

MATERIALS AND INSTRUCTIONS FOR EXPERIMENTS NO. 2 AND 5

BASIC TECHNOLOGY OF POLYMERS

4.1. INTRODUCTION

Term “**polymer**” comes from Greek *polymeros* (consisting of many parts) and means large molecule made up of repeating simple molecules (**mers** or **monomers**) that have low molecular weight. Polymer composed of one kind of starting molecules is called **homopolymer**, and polymers composed of various kinds of monomers are called **copolymers** or multipolymers. Polymers are formed during polymerization reactions (if different kinds of monomers form copolymer or multipolymer, the reaction is a copolymerization or a multipolymerization, respectively) [1,2].

The main subject of interest in macromolecular chemistry are stable polymers containing a covalent or coordination bonds between the mers. However, in a broader spectrum macromolecules having electron deficient bonds (borates, polymeric PdCl_2) or hydrogen bonds (polymeric H_2O , liquid HF, crystallized methanol) are also considered as polymers. However, the practical value have the polymers with mers connected with covalent chemical bonds. Many **inorganic polymers**, e.g., polysilicates, polyphosphates, polymeric sulfur, sand, diamond are common in nature. Others, like glass, porcelain, molecular sieves, are produced synthetically. **Organic polymers** are separate and very common class of macromolecular compounds and some of them are fundamental to life, for example, polysaccharides, ribonucleic acids and deoxyribonucleic acid, or polypeptides. Many of the **natural organic polymers** are also important for economy, such as natural rubber and gutta-percha, cellulose, starch, wool, vegetable and animal proteins. On the other hand synthetic polymers are also employed in an enormous range of applications. Plastic industry is producing and processing huge amounts of synthetic organic polymers. Synthetic polymers or chemically modified natural polymers belong to a group of **plastics**, although in common sense plastic is considered as the polymer enriched with all the accessories needed in the manufacturing process, i.e. fillers, pigments, antioxidants, processing aids and flammability reducers etc. [2]

Plastics, depending on the physic-chemical properties and applications can be divided into four categories: thermoplastics, thermosetting plastics, elastomers (rubbers) and fiber plastics. This classification is often used, but still vague, since some polymers can be at the

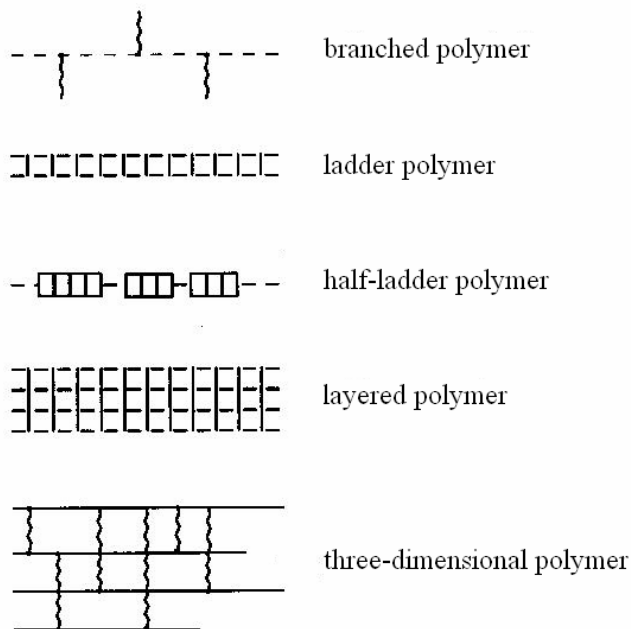
same moment classified into two groups , such as polypropylene (a polymer that is typically a thermoplastic material and is also used for production of synthetic fibers). Another example is a copolymer of ethylene and propylene - being thermoplastic and elastomer.

It is difficult to unambiguously define what the minimum size of particles can be considered as polymers. Macromolecule is defined conventionally as a molecule with at least 2000 atoms assembled together covalently. The number of repeating units (mers) in the macromolecule is called a **degree of polymerization**. Degree of polymerization, \bar{P} , can be calculated from the molecular weights of polymer (\bar{M}) and monomer (M_M):

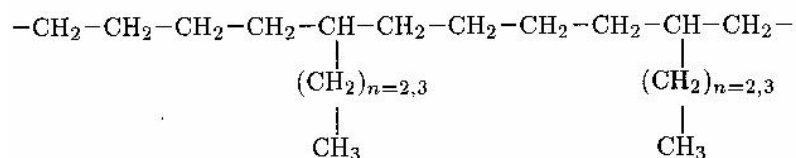
$$\bar{P} = \frac{\bar{M}}{M_M}$$

An increase of the degree of polymerization beyond 1000 practically does not cause significant changes in physical properties of polymer, like softening point and mechanical strength. So, $\bar{P}=1000$ can be considered as the limit above which the polymers occurs. Molecules below this limit are called **oligomers**. According to this distribution, solutions of oligomers form a hemi- or mesocolloids, and polymers - eucolloids.

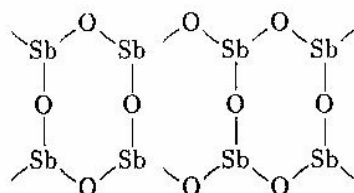
Macro-and microstructure of polymers has a significant impact for their properties. According to the macrostructure criterion, polymers can be divided into linear, branched, ladder, half-ladder, layered and three-dimensional. Schematically these structures can be depicted as follows:



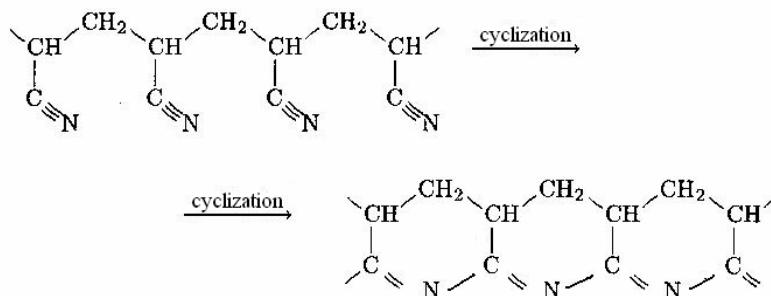
Typical representatives of **linear polymers** are polymeric sulfur: $-S-S-S-S-$ or tetrafluoroethylene (or perfluoroethylene): $-CF_2-CF_2-CF_2-CF_2-$. An example of a **branched polymer** is high-pressure polyethylene industrially obtained at the pressure $p > 1200$ atm and temperature $T = 200^\circ C$:



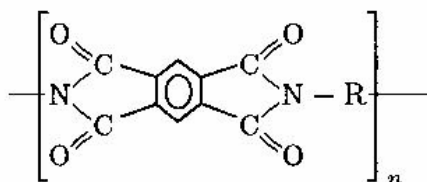
Among the natural inorganic **ladder polymers**, polymeric antimony trioxide is a good example:



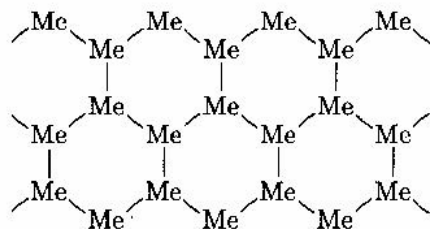
An example of synthetic organic **ladder polymer** is polyacrylonitrile subjected to thermal cyclization:



Half-ladder polymers like polypyromellitimide were obtained so far only by synthetic methods:



There are numerous examples of natural layered polymers, including black phosphorus, gray arsenic and metallic antimony:

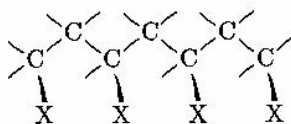


where Me = P, As, Sb.

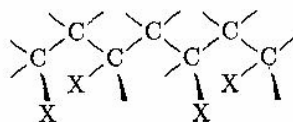
The most famous example of three-dimensional pure carbon polymer which have regular structure is diamond. Extremely high hardness of diamond can be explained by the fact that the crystal lattice is formed by covalent bonds only. However, the polymers are mainly organic thermosetting plastics, as well as crosslinked rubbers [2,3].

Macrostructure of polymers has a big impact on their physical properties. Compared to linear polymers, branched polymers are generally more amorphous, have a lower softening point and glass transition, and thus, are more flexible. Ladder and half-ladder polymers are generally poorly soluble, they are rigid and have increased resistance to temperature. The three-dimensional polymers are completely insoluble and at elevated temperatures did not melt but decompose. Spatial **cross-linking** of polymers also causes an increase of their mechanical strength parameters.

A significant impact on the properties of polymers has their microstructure associated with the configuration of units in the macromolecule. If the polymer chain is composed of substituted monomeric units linked together on a regular basis, "head to tail", the spatial location of the substituents determines their so-called **tacticity**. When the mer substituents are located on the same side of polymer chain (the same plane) - the polymer is isotactic. When the location of substituents cannot be assigned to one plane (substituents are located regularly on both sides of the polymer chain) the polymer is syndiotactic.



isotactic polymer



syndiotactic polymer

Atactic polymers shows lack of any regularity in the arrangement of substituents. Tacticity, regularity of "head to tail" linking and a presence of geometric isomers (e.g. 1,4-*cis* or -*trans* polydienes) are very important for degree of crystallinity and the physicochemical properties

of polymers. High iso-or syndiotacticity of polymer favors greater crystallinity and, thus, , causes a distinct melting point and generally better parameters of mechanical strength.

4.2. POLYMERIZATION PROCESSES [1-4]

4.2.1. General remarks

The reactions leading to the formation of polymers are very diverse in nature. This applies to both, the mechanism and kinetics of these reactions. Although different approaches to this issue can be found in the literature, the classification of reactions according to the mechanism of polymer chain growth dominates. According to this classification, polymerization reactions can be divided into **chain polymerizations** and **step polymerizations**.

Chain polymerizations are typical reactions in kinetic sense: the polymer molecule is formed in several stages, the first is a **start of kinetic chain reaction**, in second, a large number of identical monomer molecules undergo very rapid reaction / addition with other monomer molecules (**growth reaction**), broken finally by the end of either polymer chain reaction and the kinetic chain. After each single growth reaction, length of reacting polymer chain grows by one mer. Start, growth and **termination** reactions are three different kinds of chemical reactions with different mechanism and speed.

Step polymerizations have only one type of reaction, which is the reaction of growth. There is no difference here between the start, growth and termination, as both the start and end have the same nature as the growth reaction, which in relation to the chain reaction proceeds much more slowly. Macromolecules with a high degree of polymerization are achieved only at very high degrees of conversion. This slow increase of polymerization degree follows from the fact that during the step polymerization all molecules of monomer are transformed into dimers, then into trimers, tetramers and so on, until finally the polymeric macromolecules are obtained.

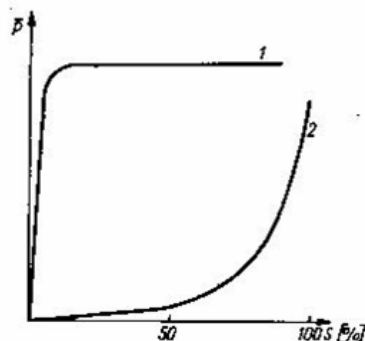
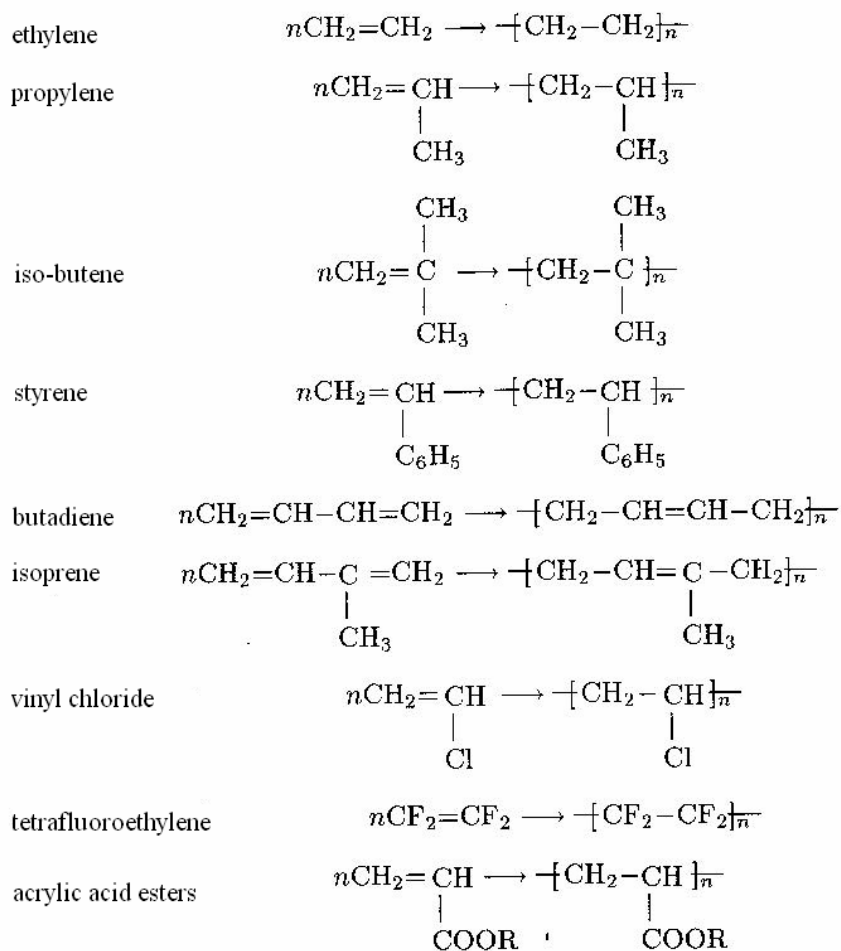
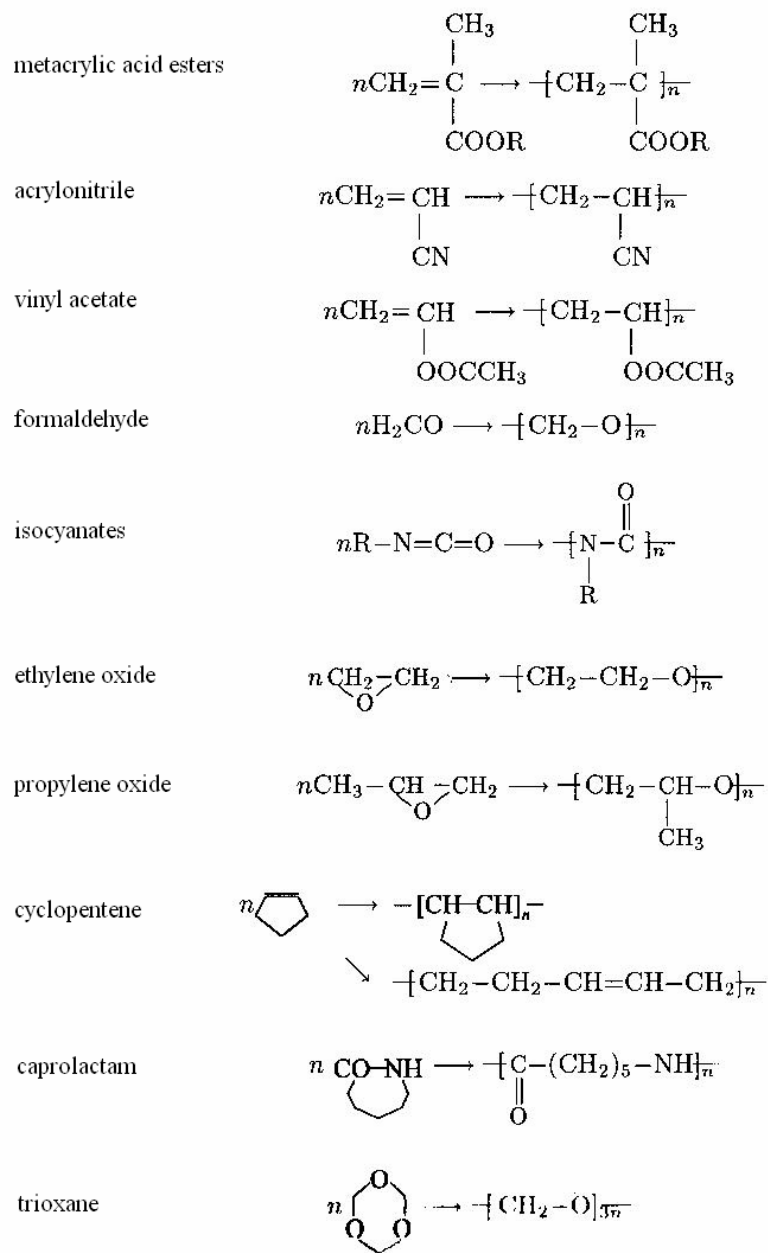


Figure 1. Relationship between degree of polymerization and degree of conversion for the chain (1) and step (2) polymerization.

Comparison of the chain and the step polymerization processes is shown in Figure 1. Graph shows the correlation between the degree of polymerization and the degree of conversion (fraction of reacted monomer). Chain polymerization usually occurs with the opening of the double bond, triple bond or ring opening. Monomers with double or triple bond include olefins, dienes, vinyl compounds and aldehydes, ketones, thioketones, nitriles, azo compounds, Schiff bases, SO_2 , diazoalkanes, isocyanates and others. As you can see monomers of these groups may have multiple bond: carbon-carbon, carbon-heteroatom, or heteroatom-heteroatom. Group of cyclic monomers include cycloalkanes and cycloalkenes, cyclic ethers, lactams, lactones, dioxoles, and many others. Below are listed examples of common monomers which undergo chain polymerization:



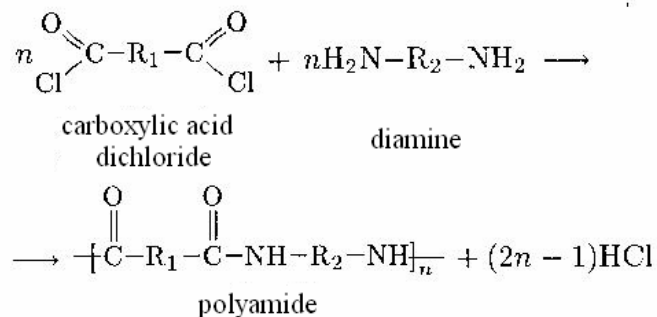
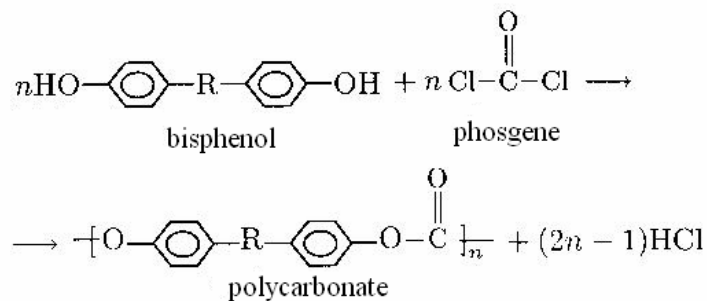
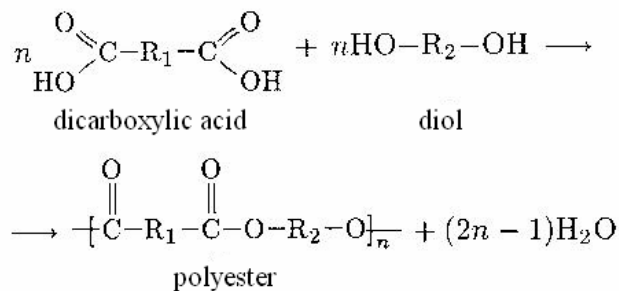


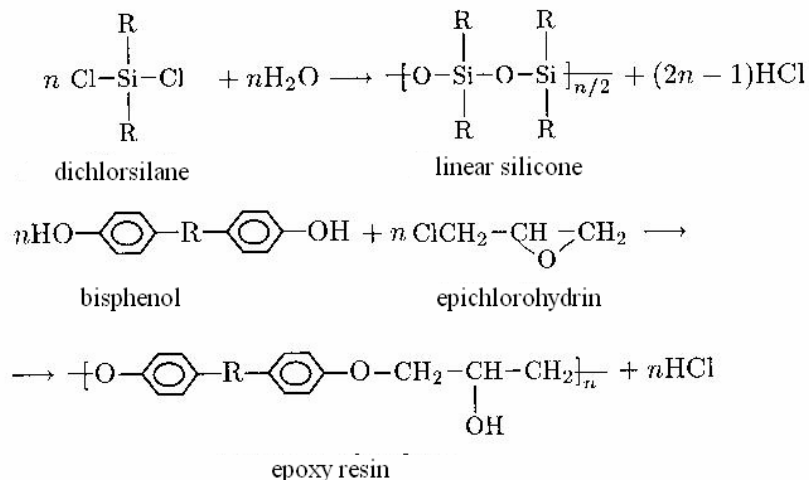
These compounds are just most popular examples of the wide range of monomers polymerizable by the kinetic model of chain reactions.

Step polymerizations include two subgroups of polyreactions: polycondensation and polyaddition. These are reactions that occur with monomers with two functional groups. The difference between polycondensation and polyaddition lies in the fact that in the first of these polyreaction growth of the polymer chain is accompanied by the formation of low molecular weight condensation by-products (for example, NH_3 , HCl , H_2O) whose removal shifts the reaction equilibria and is necessary for the progress of the reaction. In the case of

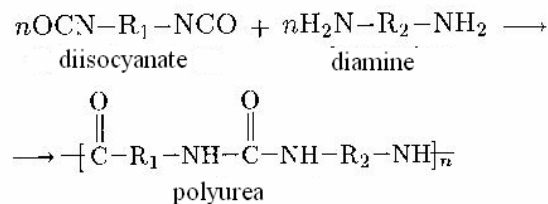
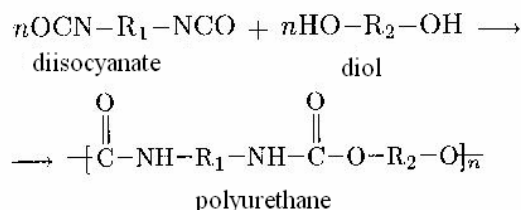
polyadditions this condition does not occur and the reaction can occur even spontaneously. Among the well-known step polyreactions, polycondensation reactions are far more common. This also applies to polyreactions that have industrial importance. Below are some of the well-known systems of monomers undergoing polycondensation and polyaddition.

Polycondensations

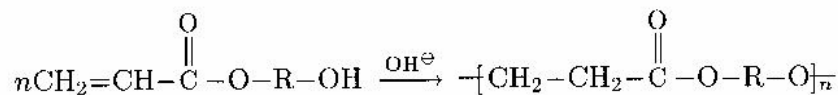




Polyadditions



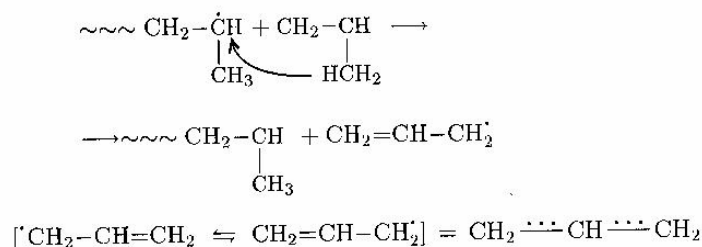
Polycondensations also proceed with the participation of one type of monomers with two different functional groups, for example, polyesters can be prepared from hydroxyacids, polyamides from amino acids containing more than 7 carbon atoms per molecule. There are also analogous monomers undergoing polyaddition. Monoesters of acrylic acid and diols polymerize by Michael addition mechanism:



4.2.2. Chain polymerizations

Chain polymerization may be carried out using free radical mechanism, anionic mechanism, cationic mechanism and coordination mechanism. Type of mechanism depends on the chemical properties of monomer and initiator used. The best known and most

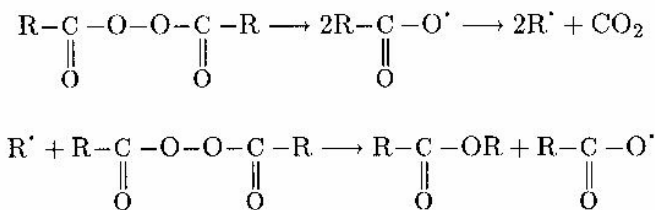
widespread are free-radical polymerizations, where monomers have carbon-carbon double bonds (vinyl monomers). The most popular are: ethylene, butadiene, styrene, vinyl chloride, acrylonitrile, esters of acrylic and methacrylic acid, vinyl acetate, tetrafluoroethylene and many others. Monomer polymerizes more readily radical, when the start of the chain reaction's energy of activation is lower and radical formed from the monomer is more resonance stabilized. For example, the ethylene produces highly reactive radicals, but the activation energy of the start of polymerization is also very large. Since this is also a gaseous monomer with low boiling point (b.p.= -103.7°C), its radical polymerization occurs only at pressures above 1200 atm and at temperature $T = 200^{\circ}\text{C}$. The role of substituents in the monomers might be various: a substituent can affect the resonance stabilization of the radical formed, but on the other side, inductive effects cause the polarization of the double bond and lowering the activation energy of the start and growth reactions. A big impact, especially at higher substituted derivatives of ethylene, has the steric hindrance. Homopolymerization of 1,2-di- and higher substituted ethylene is in principle impossible, if the volume of substituents is greater than the fluorine atom. Alkyl substituents (e.g. in propylene) cause very strong growth trends in the occurrence of radical transfer of hydrogen from the monomer to the alkyl radical, which leads to the formation of allyl radical with a very good resonance stabilization:



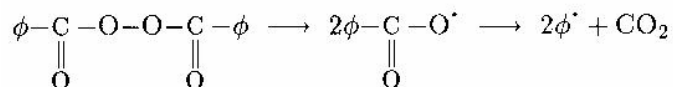
According to the above mechanism, the monomers like propylene, 1-butene, 2-butene, isobutene, vinylcyclohexane, cyclopentene, and unconjugated dienes such as 1,4-pentadiene, can be considered as not suitable for radical homopolymerization, since even in extreme conditions (high temperature and pressure) their polymerization leads at most to the formation of short oligomeric chains. In the case of these monomers we can observe effect of polymerization autoinhibition [2].

Initiators of free radical polymerization are the compounds or their combinations, which by chemical reaction (thermal decomposition, redox reactions, and others) generate radicals with short lifetime and low resonance stabilization or even unstabilised by resonance. The most widely known and common are initiators decomposing thermally: dialkyl- and diarylperoxides, hydroperoxides, dicarbonateperoxides, peroxyesters,

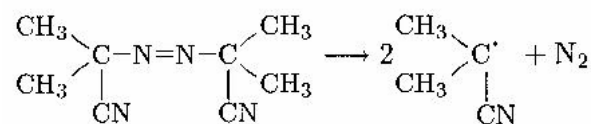
sulphonylacetylperoxide, azocompounds, and inorganic water soluble persulfates (sodium, potassium, ammonium) and hydrogen peroxide. Thermal decomposition of peroxides is homolytic break of -O-O- bond in which there is an additional number of secondary reactions [4]:



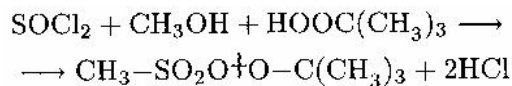
One of the most frequently used peroxide initiators - benzoyl peroxide - decomposes under the above reaction to the benzoyl and phenyl radicals, both of which are able to initiate the polymerization reaction:



Another well-known initiator from the group of nitrogen compounds is AIBN (*azoisobutyronitrile*), which decays almost purely with emission of molecular nitrogen:

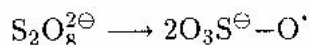


An interesting example of a peroxide initiator, decomposing at a temperature below 0°C is tert-butyl methyl peroxy sulphonic acid ester, a compound produced directly in the place of polymerization reaction:

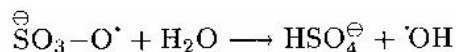


however, industrial importance of this initiator is rather small.

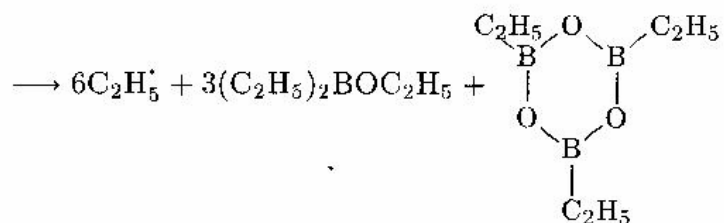
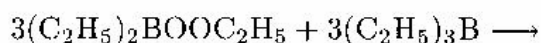
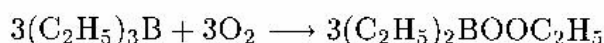
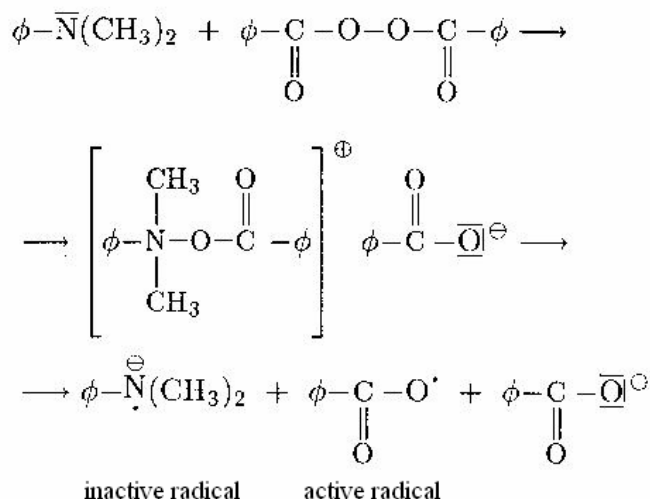
Water-soluble persulfates in an alkaline medium undergo monomolecular thermal decomposition according to reaction:



but active radicals are hydroxyl radicals that are subsequently formed in reaction with water:



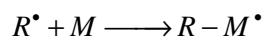
In acid environment the yield of generation of radicals can be smaller because of useless proton-induced decay of $\text{S}_2\text{O}_8^{2-}$ anion:



The other methods of radical polymerization initiation include physical methods: **thermal initiation** (without initiating mediators), **UV light**, **α , β , γ -rays**, as well as **electrochemical** and **mechanical methods**. However, technological importance is limited to thermal initiation and initiation using γ -ray.

Kinetic model of radical polymerization include a number of reactions that represent individual stages of the process.

Start reaction:



where: R^{\cdot} - radical initiating a polymerization, M – molecule of monomer.

The reaction rate, v_{st} , can be written in the form of equation:

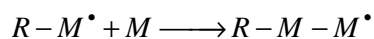
$$v_{st} = \frac{+d[R-M^{\cdot}]}{d\tau}$$

and v_{st} is determined by slow reaction of decomposition of initiator generating radicals R^\bullet . Assuming monomolecular initiator decomposition, from one molecule two R^\bullet radicals can be obtained. At the same time, not all radicals are involved into polymerization. Therefore it becomes necessary to introduce radical efficiency factor f , which is the ratio of the number of radicals used in the polymerization to the total number of produced radicals. Thus, the equation can be converted to the form:

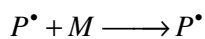
$$v_{st} = 2fv_r = 2fk_r[I]$$

where: v_r is a rate of initiator decomposition, k_r – rate constant of initiator decomposition, and $[I]$ is concentration of initiator.

Chain growth reaction:



Assuming that the activity of the radical $R-M-M^\bullet$ is the same as reactivity of $R-(M)_n-M^\bullet$ radicals with different number n , we can replace both of the above with general symbol of a macroradical, P^\bullet , and write the above reaction in the form:



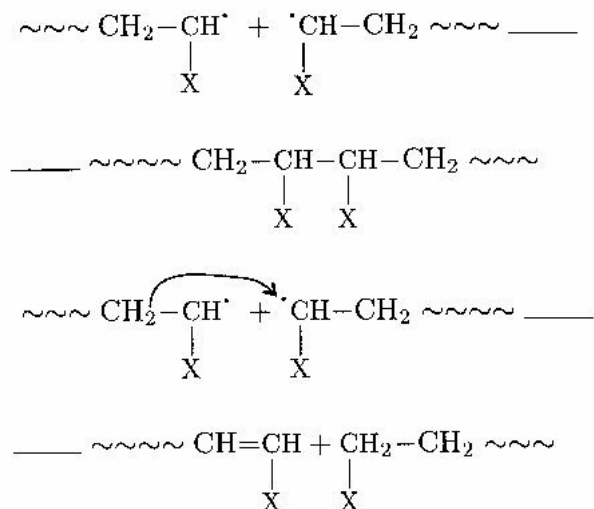
The corresponding kinetic equation will take the form:

$$v_w = -\frac{d[M]}{d\tau} = k_w[P^\bullet][M]$$

where: $[M]$ – concentration of monomer, k_w – rate constant of chain growth, $[P^\bullet]$ – concentration of macroradical.

Polymer termination

This reaction can occur by recombination or disproportionation of two radicals:

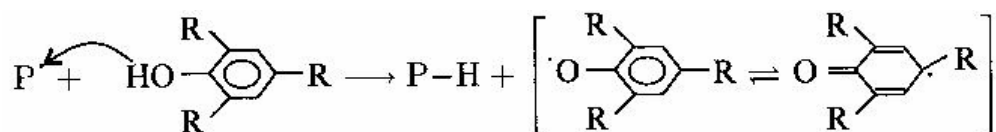


The reaction of recombination increases the degree of polymerization and polymer molecular weight. Participation of both reactions in the chain termination depends strongly on reaction temperature. Disproportionation is characterized by a higher activation energy than the recombination reaction, so, its contribution increases with temperature. Both reactions are bimolecular and can be described by equation:

$$\begin{aligned}
 v_z &= -\frac{d[P^\bullet]}{d\tau} = v_{z,rec} + v_{z,dysp} = \\
 &= 2k_{z,rec} [P^\bullet]^2 + 2k_{z,dysp} [P^\bullet]^2 = 2k_z [P^\bullet]^2
 \end{aligned}$$

where: $v_{z,rec}$ – chain termination by recombination rate, $v_{z,dysp}$ – chain termination by disproportionation rate, $k_{z,rec}$ – chain termination by recombination rate constant, $k_{z,dysp}$ – chain termination by disproportionation rate constant, k_z – overall rate constant of chain termination.

Chain reaction can also be deliberately stopped by addition of inhibitors, acting in two ways. The first group of inhibitors are stable radicals deactivated in the recombination reactions with active radicals arising from the monomers. As examples may serve: diphenylpicrylhydrazyl (DPPH - ESR spectroscopy standard), nitric oxide, para-substituted triphenylmethyl radicals, etc.¹ The second group consists of chemicals that react with the P^\bullet radical to form a new inactive radical, stabilized by resonance. As example of this method a reaction involving alkylphenols can be demonstrated:

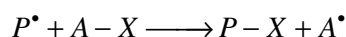


¹ Can we use molecular oxygen as inhibitor of oxidation?

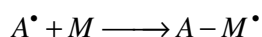
In addition to alkylphenols this group of inhibitors also includes: p-benzoquinone, chloranil, aromatic nitro compounds, methylene blue, thiocarbamates, amines, and many others. Polymerization inhibitors are used both to stop the polymerization, and as compounds preventing the monomers against polymerization during storage and transport.

Chain transfer reactions

Apart from the aforementioned propagation, termination and inhibition reactions, some other reactions are also important. For example, polymerization chain transfer reactions, when the **polymer chain termination** occurs but the **kinetic chain** of polymerization is not stopped. The mechanism of these reactions involves the transfer of a radical X (usually $X = H^\bullet, Cl^\bullet, Br^\bullet$) from neutral molecule AX to macroradical P^\bullet :



Therefore, a terminated polymer chain P-X is obtained, while A^\bullet is able to continue the kinetic chain of polymerization by attack on the next molecule of monomer and a growth of new macroradical is started:

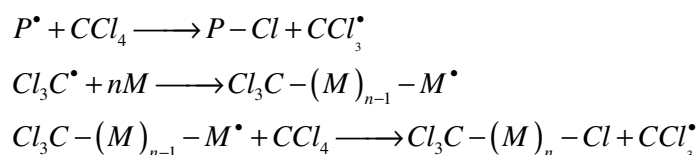


The rate of chain transfer can be described by the kinetic equation:

$$v_p = -\frac{d[A-X]}{d\tau} = k_p [A-X][P^\bullet]$$

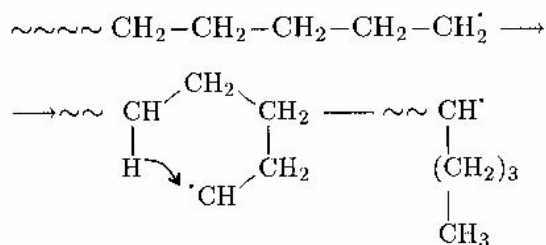
where [A-X] is a concentration of chain transfer agent and k_p is a rate constant of chain transfer.

These reactions (chain transfer) are competitive to the reactions of chain growth and can significantly affect the molecular weight of polymer. They can occur with the participation of each of the reaction mixture components, this means that the chain transfer can take place at the initiator, monomer, solvent, polymer and other chemical compounds which are additives for polymerization. Polymerizations with the use of very high chain transfer ability solvents is defined as **telomerization**, and solvents are called **telogens**. Low molecular weight, usually liquid polymerization products are called the **telomers**. An example of such a solvent is carbon tetrachloride:



When using CCl_4 as a telogen, the terminal fragments of the received telomere chains will contain Cl atoms. Telogens as well as other compounds of very high ability to chain transfer reactions (e.g. aliphatic mercaptans) can be used in small quantities as regulators of polymer molecular weight.

Intramolecular chain-transfer reactions are responsible for the formation of branched polymers:



If all the molecular reactions during the polymerization are known, we can draw the kinetic equation for the rate of polymerization. Taking into account the Bodenstein Steady-State Approximation (*The Stationary State Theory*), it can be assumed that the concentration of radicals P^\bullet supplied by the start reaction after a few seconds, reaches a constant value of $[P^\bullet]$. This assumption is well justified because the rate of formation of radicals v_{st} is the same as the rate of their disappearance by the end of the chain reaction v_z :

$$\begin{aligned} v_{st} &= v_z \\ 2fk_r[I] &= 2k_z[P^\bullet]^2 \\ [P^\bullet] &= \left(\frac{fk_r[I]}{k_z} \right)^{\frac{1}{2}} \end{aligned}$$

Assuming that the reactivity of radicals and thus k_w , k_z and k_p are independent of the length of macroradical and that monomer is consumed exclusively by the reaction of growth, we can write:

$$-\frac{d[M]}{d\tau} = v_w = v_{pol} = k_w[M][P^\bullet]$$

where v_{pol} is overall rate of polymerization. After entering the expression for $[P^\bullet]$ we obtain therefore:

$$v_{pol} = \frac{k_w k_r^{\frac{1}{2}} f^{\frac{1}{2}}}{k_z^{\frac{1}{2}}} [M][I]^{\frac{1}{2}} = k_{pol} [M][I]^{\frac{1}{2}}$$

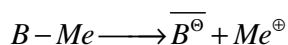
where k_{pol} is rate constant of polymerization. *So, the rate of radical polymerization is first-order reaction with respect to monomer and half-order reaction in the concentration initiator.*

Chain polymerizations can also be carried out according to the anionic mechanism, cationic mechanism and coordination mechanism. The kinetics of these reactions is not as clearly described as in the case of radical polymerization and depends on many factors, such as the type of initiator, solvent effects, solvation, association and temperature. Therefore, in further considerations the kinetics of these reactions will not be described.

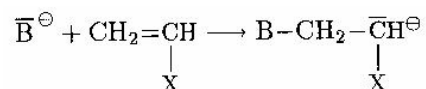
Several monomers can polymerize with anionic mechanism: vinyl monomers carrying substituents with a negative inductive effect (-I), monomers containing heterocyclic and heteroatom-carbon double bond. Among the popular vinyl monomers the following should be mentioned: acrylonitrile, nitroethylene, acrylic and methacrylic esters, vinyl halides, butadiene, styrene. The stronger the inductive effect in monomer (strong electron withdrawing substituents pull the electrons out of a double bond) the easier anionic polymerization occurs.

Initiators of anionic polymerization are usually bases with different basicity strength. Depending on the monomer tendency to polymerization, stronger or weaker base must be used as an initiator. Very strong bases are needed to initiate polymerization of styrene or butadiene (weak negative effect of a substituent), and alkali metal amides or metalorganic compounds (R-Me aliphatic or aromatic, e.g. butyllithium or phenylsodium) have to be applied. Moreover, as initiators can be used: alkali metals alkoxides and enolates, ammonium bases and alkali metal hydroxides, or Lewis base compounds (alcohols, amines). The last ones cause the polymerization only of monomers with a very strong tendency to anionic polymerization, for example nitroethylene, vinylidene cyanide, cyanoacrylate. These monomers are used as fast-acting adhesives. For pure anionic mechanism (polar solvents, dissociation of the initiator) the polymerization proceeds as follows:

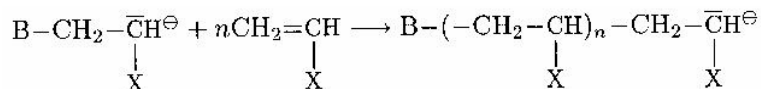
- dissociation of initiator

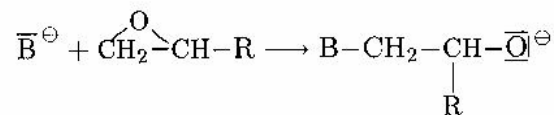


- start of polymerization

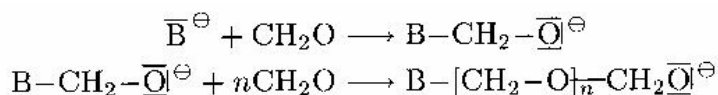


-chain growth





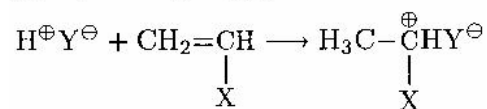
Monomers containing carbon-heteroatom double bond (aldehydes, ketones, tioketones, isocyanates, Schiff bases, and other) also can undergo anionic polymerization. The above-mentioned monomers polymerize in a manner similar to vinyl monomers, like formaldehyde:



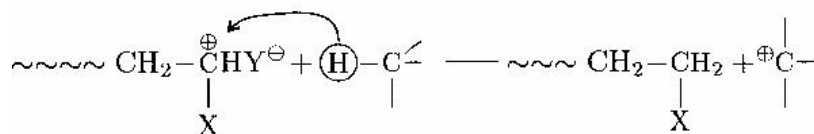
Industrial importance of anionic polymerization is rather small. In technology of plastics, much more often are used polymerizations which occur according to the cationic mechanism. Polyethylene oxide and polyisobutene are valued polymers produced by this method in large scale.

Cationic polymerization undergo vinyl monomers with substituents with inductive effect + I or mesomeric effect + M, including iso-butene, alkyl vinyl ethers, isoprene, butadiene, styrene. Cationic mechanism of polymerization is preferred for cyclic unsaturated hydrocarbons (cyclopentadiene, indene, pinene), monomers with carbon-heteroatom double bonds (aldehydes, tioketones) and heterocyclic compounds (trioxane, epoxides, cyclic imines, lactams, lactones).

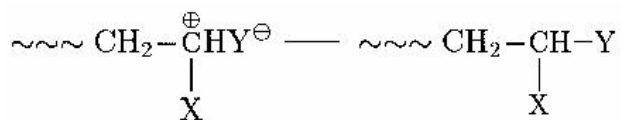
Cationic polymerization initiators can be strong protic acids, Lewis acids (AlCl_3 , BF_3 , TiCl_4 , etc.), carbocations (tropylium cation, triphenyl carbocation), and even iodine and its halides (iodine chloride, iodine bromide). In highly polar solvents the mechanism of polymerization of vinyl monomers involves ionic structure of the initiator H^+Y^- , where the cation initiates a polymerization process:



Lewis acids can also be transformed into their protic acid forms in the presence of trace amounts of co-catalysts in the reaction system: water, alcohol or other protic acid. For example, a reaction of AlCl_3 with water gives $\text{H}^+[\text{AlCl}_3\text{OH}]^-$ acid. Chain growth reaction involves successive addition of monomer molecules to growing carbocation. Transfer reactions in cationic polymerization occur frequently, but they are associated generally with the transfer of hydride ion from the monomer, solvent or polymer to the carbocation by the scheme:



Mechanism of chain termination is not clear to this day and probably occurs via deactivation of carbocation:



and it can be induced by the addition of basic compounds.

The mechanism of cationic polymerization is generally more complicated and polymerization occurs without the participation of free ions, so, it has pseudocationic mechanism. Also, polymerizations of monomers containing carbon-heteroatom double bond and cyclic and heterocyclic monomers proceed by complicated and different mechanisms.

Last group of chain polymerizations of industrial importance are coordination polyreactions [9,10]. The method is associated with the discovery of an active catalyst for polymerization of olefins composed of $\text{Al}(\text{C}_2\text{H}_5)_3$ and TiCl_4 by Ziegler in 1955, which allowed polymerization of ethylene under normal pressure. The works of another scientist, Natta, on the polymerization of other α -olefins, and the discovery of stereospecific action of these catalysts resulted in that we are talking today about Ziegler-Natta catalysts, for which these two scientists received the Nobel Prize. The Ziegler-Natta catalysts make possible to obtain iso- and syndiotactic polyolefins and polydienes with a high participation of a desired structure 1,4-*cis*. Cycloalkenes also polymerize in the presence of these catalysts, with or without ring-opening. Until the discovery of the Ziegler-Natta catalysts, many olefins were considered as not able to homopolymerization (for example, propylene).

Ziegler-Natta catalysts for coordination polymerization are the combinations of transition metals halides with organic derivatives of nontransition metals, particularly alkyl aluminum compounds. For polymerization of α -olefins some compounds of titanium, vanadium and chromium are suitable, whereas for stereospecific polymerization of dienes (butadiene, isoprene) some nickel and cobalt compounds are used. Molybdenum and tungsten compounds are applied for polymerization of cycloolefins with the ring opening. In contrast, application of vanadium and chromium compounds does not cause ring opening during polymerization. Today at least about several hundred combinations of organometallic and transition metal compounds are known. They are used both as homogeneous and heterogeneous catalytic systems. Among the organometallic compounds most frequently used

are: aluminum, zinc, diethyl beryllium, dimethyl cadmium, phenyl- and butyllithium, and also Grignard compounds. Transition metal compounds are mainly halides of titanium, vanadium, chromium, cobalt, zirconium, molybdenum and tungsten, but also chloride oxides (VOCl_3), acetylacetonates [$\text{V}(\text{acac})_3$, $\text{Cr}(\text{acac})_3$] and cobalt and nickel naphthenates.

Polymerization mechanism in accordance with the current state of knowledge is very complex. In short we can say that it involves the formation of a transition state between metal complex and olefine, which opens the double bond.

4.2.3. Step polymerization [5-8]

In contrast to the chain polymerization, step polymerizations mechanisms are generally well-known and typical polycondensations and polyadditions have ionic nature (cationic or anionic). A deeper discussion on these reactions is not necessary, because the mechanisms are the same that we know from organic chemistry course for low-molecular compounds. Kinetic model of these reactions can also be applied to analogous reactions: esterification, addition, ammonolysis, etc. Using the polycondensation of diols and dicarboxylic acids, we can therefore construct a general scheme. The rate of polycondensation reaction catalyzed by protons H^+ is described by the equation:

$$v_{pol} = k [\text{H}^+] [-\text{COOH}] [-\text{OH}]$$

where: k - rate constant for polycondensation reaction.

Because the carboxyl and hydroxyl ($-\text{COOH}$ and $-\text{OH}$) groups are present in the reaction mixture in the same quantities, we can write:

$$[-\text{COOH}] = [-\text{OH}] = X$$

hence:

$$v_{pol} = -\frac{d[X]}{d\tau} = k [\text{H}^+] [X]^2$$

Integration within the time interval from 0 to τ at constant catalyst concentration gives the following relationship:

$$\frac{1}{[X_t]} - \frac{1}{[X_0]} = k [\text{H}^+] \tau$$

The degree of conversion, S , is defined as:

$$S = \frac{X_0 - X_t}{X_0}$$

hence:

$$X_t = X_0(1-S)$$

and therefore:

$$\frac{1}{1-S} = 1 + k[H^+][X_0]\tau$$

For the step polymerization the expression $1/(1-S)$ is another form of degree of polymerization \bar{P} , therefore, for known rate constant k and known concentrations $[H^+]$ and $[X_0]$, we can calculate both the degree of conversion and the degree of polymerization \bar{P} at time τ . If the reaction proceeds without the participation of an acid catalyst (carboxylic acids give protons to catalyze the reaction), the equation for the rate of polymerization reaction takes a form:

$$v_{pol} = k[X]^3$$

Following the scheme outlined above, we can formulate the kinetic equation for any step polymerization.

4.3 METHODS OF POLYMERIZATION

Method of polymerization in industrial as well as in laboratory scale depends mainly on the mechanism of polymerization. The most possibilities in this field are for radical chain polymerizations, that can be carried out in mass, in solution, in aqueous suspensions and emulsions [4-8].

Block polymerization (bulk polymerization or polymerization “in mass”) may be either **homogeneous** or **heterogeneous**. It runs only with the participation of undiluted monomer and initiators with optional additives. It is characterized by the formation of polymers with high molecular weight and a high purity. Technical problems sometimes are caused because of non-homogeneous heat dissipation.

If the formed polymer is soluble in the monomer the process is called **homogeneous polymerization** and some industrially important polymers are obtained by this method: polystyrene, polyethylene and its copolymers, polyvinyl acetate and polymethyl methacrylate. Another method of block polymerization is **heterogeneous method**, for example, during production of polyvinyl chloride formed polymer precipitates from the liquid monomer.

Polymerizations in solution may also occur in homogeneous and heterogeneous phase. Polymers soluble in the reaction solvents are used most often as varnishes, adhesives, impregnation agents or fibers (polyvinyl acetate, polyacrylates, polyacrylonitrile). Their molecular weight is lower than the polymers obtained in previously discussed method.

Polymerizations in solution, where precipitates the formed polymer, also have industrial uses (acrylonitrile in water, a copolymer of styrene and maleic anhydride in benzene) because the operations for separating the solvent from the polymer are simple and rely only on filtration and drying.

During polymerization in aqueous suspension (**bead or pearl polymerization**) a water-insoluble monomer is dispersed by rapid stirring to form small droplets containing dissolved initiator (which also is not soluble in water). Thus, this type of polymerization can be compared to the method of block polymerization as the polymerization in aqueous suspension is in fact polymerization in a large number of microblocks. To prevent the pearls from sticking together (viscosity is growing with reaction progress) protective colloids are used at a concentration of 0.1-1% by weight in relation to water. For this purpose some water-soluble macromolecular compounds³ and water-insoluble finely ground minerals⁴ are used. Bead size can be adjusted by intensity of mixing and concentration of protective colloid, whereby the greater the intensity of mixing, and colloid concentration, the smaller beads are obtained.

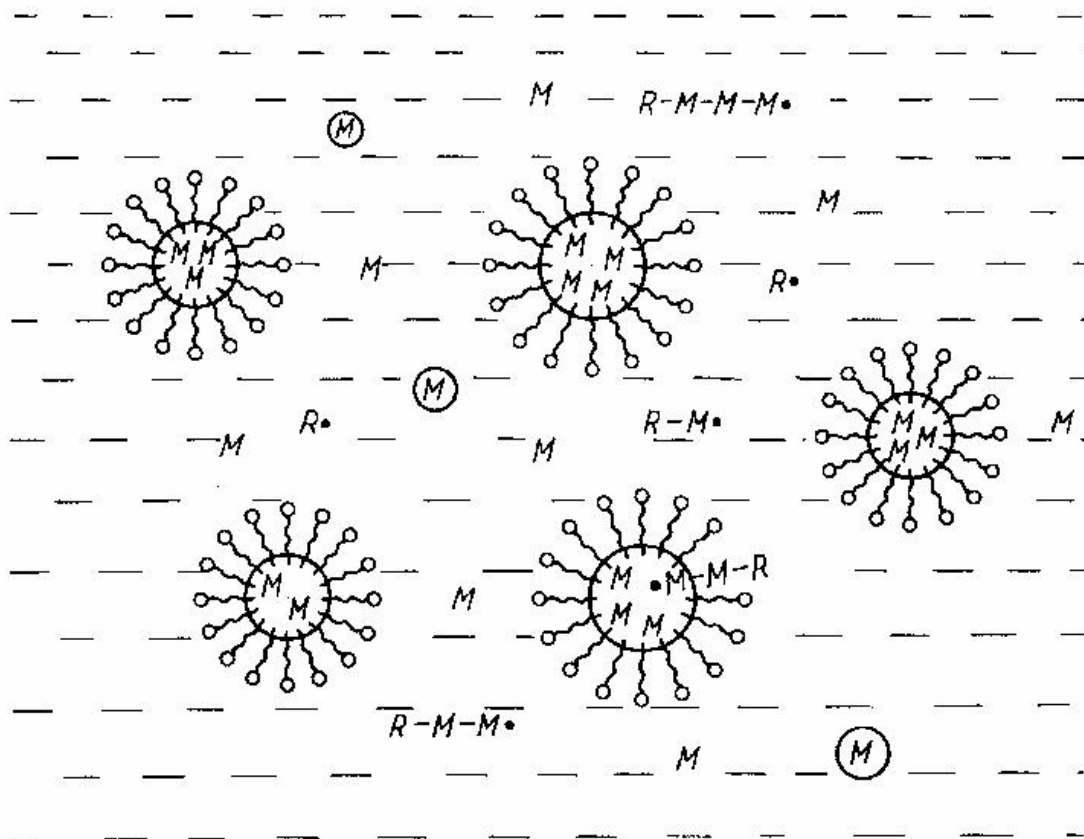
Pearl polymerization has a high technical value, as the problem of non-homogeneous heat dissipation is avoided due to fast heat exchange between beads and water, the polymers are characterized by a high molecular weight and have an easy form for processing. By this method we obtain polyvinyl chloride, polystyrene, polymethacrylates, teflon and crosslinked copolymers of styrene and divinylbenzene. If light hydrocarbon (pentane, hexane) is dissolved in styrene before polymerization, and the reaction will be conducted at little overpressure, received beads will also include dispersed hydrocarbon, which when melting causes foaming of the polymer (polystyrene). Diameter of the obtained beads may be from the 50 μ to 1cm, and at a concentration of protective colloid about 4-5% we can obtain suspension with properties similar to latex (particle diameter 1 μ m).

The most complex method of radical polymerization is carried out by emulsifying monomers in water emulsion. This type of polymerization (called emulsion polymerization) occurs with good heat dissipation and is applied to produce polymer emulsions for use as adhesives, emulsion paints, impregnating. In the latter case, the obtained emulsion is subjected to coagulation by the addition of electrolytes (salts, acids), methanol or by freezing. Emulsion polymerization is carried out by adding the water-insoluble monomer to an aqueous

³ Gelatin, agar, pectin, polyvinyl alcohol, polyvinylpyrrolidone, copolymers of styrene and maleic acid, propoxy- and etoxymethylcellulose and others.

⁴ Diatomaceous earth, barium sulfate, bentonite, calcium phosphate and others.

solution of an emulsifier having a concentration of 0.2 to 3% by weight, which by intensive mixing forms an emulsion with water (with the appearance of milk). After adding water-soluble radical polymerization initiator, pH buffers and optionally, an agent controlling the molecular weight of polymer. The product is a water emulsion containing polymer particles with a diameter of 0.05-1 μm , which are impossible to see in the optical microscope. In the average reaction system 1cm^3 of emulsion contains about 10^{18} micelles, 10^{10} monomer droplets, and also the minimum amount of monomer is dissolved in water. Initiator (dissolved in water) generates radicals that after joining a few monomer molecules are absorbed by the micelles, where the radical polymerization is continued. Growing macroradical is absorbed by micelle, rather than by microdroplet of monomer due to a difference in concentration, much higher in the case of micelles. Addition of the next portion of the monomer to the micelle takes place by diffusion of the droplets through the aqueous phase with dissolved monomer. The number of micelles, in which the polymerization occur, grows very fast. Growing macroradicals cause an increase of micelle dimensions, and these new bigger micelles need more emulsifier to cover their growing surface. Emulsifier is taken from the solution, and a non-active (not polymerizing) micelles are destroyed. After some time, inactive micelles disappear, which at constant monomer concentration in reacting micelles (continuous diffusion of monomer from droplets) causes a constant rate of polymerization. This rate decreases when the reserves of monomer from droplets are exhausted. Emulsifier concentration must be always higher than **the critical micelle concentration**, to ensure the polymerization inside the micelle rather than inside microdroplets of monomer, which after polymerization would not be able to create a stable polymer emulsion. Picture of the aqueous emulsion during the polymerization is shown in figure below:



Illustrative image of the emulsion during the emulsion polymerization

For emulsion polymerization the water soluble initiators are used, thus, persulfates of sodium, potassium, ammonium, hydrogen peroxide, as well as soluble in water redox initiating systems are suitable. Since persulfates and redox systems simultaneously generate radicals by changing the pH of the solution (followed by acidification), so there is often need to buffer the emulsion to slightly alkaline pH.

Emulsifiers used in emulsion polymerization may be alkali salts of fatty acids: palmitic, stearic, oleic and alkyl sulphonic and alkyl aryl sulphonic acids. Alkaline salts of phthalic and amber acid halfesters with long alcohols are also used as emulsifiers. These salts belong to the group of anionactive emulsifiers. Nonionic emulsifiers, which include products of addition of ethylene oxide to alkyl phenols and fatty alcohols, are indeed less able to emulsify, but advantageously, these non-ionic emulsifiers are insensitive to the change in pH of the solution.

Molecular weight regulators are usually aliphatic mercaptans.

Kinetic model of emulsion polymerization assumes that the micelles and latex particles containing macroradical chain are protected from mutual recombination and disproportionation reactions of radicals, by a layer composed of an emulsifier particles. Small size of micelles cause that in each of them only one growing macroradical is reacting. Penetration into the second macroradical causes immediate recombination. Another radical initiates new polymerization reaction, etc. Monomer concentration inside the latex particles is in constant kinetic equilibrium and without external influences, under these conditions, the polymers reach very high molecular weights, which sometimes have to be reduced by the addition of mercaptans.

Method of emulsion polymerization is used on industrial large-scale for production of synthetic rubbers, polyvinyl chloride, polystyrene, polyvinyl acetate, acrylic polyester and copolymer of ethylene with vinyl acetate.

Polymerization methods described above are also used in place according to mechanisms of non-radical polyreactions. Chain polymerizations: anionic, cationic and coordination are generally carried out in a solvent, both homo- and heterophase. Step polymerizations are performed in solvent (resin synthesis) and in mass (fibers, polyurethane foams). Another, very specific method of the polycondensation is polymerization of carboxylic acid dichlorides on phase border. One of the monomers (diol, diamine, bisphenol) and hydrogen chloride binding agent (amine, NaOH) are dissolved in aqueous phase, whereas another monomer (dicarboxylic acid dichloride) is dissolved in organic phase. Polycondensation occurs at the inter-phase region and a thin layer of polyamide, polyester or polycarbonate is formed. Removing this layer causes its immediate restoration, and in this manner a continuous polymerization takes place until all the monomer is consumed. If two phases are emulsified or dispersed each other, the condensation product precipitates from the reaction mixture in powder form.

4.4 POLYMERS MOLECULAR WEIGHT

One of the specific properties of polymers is their **polydispersity (polymolecularity)**. This means that in a given sample of polymer macromolecules are present with varying degrees of polymerization, thus with different molecular weights. So, for a given polymer sample we can at most determine the average molecular weight, depending on the method of determination and molecular weight distribution, different numerical values are obtained. Therefore, we can define different types of molecular weight:

- the number average molecular weight (M_n)

$$\overline{M}_n = \frac{n_1M_1 + n_2M_2 + \dots}{n_1 + n_2 + \dots} = \frac{\sum n_i M_i}{\sum n_i}$$

where n_i is number of moles of molecules with a molecular weight M_i

-the weight average molecular weight (M_w)

$$\overline{M}_w = \frac{n_1M_1^2 + n_2M_2^2 + \dots}{n_1M_1 + n_2M_2 + \dots} = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

The value of \overline{M}_n is in greater extent dependent on the smaller macromolecules, while the \overline{M}_w is mostly dependent on macromolecules of higher molecular weight. It is described by relation:

$$\overline{M}_w \geq \overline{M}_n$$

It turns out that with the same values of \overline{M}_n for different polymer samples different values of \overline{M}_w can be obtained. It depends on the weight distribution inside the samples, thus comparison of both molecular weights can give information on the polydispersity. If $\overline{M}_w / \overline{M}_n = 1$, then a sample is homodisperse and *all chains are the same length*. This situation is rather theoretical. The greater dispersion of molecular weights, the larger the ratio $\overline{M}_w / \overline{M}_n$. The measure of polydispersity is called the degree of polydispersity, which is zero for homodisperse samples .

$$U = \frac{\overline{M}_w}{\overline{M}_n} - 1$$