

POLYMER SCIENCE AND TECHNOLOGY

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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 \longrightarrow 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:

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

$$L_0 = size of the pearls, cm$$

- \overline{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* **1-10** μ .

Polymer is obtained as stabile emulsion – <u>latex</u> 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



2nd phase: initiation



<u>3. phase</u> the end of formation of emulsifier micelles

active micelles grow during the polymerization



4. phase of monomer drops disappearance

propagation



5. the end of polymerization rection -

termination



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 °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.

 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
- <u>Viscosity of the emulsion</u>
 i.e. polymer molecular masses are easily controlled and measured



<u>Emulsifiers</u>

-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 value 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*).

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Laboratory reactors







COPOLYMERIZATION

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product: copolymer

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

The mixture of 2 monomers:

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



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

2) Alternated copolymer

- equal quantity of each monomer in the polymer structure

3) Block copolymer

- longer blocks of one monomer in the polymer chain

-A-A-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