UNIVERSITY OF ZAGREB

FACULTY OF CHEMICAL ENGINEERING AND TECHNOLOGY

POLYMER SCIENCE AND TECHNOLOGY

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Heterogeneous polymerizations

1. Bulk polymerization

- **monomer + initiator**

- polymer is not soluble in monomer

- Monomer and polymer separate in reactor–
  two phases in reaction mixture
  – monomer and polymer layers are separated

- **Polymerization with precipitation**

2. Solvent polymerization

- **monomer + initiator + solvent**

- **monomer is soluble in solvent, polymer is not soluble in solvent –**
  two phases in reaction mixture

- **solvent provides good heat transfer**
- **Polymerization with precipitation**

Advantages:

- low viscosity
- efficient mixing

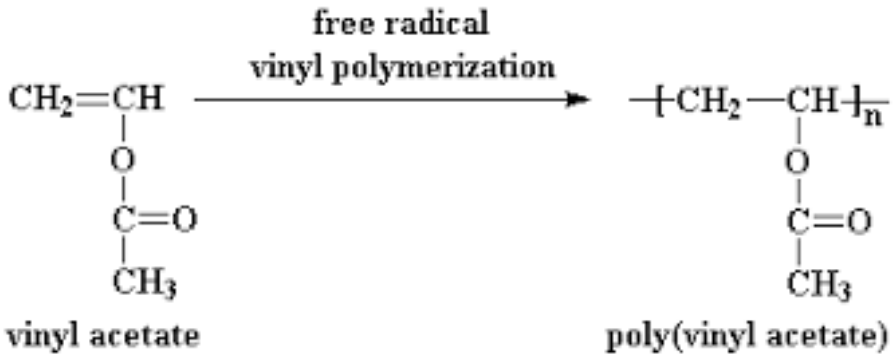
3. Suspension polymerization

- heterogeneous polymerization
  monomer + initiator + water

Suspension polymerization (**pearl** polymerization)

- monomer is slightly soluble or nonsoluble in water
- ratio of monomer and water - 1:2

Monomer is suspended in the shape of small pellets (pearls) in water phase.



The initiators: organic peroxides

- soluble in the liquid phase of **monomer**

Droplets of monomer

- polymerize during heating and strong stirring.
- the result: suspension in which polymer in the shape of little pearls will be obtained

- product of this process: ⇒
  polymer in the form of pearls of different sizes

pearl polymerization

Phases of suspension polymerization

phase 1 – initiation period

- the start of polymerization, monomer is suspended in water
- mechanical stirring prevents the formation of large monomer drops (little drops of monomer are separated by stirring)
- mechanical stirring prevents separation of monomer and water layer

Stirring prevents the formation of monomer aggregates!

phase 2 – propagation period

- a fast formation of
  large pearls → globules of growing polymer chains

- pearls are viscous and sticky and can not be separated by stirring
  Addition of protective colloid (stabilizer) prevents formation of agglomerates of the pearls!

Protective colloid becomes adsorbed on the surface of the pearls and prevents their sticking.

phase 3 – termination period

- the termination of polymer occurs:
  the temperature must be raised!

- the pearls of polymer are firmer after raising the temperature, they are solid and suspended in water, the pearls are not sticky in this phase

- the sticking (aggregation) is prevented by adsorbing of stabilizers on the surface of the polymer in the phase of propagation

Stabilizers are:

- polymers soluble in water ⟶

poly(vinyl-alcohol),
poly(methacrylic-acid),
starch,
gelatin

- inorganic substances ⟶

barium sulphate,
aluminium hydroxide…

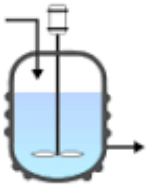
Obtained polymers:

- high molecular masses
- narrow curve distribution of molecular masses

Problems of suspension polymerization:

a) to obtain a homogeneous suspension of monomers in water phase

b) to prevent sticking of polymer droplets during the polymerization



Stirring – one of the most important conditions **for maintaining the stable suspension**

Phase 1 – initiation period

- vigorous stirring enables good dispersion of monomer droplets in water

Significant difference in density of monomer and water phases will affect their separation when stirring is not applied.

Phase 2 – propagation period

- the viscosity of droplets increases and they become sticky - strong stirring prevents their agglomeration but the adding of stabilizer is necessary

Stirring allows:

- efficient heat transfer

Stirring prevents:

- the sticking of polymer on the reactor walls.

Stirring rate significantly affects:

- utilization of residual monomer
- the size of the molecular weight
- the size of polymer particles

Higher speed stirring → the smaller polymer pearls

The form and the type of stirrer is highly important.

The empirical **equation for the size of the pearls**
- the Swiss researcher Hopff:

$$\log L_0 = a_{n\bar{D}} + b_n \log n + b_{\bar{D}} \log \bar{D} + b_n \log N_w$$

L_0 = size of the pearls, cm
$\bar{D}$ = diameter of reactor, cm
N_w = viscosity solutions of protective colloids
n = rpm, s^{-1}
a,b = constants

4. Emulsion polymerization

Heterogeneous polymerization

Components for emulsion polymerization are:

- water
- monomer - insoluble in water
- initiator - soluble in water
- emulsifier- surfactant (contains hydrophilic and hydrophobic groups)

Liquid monomer is emulsified by adding the suitable **emulsifier** and the emulsion is obtained. This emulsion contains *spheral particles (micelles) with size from* ***1-10μ***.

Polymer is obtained as stabile emulsion – **latex**

used for production of **dyes and coatings.**

Mechanism of emulsion polymerization

This type of polymerization is **completely different type** than the other polymerization techniques.

The main difference is that the **emulsion polymerization takes place in a very small volume.**

The important stages are:

1. phase prior to initiation

2. initiation phase

3. the end of formation of emulsifier micelles

4. phase of the monomer disappearance
   propagation

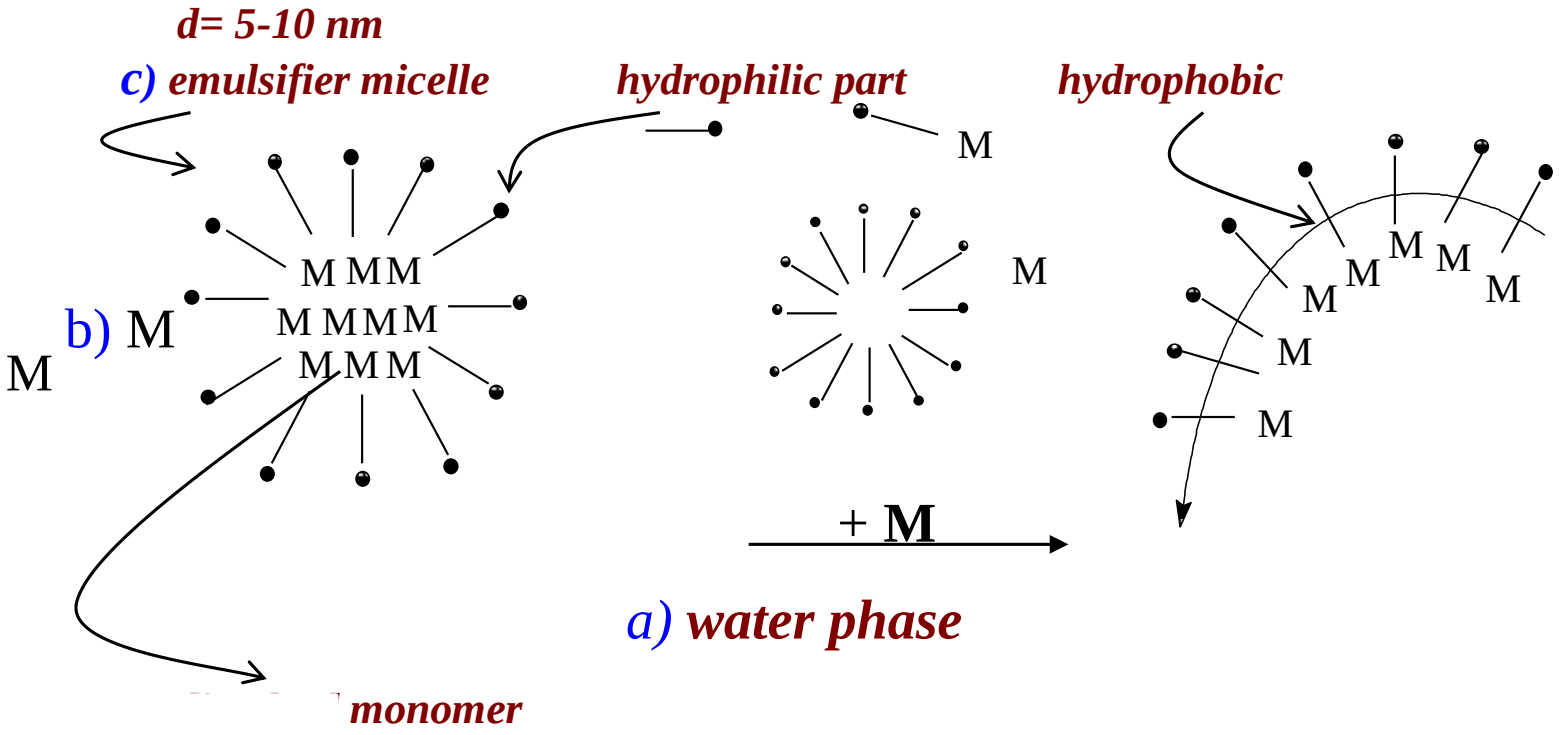
5. end of the polymerization, termination

1st phase: **prior to initiation**

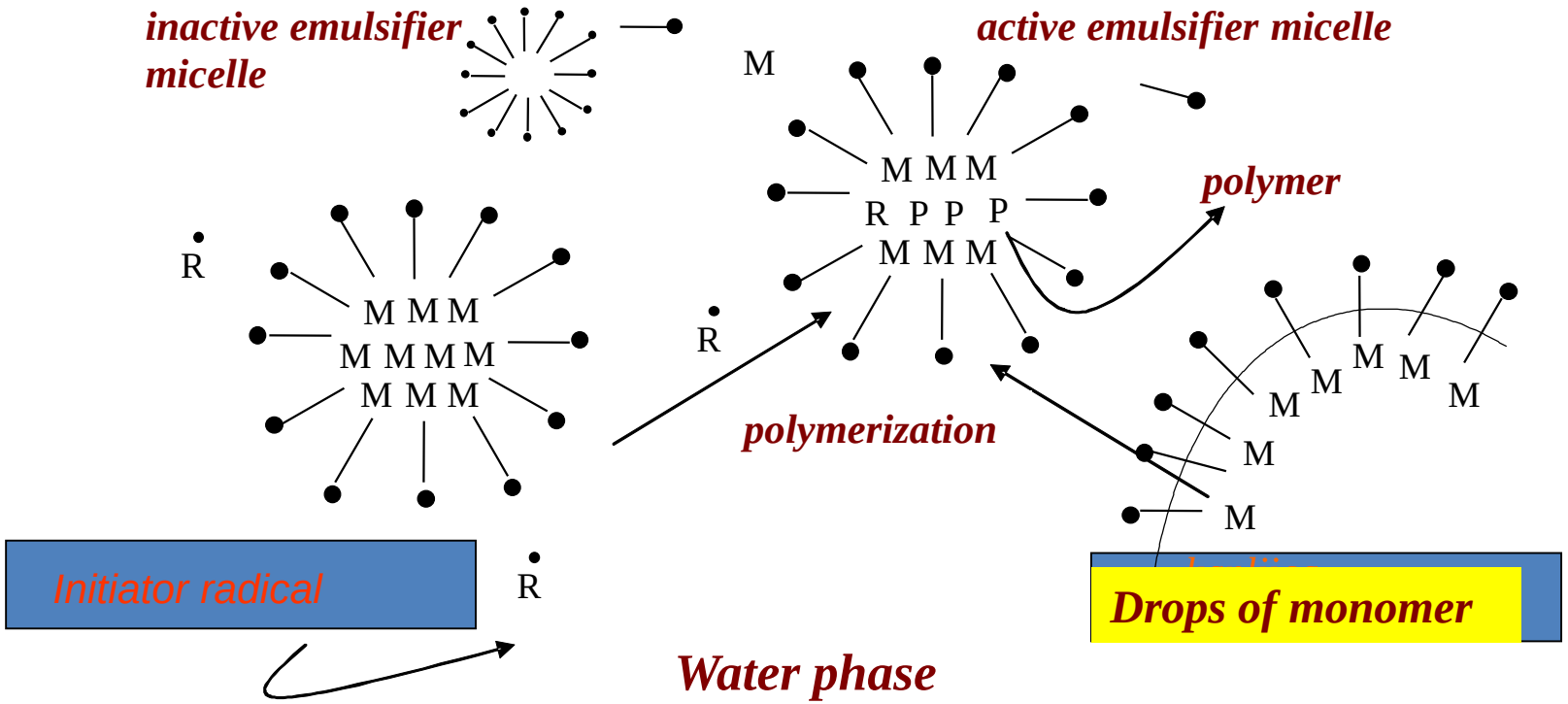
At this prepolymerization state there are:
- water phase,
- monomer drops distributed in water
- emulsifier micelles with dissolved monomer.

Emulsifier molecules form micelles in the aqueous phase: - hydrophobic parts
- hydrophilic parts

When the insoluble monomer is added to water, mixing causes **spliting of monomer** into form of tiny droplets

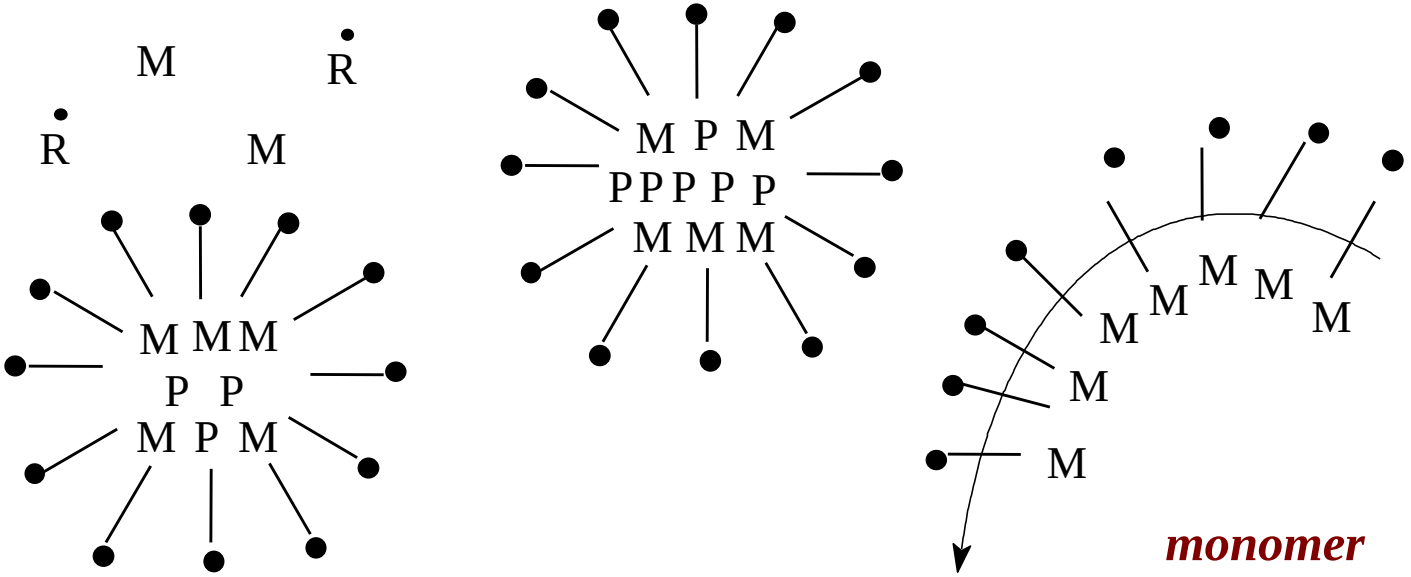

d= 5-10 nm
c) emulsifier micelle
hydrophilic part
hydrophobic
M
M
M M M
M M M M
M M M
b) M
M
+ M
a) water phase
monomer

2nd phase: **initiation**



3. phase the end of formation of emulsifier micelles

active micelles grow during the polymerization

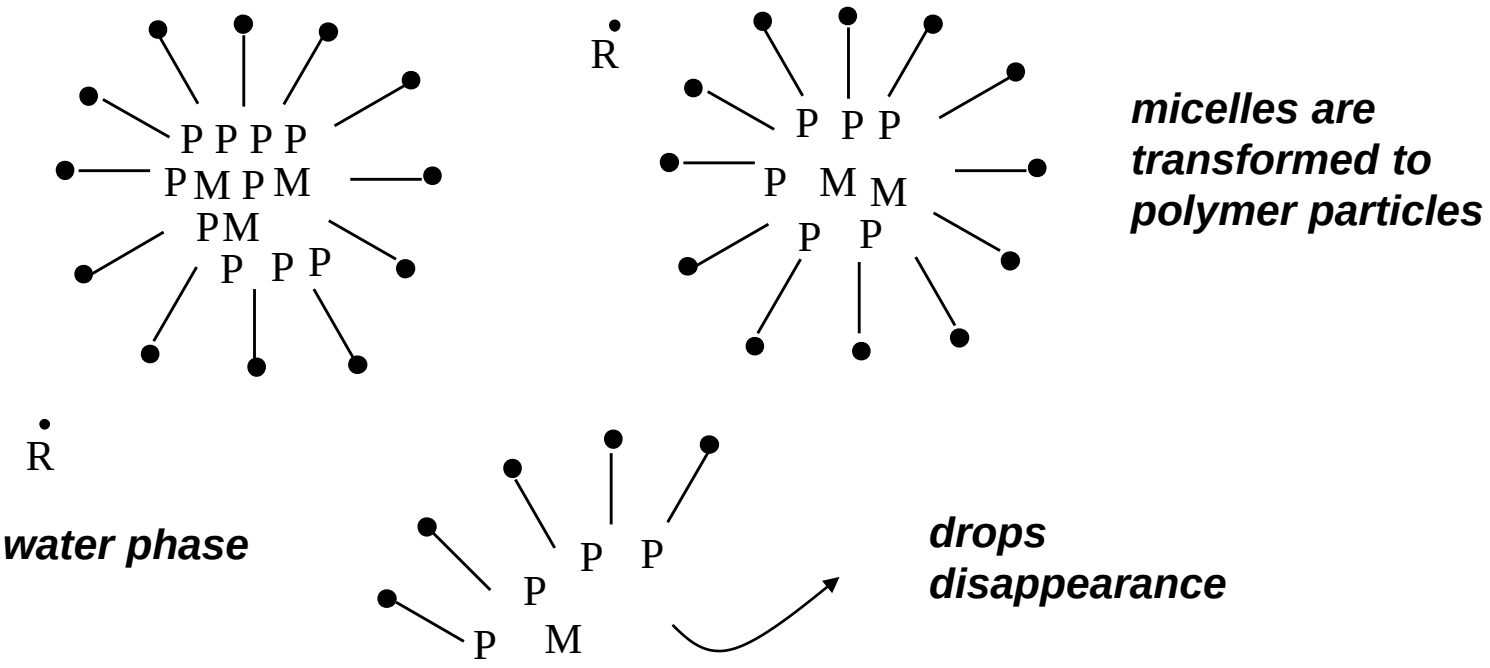


monomer drops

Water phase

4. phase of monomer drops disappearance

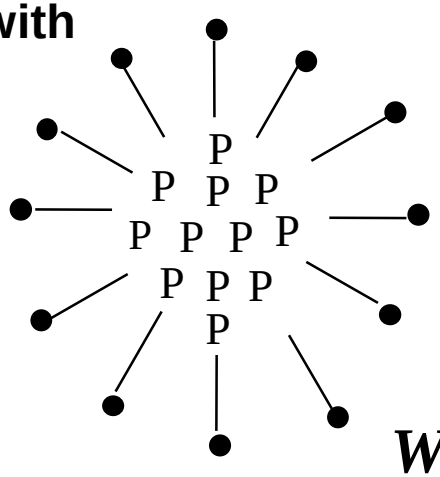
propagation

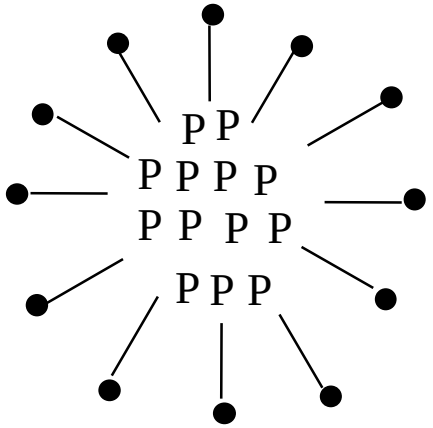


5. the end of polymerization rection - termination

polymer particles with

adsorbed emulsifier





Water phase

Advantages of the emulsion polymerization

1. Water as the dispersive medium
   - low price,
   - nonflammable,
   - nontoxic,
   - system is relatively colourless

2. Efficient temperature control
   - system is diluted and the heat transfer to water medium is better and faster
   - there is no overheating

3. Polymerization
   - relatively low temperatures (20-80 ^{o}C)

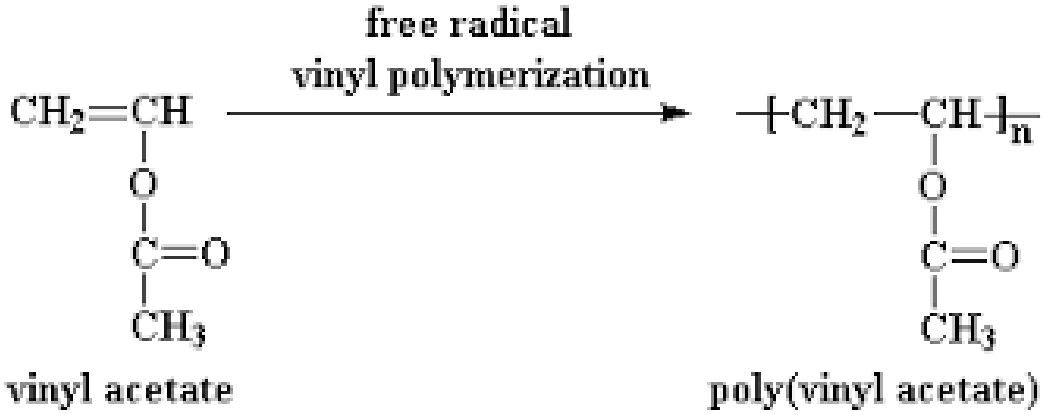
4. Production of polymer
   - with high molecular masses
   - with high polymerization rates

5. Polymerization product
   - directly suitable for use:
     for adhesives, paper impregnation, coatings (colours) etc.

6. Possibility of the polymerization reaction stopping
   - at the all polymerization steps in order to add the modifiers

7. Minimal unwanted side reactions
   - chain breaking and cyclization

8. Viscosity of the emulsion
   i.e. polymer molecular masses are easily controlled and measured



Emulsifiers

-anionic, **kationic** and **nonionic** emulsifiers.

Anionic emulsifiers:

- alkylsulphates,
- alkylarylsulphates and
- phosphates

Many of them are the soaps:

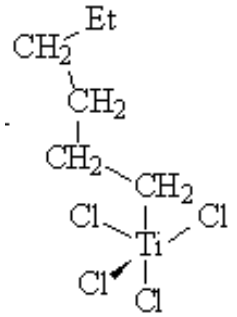
sodium-lauryl sulphate

Nonionic emulsifiers:

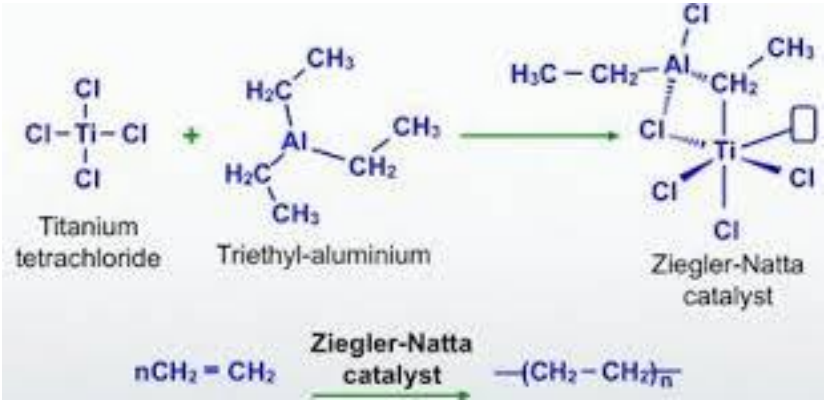
-modified cellulose

-different derivatives of poly(ethylene-oxide)

5. Polymerization in the gas phase



- In production of polyolefins
- at temperatures 20 do 50 °C below polymer softening temperature
- reactor with fluidized particles of active initiators (Ziegler-Natta) – gaseous monomer reacts - polymer is formed at initiator particles in the form of powder
- unreacted monomer is recycled, powdery polymer is separated



6. Interfacial polycondensation

- **Step by step polymerizations**
  - when other polymerization processes are not efficient
- very high reaction rate
- Obtained polymers have high molecular masses
- polyesterifications and polyamidations

- The first monomer component
  – dissolved in a water phase
- The second monomer component
  - dissolved in a some type of organic solvent (insoluble in water)

- Reaction occurs at the interface
  - difussion of the reactants from one phase to another phase – polymerization at the interface

1. Reactors

Polymerization is performed in **reactors of diverse design which have:**

- different conditions of stirring
- different heat transfer

Material for reactors depends on:

- type of polymers
- durability of reactor
- corrosion resistance

Mostly are in use stainless or enamel steel.

Enamel steel

Advantages:

- chemical inertness *(important in all types of reactors)*
- it prevents an adhesion of the polymer to the reactor walls

Polymer is easily and quickly removed from the enamel which isn't the case in materials with steel surface. Extraction of the iron from steel polymer negatively effects on the process of polymerization *(iron participates in chain-growth transfer with initiator)*.

2. Equipment for temperature control

Temperature is important fact for the final properties of the finished product.

Effects:

- on the size of particles
  (effect on solubility of protective colloid and its power of adsorption to polymer)

Equipment for temperature control consists of:

- thermoregulator in reactor
- control valve in the cooling system in the double shield of the reactor

3. Auxiliary equipment of the reactor

Equipment that determines the end of polymerization; the desired degree of conversion.

This is accomplished by several methods:

a) decrease of cooling - at the end of reaction its rate decreases and thermo control element gives impulses for slower opening of cooling media valve

b) partial pressure lowering - indicates the consumption of volatile monomer; monomer provides certain pressure (which decreases with the consumption of monomer)

c) Weight viscosity increasing

Before the termination of polymerization reaction viscosity of reaction mass is rapidly increasing.

It can be measured by:

- integrated viscometer
- measuring the power required to drive the stirrer

Monomer which is present after the polymerization reaction, can be removed with nitrogen flow or destilation with water steam.
Residual monomer must not be higher than 0,8 – 1 mass. % - some monomers are very toxic!

Water is removed by centrifugation up to 90%.
Drying the polymer is performed very carefully so that increased temperature wouldn't affect the final properties (*drying at room temperature*).

Laboratory reactors