

## Polymeric materials- laboratory

## Preparation of polymers by suspension polymerization

Based on J. Pielichowski, A. Puszyński: *Preparatyka związków wielkocząsteczkowych*PART A – Suspension polymerizationIntroduction

Polymers are macromolecular compounds with macromolecules built of repeating elements of the structure, so-called mers. The polymerization reaction is the process of combining the substrate molecules - the monomer, into product - polymer molecules, without isolating any side substances. The most common substances which are susceptible of polymerization reactions include those compounds containing double bonds. As a result of the polymerization of bifunctional monomers containing one double bond or two reactive groups in the molecule, linear polymers chains are formed, which can be fusible and soluble in solvents of similar polarity. The presence of two or more double bonds or at least three functional groups on the monomer molecule may result in a spatially crosslinked polymer that is insoluble and insoluble.

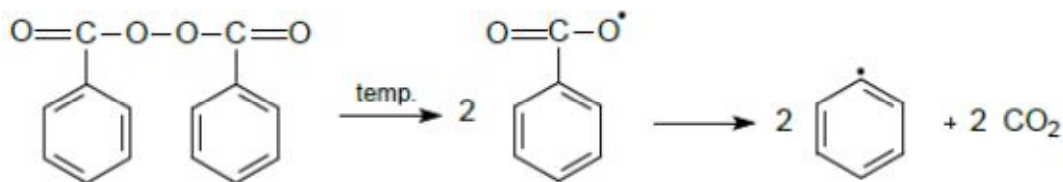
Vinyl monomers (containing double bonds) are most often polymerized according to the free radical mechanism. Free radical polymerization takes place in three stages:

- polymerization initiation,
- polymer chain growth (propagation),
- chain ending.

The initiation of free radical polymerization is the process by which the free radical is formed on the carbon atom of the monomer molecule. The factors that enable the initiation of free radical polymerization are:

- free radicals, formed as a result of the breakdown of peroxide or azo initiators,
- thermal energy (thermal polymerization),
- UV rays (photopolymerization), X or gamma rays (radiation polymerization),

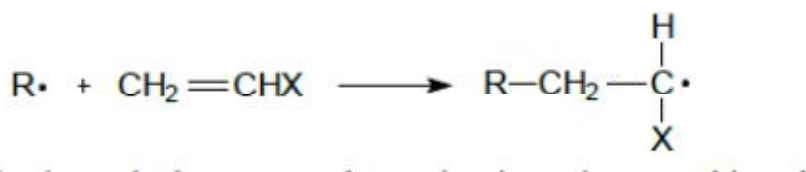
ultrasounds A typical example of the dissolution of the initiator into free radicals is the breakdown of dibenzoyl peroxide, called benzoyl peroxide:



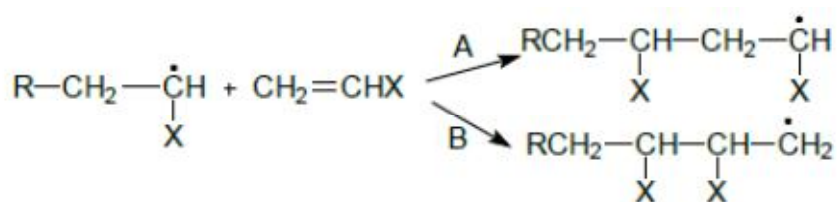
An important factor characterizing the polymerization initiation stage is the induction period. This is the time counted from the initiation of polymerization to the beginning of chain growth. It depends on the reaction temperature, the structure and concentration of the monomer, the presence of inhibitors, etc.

The second stage of radical polymerization is the growth of the chain, called propagation. Wzrost ten polega na kolejnym przyłączaniu się cząsteczek monomeru początkowo do

wolnego rodnika, powstałego w etapie inicjowania polimeryzacji, a następnie do wciąż wzrastającego makrorodnika.



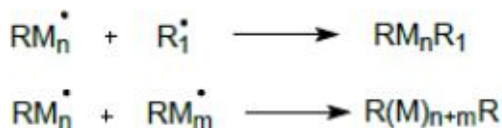
The speed of chain growth is so high that it practically does not affect the polymerization kinetics. This step, however, determines the chain configuration of the resulting polymer. The attachment of the monomer molecule containing the X substituent to the growing macro-radical can occur in the "head to tail" system (scheme A) or "head to head" (scheme B).



Due to the possibility of resonance of an unpaired electron with the substituent X and for steric reasons, the formation of a "head-to-tail" configuration is more favored and in most polymers the content of these structures is 98-99%.

The last stage of free radical polymerization is the end of the chain. It can take place:

- by the collision of two macro-radicals with each other (so-called recombination):



where: M=CH<sub>2</sub>CHX a **RM<sub>n</sub>·** and **RM<sub>m</sub>·** - growing macro-radicals,

- by chain transfer reactions resulting from collision with an inert monomer, solvent or polymer molecule; then the growth of the macro-radical chain ends with the simultaneous creation of a new radical:



Depending on the method and conditions of the polymerization, polymers differing in molecular weight and polydispersity, and thus in physical and functional properties, can be obtained.

### Suspension polymerization

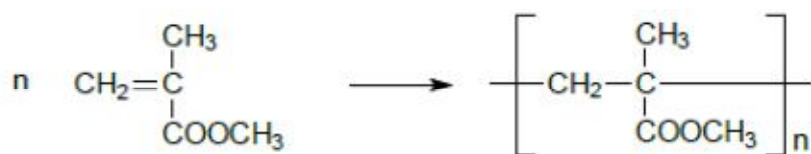
The suspension polymerization, also known as polymerization in the micro-blocks or pearl polymerization, is carried out with water-insoluble monomers. The process takes place under the influence of the initiator dissolved in the monomer dispersed in an aqueous solution of organic colloids, which are suspension stabilizers. The suspension polymerization and the

properties of the resulting polymer are strongly influenced by: protective colloids (suspension stabilizers), polymerization initiators and mixing. When dispersing the monomer in excess (2- to 4-fold) demineralized water, small beads with a diameter of 0.1-1 mm are formed. As polymerization progresses, these beads, often referred to as pearls, increase the viscosity and assume sticky consistency. To prevent sticking of the beads the hydrophilic protective colloids are added to water phase. Even the minimum concentration of protective colloid (0.1% -wag.) Causes the formation of a protective coating on the boundary surface that prevents the coalescence of monomer droplets. Excessive reduction of the viscosity of the aqueous phase may result in the formation of an emulsion, whereas too high viscosity of this phase makes it difficult to disperse the monomer during mixing, which can lead to the formation of a coarse polymer. Protective colloids include water-soluble organic macromolecular compounds such as poly(vinyl alcohol), salts of polyacrylic and polymethacrylic acids, methylcellulose and their derivatives, gelatine, starch, etc. Well-grounded, water-insoluble inorganic compounds, such as water, can also be used.: bentonites, silica gel, calcium phosphates, aluminum and magnesium hydroxides. In the suspension polymerization process, various additives that modify the activity of the protective colloid are also used. These additives, also called auxiliary suspension stabilizers, improve the hydrophilic-hydrophobic balance of the colloid and correct the surface tension at the water-monomer interface. In the course of suspension polymerization, mixing plays a very important role, because its intensity affects the size of the beads, their shape and polydispersity. Too slow mixing can promote agglomeration and too fast product fragmentation. The problem of mixing is particularly important in the first polymerization period when the monomer reaction is 10-60%. Stop the mixer, even for a very short period of time causes irreversible agglomeration. The advantages of suspension polymerization are: the ability to synthesize a particulate polymer that is easy to isolate by filtration or centrifugation; easy removal of the protective colloid; obtaining a product with reproducible properties, and low polydispersity and the ease of discharging the heat released during the polymerization reaction.

This method has been widely used for the industrial production of polymers such as poly(vinyl chloride) - PVC, poly(methyl methacrylate) - PMMA, polystyrene - PS, poly(vinyl acetate) - PVAC.

### Aim of exercise

The aim of the exercise is to follow the course of the process of suspension polymerization of methyl methacrylate, isolation of the resulting polymer and determination of reaction yield.



### Materials:

- methyl methacrylate (MMA)- 21.25 g,
- benzoyl peroxide (BPO)- 0.6 g,
- poly(sodium acrylate) (Rokrysol WF-2) - 5.0 g,
- Na<sub>2</sub>HPO<sub>4</sub> – 0.7 g,
- NaH<sub>2</sub>PO<sub>4</sub> – 0.045 g,
- - NaOH in tablets - 1 pastil

- nitrogen from the bottle.

**The apparatus and the glass:**

- reactor, vol. 500 cm<sup>3</sup>,
- reflux condenser,
- mechanical stirrer,
- thermometer,
- nitrogen supply pipe,
- beaker 150 cm<sup>3</sup>,
- Büchner sieve, Ø 9 cm
- suction flask, vol. 1000 cm<sup>3</sup>,
- water pump,
- electric water bath.

**Procedure:**

To the reactor put 125 cm<sup>3</sup> of distilled water, 5.0 g of poly(sodium acrylate), 0.7 g of Na<sub>2</sub>HPO<sub>4</sub>, 0.045 g of NaH<sub>2</sub>PO<sub>4</sub> and 1 pellet of NaOH. The reactor, after closing with a cover with the stirrer, is supplied with a reflux condenser and a thermometer, and then placed in a water bath. The contents of the reactor are heated at 30-35°C until the components are completely dissolved. In a beaker 21.25 g of MMA are weighed, in which 0.6 g of BPO is dissolved. The initiator solution in the monomer is introduced into the solution in the reactor and then purged with nitrogen to remove oxygen. After starting the mixing (about 250 rpm) the reaction mixture is heated in a water bath to 78-80°C and maintained at this temperature for 2 hours. After completion of the reaction, the product is cooled to room temperature, filtered under vacuum on a sieve, washed with distilled water and dried in an oven at 65°C for 5-10 h. The product is weighed and the yield of the polymerization reaction must be calculated.

**PART B**

During polymerization, you will also prepare membrane from polysulfone UDEL 1700 (PSU), which you will be used them during the exercise **No. 5.**

**Chemicals:**

- PSU solution with known concentration in N, N-dimethylformamide,
- Methanol for cleaning glass surface,
- Water bath.

**The apparatus and the glass:**

- Knife for forming the membranes,
- Plastic cuvettes,
- Glass pane,
- Glass beakers,
- Sponge.

Procedure:

The glass, on which the individual membrane sheets will be formed, should be thoroughly washed with water, then degreased with methanol and then dried. The glass is placed on a special sponge. The knife for forming the membranes is placed on the edge of the glass. A polysulfone solution is poured into the knife's gap and then spread evenly over the glass pane using this knife. Then the poured film together with the glass is transferred to a plastic tray filled with water. The precipitated polymer film is transferred to a fresh supply of water. The obtained membranes are left in the water for the next exercise (**exercise 5**), during which their physicochemical and filtration properties will be determined.

### **Issues for parts A and B**

- **Definition of polymer, division of polymers,**
- **Polymerization - basic information about the polymerization process,**
- **Methods for obtaining spherical polymeric materials,**
- **Membrane definition, membrane division,**
- **Methods for obtaining polymer membranes,**