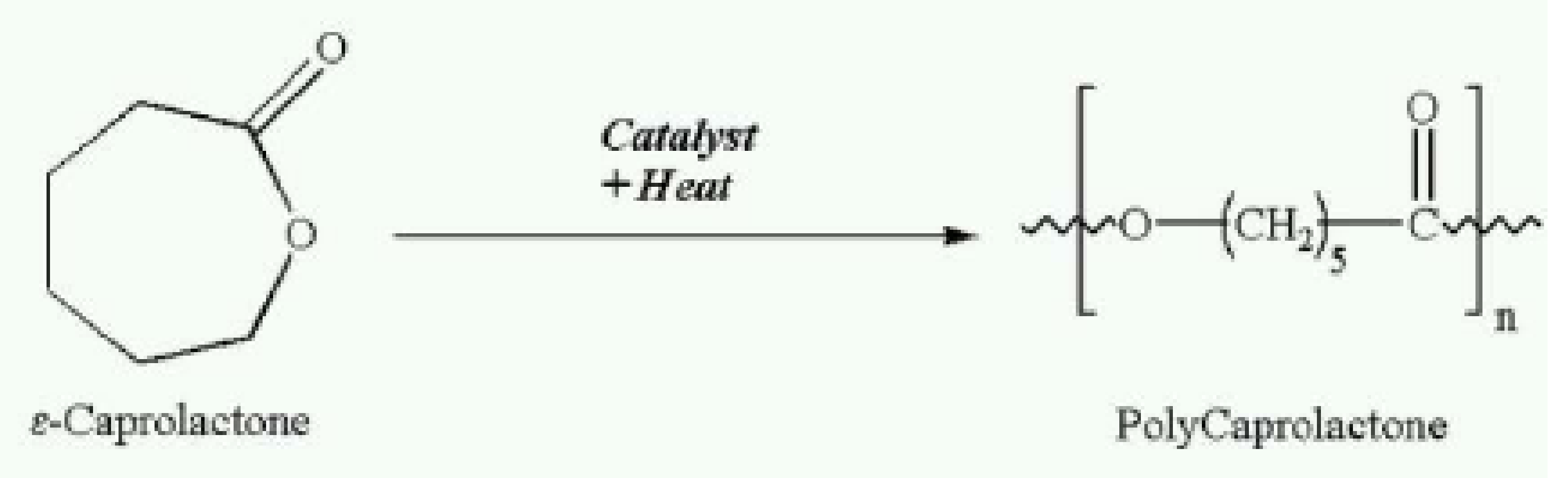
breaking of the double bond $\longrightarrow$



Cyclopentene



caprolactone: polymerization to polycaprolactone (PCL)



IONIC POLYMERIZATION

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 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:

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

carbanion

Initiation:

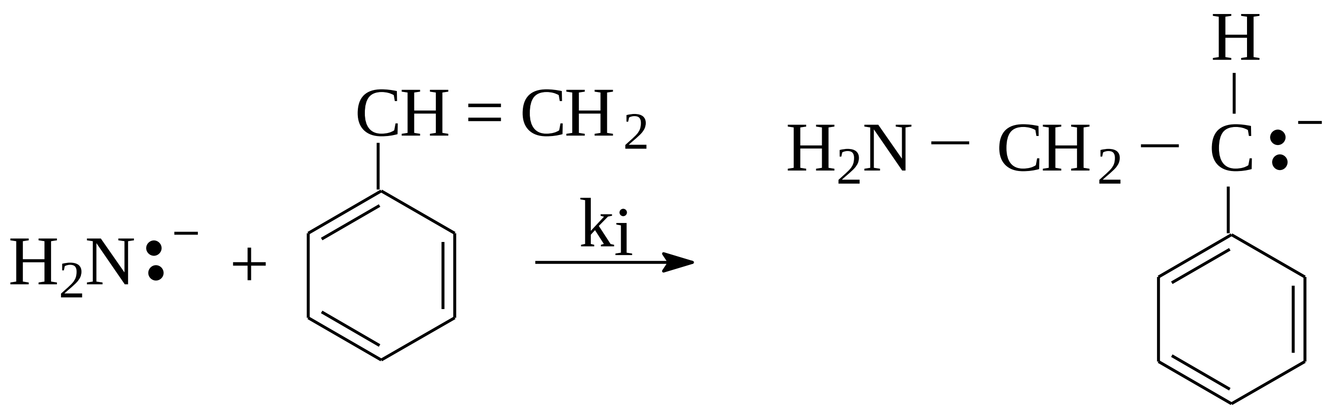
a) by metal amides
b) by electron transfer
c) by metal alkyls

a) by metal amides:

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

$$KNH_2 \underset{}{\overset{K}{\rightleftharpoons}} K^+ + H_2N\colon^-$$

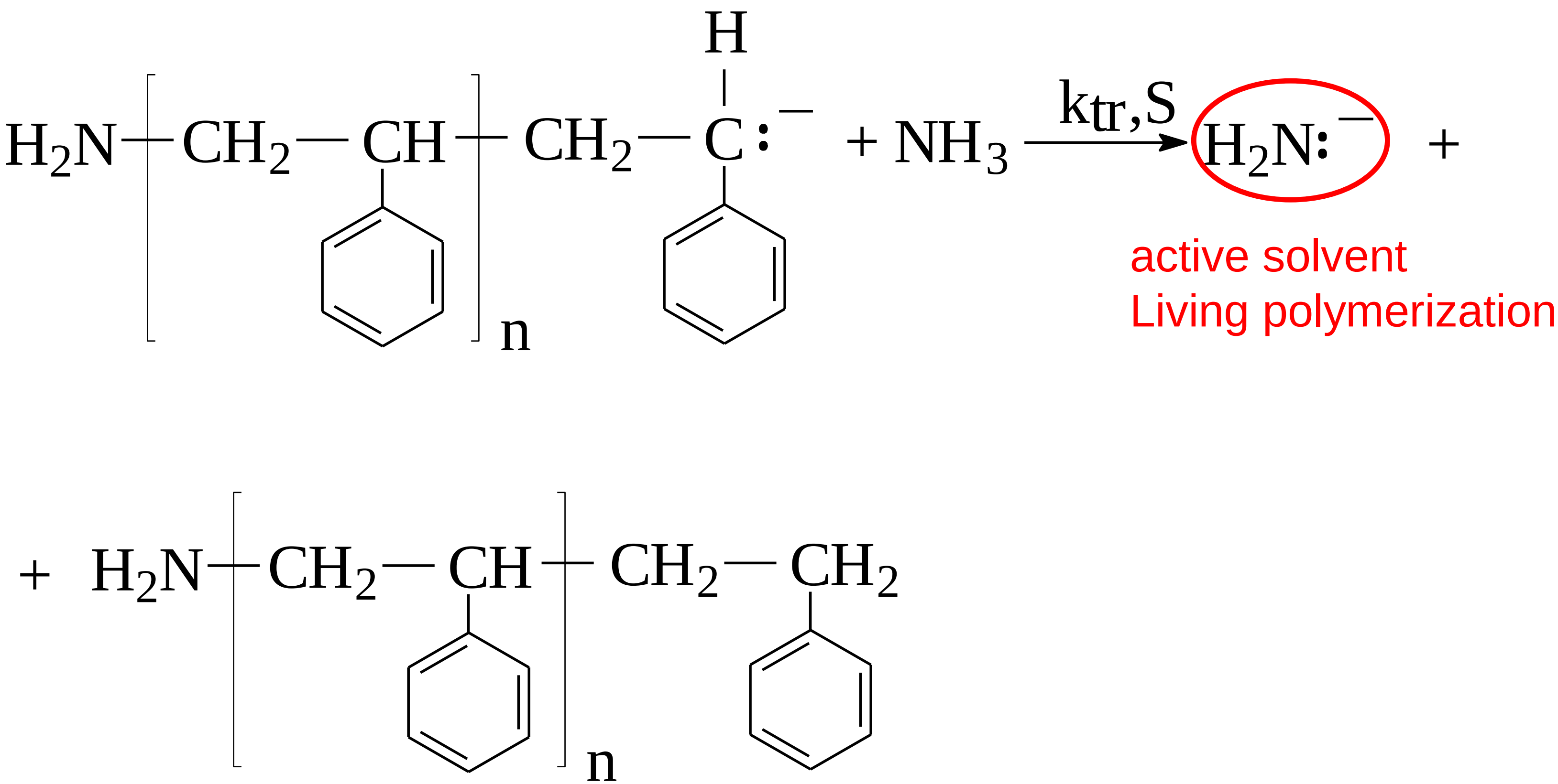
amide ion



propagating anionic center

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

Chain-growth transfer termination to solvent:



The final polymer product

2. CATIONIC POLYMERIZATION

Active end of the growing polymer molecule is positive ion. Ion may be carbonium, oxonium, sulphonium ion or quaterly ammonium ions.

<u>Mechanism of cationic polymerization</u>

INITIATION – initiators discharge electrons

a) protonic acids

$$HA + RR'C = CH_2 \longrightarrow RR'\overset{+}{C} - CH_3 (A)^-$$

These are perchloric, sulphuric or phosphoric acid.

b) 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 ^oC)

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

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

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

$$H\left[CH_2C(CH_3)_2\right]_n^+ (BF_3OH)^- + (CH_3)_2C=CH_2 \longrightarrow$$

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

TERMINATION

a) the 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:

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

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

Active again!
Living polymerization!

The first exam:

on Thursday,13th November 2025

- duration of the exam: 60 min, 10:00 – 11:00
- in written form
- there will be five questions

The second part of the lectures:

on Thursday, 20th November 2025

Dr. Zvonimir Katančić, Associate Prof.