We are IntechOpen, the world's leading publisher of Open Access books
Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

154
Countries delivered to

Our authors are among the
TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

An Advanced Approach on the Study of Emulsion Polymerization: Effect of the Initial Dispersion State of the System on the Reaction Mechanism, Polymerization Rate, and Size Distribution of Polymer-Monomer Particles

M. Khaddazh, I.A. Gritskova and G.I. Litvinenko

1. Introduction

Emulsion polymerization (EP) is a complex heterophase process which involves many components and also runs sequentially and in parallel physicochemical processes that determine the composition of the emulsion, the formation mechanism of polymer-monomeric particles (PMP), conditions for the formation of interfacial layer, etc. There are a number of factors that collectively affect the kinetics of emulsion polymerization, among them:

- initiator decomposition,
- dispersion of the monomer,
- emulsifier redistribution between phases,
- microemulsification,
- formation of interfacial adsorption layer,
- initiation of polymerization,
- PMPs formation,
- diffusion of monomer into PMPs.

The initial stage of emulsion polymerization defines the basic parameters of the process: the rate of polymerization and the formation of interfacial layer, the number of particles, their size distribution, molecular masses of polymers and molecular mass distribution. The mechanism of formation of PMPs has been widely discussed in the literature and the researchers can not possibly come to a consensus.

This can be explained by the fact that in the original system, different types of particles may be present depending on the nature of system components and their concentrations:

- individual molecules of surfactant
- micelles of surfactant
- monomer swollen surfactant micelles
- surface-active oligomers formed during the initiation of polymerization in the aqueous phase
- mixed micelles (surfactant + oligomers)
- macro- and microdroplets of the monomer.

In addition to these particles, the emulsion of the monomer may contain specially added low-molecular-weight substances necessary for the preparation of polymeric suspensions with desired properties.

2. Mechanisms of polymer-monomer particles formation in emulsion polymerization

In the literature there are various hypotheses about the mechanism of particle formation in emulsion polymerization, the main ones assume the formation of PMPs from:

- micelles of emulsifier,
- macromolecules of the polymer dropped out in water (the mechanism of homogeneous nucleation),
- by the mechanism of nucleation aggregative which combines elements of different modes of particle formation
- microdroplets of monomer.

None of the hypotheses proposed to date is confirmed by reliable experimental data. Hereinafter we briefly recall these hypotheses.

2.1. Micellar mechanism

Micellar mechanism of particle formation is based on a qualitative model proposed simultaneously and independently by Harkins [1,2] and Yurzhenko [3,4]. The basic points of such mechanism are as follows:

1. Emulsion polymerization is a usual process of a radical polymerization, its features are explained by the fact that the main site of reactions - micelles and PMP - have discrete volumes.
2. At the initial stage of the polymerization the reaction system consists of emulsifier micelles, PMP and large monomer droplets.
3. Polymerization starts only in the emulsifier micelles, which when attacked by a radical convert to PMP, monomer droplets being only the source of monomer. Diffusion of monomer from droplets through the aqueous phase and into the PMPs does not limit the process that leads to the establishment of equilibrium monomer concentration PMP, which persists as long as monomer droplets are present in the system.

According to these ideas, in the presence of surfactants, the initial emulsion consists of two kinds of particles of different sizes: the monomer droplets with diameters of 5-20 microns and colloidal degree of dispersion and monomer-swollen surfactant micelles (5-10 nm).

The mechanism of Harkins-Yurzhenko lied in the base of Smith and Ewart quantitative theory [5-7], with further refinements in the works of other authors [8-70]. The main aspect of this theory is that radicals formed in the aqueous phase are trapped by the monomer swollen surfactant micelles and turn to PMP. It is assumed that only one out of every 100-1000 micelles captures a radical and becomes PMP, and the rest of the micelles are spent to stabilize the growing PMPs. Polymer-monomer particles formation ends with the disappearance of micelles of the emulsifier in the aqueous phase, after which the number of particles remains constant.

Initial system contains monomer droplets with a diameter of 5-15 microns, their concentration being 10^{12}-10^{14} droplets/l, the monomer-swollen micelles with diameters of 5-10 nm and the number of micelles 10^{18}-10^{21} l^{-1}, and a water-soluble initiator (usually potassium persulfate) at a concentration of 1% per monomer [8]. Only a small fraction of the molecules of the monomer is located in the interior of the micelles (1-2%) and is dissolved in the aqueous phase (0.03% for styrene). In the aqueous phase, 10^{14}-10^{16} PMP / l are formed with a diameter in the range of 20-200 nm. Monomer droplets due to their relatively small surface area hardly compete with micelles in capturing radicals.

In the polymerization process PMPs increase their size due to the diffusion of the monomer from droplets and monomer-swollen micelles which contains no radicals [1-3, 5, 9-15].

Three limiting cases were considered:

1. The number of free radicals in the particles is small compared with the total number of radicals, thus the average number of radicals per particle is much less that unity.
2. The average number of radicals per particle is equal to 0.5. This case is realized under following conditions: the activity of the radical in the particle persists as long as the second radical enter the particle, and the time of chain-breaking is small as compared with the average time interval of successive absorption of radicals by the particle.

    The authors believe that case 2 corresponds to the emulsion polymerization of styrene in the presence of potassium persulfate [5]. The rate of formation of primary radicals is equal to 10^{13} radicals• $ml^{-1}s^{-1}$. The average number of polymer particles is of the order of 10^{14} -10^{16} in 1 ml of the system. If all the radicals formed by the decay of the initiator enter the polymer particles, the average frequency at which a radical enters a particle is once per 10 - 100 sec.

    At any time, the particle contains either one radical or does not contain radicals at all, since it is assumed that chain termination occurs immediately in contact with the second radical in the particle. The particle is inactive until the next radical does not enter the particle, i.e. by 10-100 sec. Consequently, half of time each particle contains a radical and another half of time does not contain radicals, i.e. one half of the particles are active and each of them contains one polymer radical. Thus, the polymerization rate, referred to 1 ml of latex, is expressed by the equation:

$$R_p = k_p \cdot \frac{N}{2}[M]$$

(1)

where N is the number of PMPs in 1 ml of latex, k_p is the propagation rate constant, [M] is the concentration of monomer in the PMP.

The rate of polymerization is determined by the number of particles and it does not depend on particle size if it is not very large.

3. If the particle size is large, they may contain several radicals at the same time, as in the case of suspension polymerization. This condition corresponds to the third case: the number of free radicals in the polymer particle is large, each particle has a certain steady-state concentration of radicals.

After completion of the formation of PMPs their concentration in water remains relatively constant until the end of polymerization. The size of particles becomes larger due to the diffusion of monomers from monomer droplets which serve as reservoirs for the growing particles. Most of the monomer is consumed in the growth stage of particles (approximately 10 to 60% monomer conversion). The stage of particle growth (interval II) ends with the disappearance of monomer droplets in the system. For case 2 the following assumptions were implanted:

1. The number of particles per unit volume of water remains constant throughout the polymerization;
2. The particle size distribution is relatively narrow;
3. No desorption of free radicals from the particles;
4. Bimolecular termination of polymer radicals, located in a particle diffusing with a radical from the aqueous phase is instantaneous.

Figure 1 illustrates the evolution of the rate of emulsion polymerization. The kinetic curve contains three phases: a relatively short stage I, characterized by the growing polymerization rate, stage II of a constant rate of the process, and stage III, where the polymerization rate decreases.

Stage I refers to a micellar stage of emulsion polymerization. It describes the formation of PMP and the increase in their number. In stage II, the formation of new particles does not occur, and the main process parameters: growth rate constant, k_p, the number of radicals in the particle, n; number of particles, N, and monomer concentration [M], respectively, and the constant changes in the rate of polymerization not observed. Stage III begins after the disappearance of monomer droplets. In this case, all the monomer is contained in the volume of PMP and the rate of polymerization of the consumption of monomer decreases.

Shortly after the publication of the Smith-Ewart theory, many other interpretations that discuss deviations from the theory were issued [8-33]. There have been many recent indications of change in the number of particles in the emulsion polymerization. In stage II, the Smith-Ewart assumption on the discreteness of the latex particles is not supported.

Nevertheless, the consideration of the number of particles in the emulsion system as the main kinetic factor remains the basic idea of the Smith-Ewart theory.
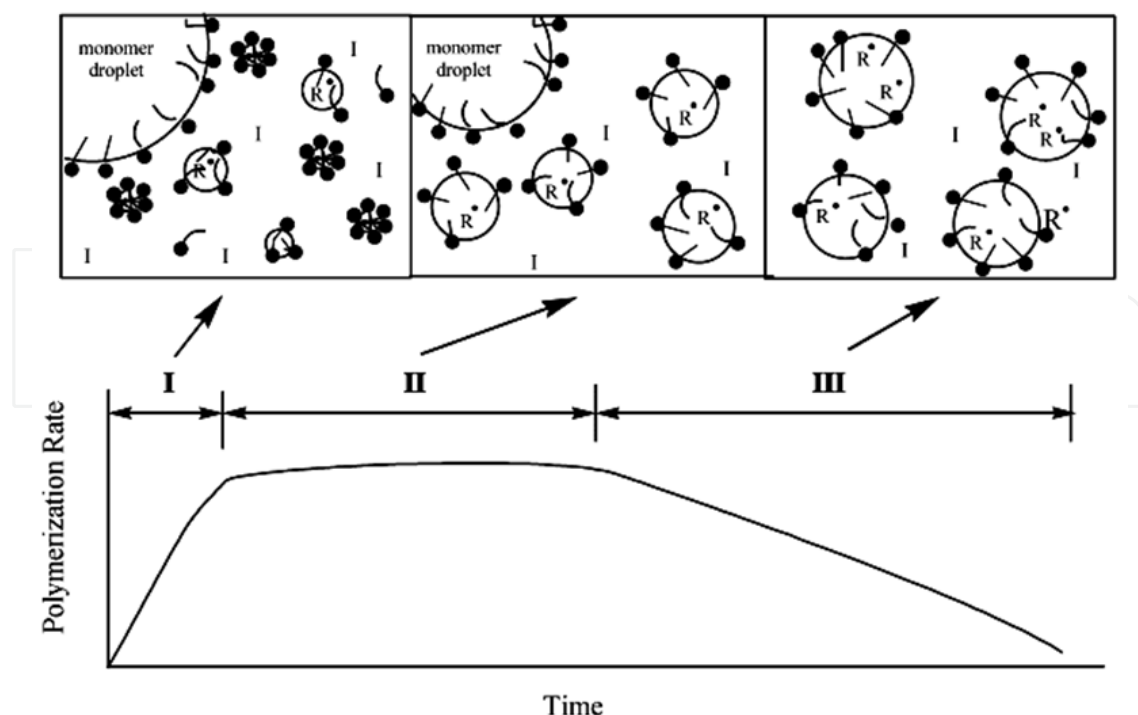
Figure 1. Three intervals of the dependence of polymerization rate on monomer conversion (from Prog.
Polym. Sci. 26, 2001, p. 2094) [16]

Today it is obvious that the observed phenomena in emulsion polymerization are extremely
diverse and can not yet be explained by a single theory.

Kinetic description of emulsion polymerization is complicated due to the difficulty of
establishing a place where elementary reactions proceed, and concentrations of reagents in
these places.

The classical theory of emulsion polymerization of the Smith-Ewart, establishing a link
between the synthesis conditions and the basic parameters of the process, proved to be
applicable only to a limited number of objects. It describes EP of nonpolar monomers in the
presence of surfactants insoluble in monomer.

Later on, these ideas have been modified by Gardon [17-23], Harada [24], Stokmayer [25],
O'Toole [26], Ugelstad [27-29], Kuchanov [30-32], etc.

A more general review of topochemistry and kinetics of polymerization of the latex were
presented by Medvedev et al. [8-11, 14]. Agreeing with Harkins-Yurzhenko's ideas
concerning particles formation, Medvedev, nevertheless, has proposed that micelles have
properties of swarms, and an exchange of molecules and radicals between (a) micelles
themselves, and (b) micelles and polymer particles takes place. This assumption considers
the processes occurring with the participation of micelles as homogeneous ones averaged
over the main parameter - the concentration of emulsifier.

Key topochemical and kinetic features of emulsion polymerization according to Medvedev
may be formulated as follows:

I. With water-soluble peroxide compounds which form initiating radicals in aqueous solution polymerization, depending on the nature of monomers, starts in water or micelles. When using oil-soluble polymerization initiators, regardless of the nature of the monomer, it begins in micelles since they contain both monomer and initiator.

The process proceeds further in 10-100 nm PMP, in which monomer concentration during the reaction remains constant (for polymers which are soluble in their monomers, this concentration is 40-50%).

It is essential that the polymerization does not start simultaneously in all the micelles, but only in a small part of them. This is because the concentration of initiating radicals is usually much lower than the number of micelles. The emulsifier contained in the polymer-free micelles is used to stabilize the increase in volume of PMP. Since initiating radicals are formed in the molecular aqueous solution or in adsorption layers of the emulsifier (which means in the micelles or at the surface of polymer particles), the polymer radicals occur near these adsorbed layers. Because of the low rate of diffusion of polymer radicals in viscous phase of PMP the reaction growth and chain termination take place not in the whole volume of the particles (especially in their relatively large volume), but in some zone near the surface. The volume of this zone is determined by the concentration of emulsifier in the process, and in some cases remains approximately constant.

II. The total rate of emulsion polymerization is 10^2-10^3 higher than the polymerization rate in homogeneous systems with the same initiators (peroxides, azo compounds, radiation). The average molecular mass of the polymers is also much higher in emulsion polymerization.

Therefore increasing the total rate of the process due to the decrease of the reaction rate of chain termination, leads to an increase in both rate and average length of the polymer molecular chains.

Reducing rate of chain termination reactions may be due to two reasons: 1) a low rate of diffusion of polymer radicals in a viscous medium, as in emulsion polymerization, even in early stages, the process takes place in concentrated solutions of polymer in monomer, 2) the radical separation to individual particles. Qualitatively, these two assumptions explain the simultaneous increase in the speed of the process and the molecular weight of polymer in latex polymerization.

Medvedev theory satisfactorily describes the quantitative relationships emulsion polymerization of many monomers.

Ivanchev and Pavlyuchenko [33, 34] attempted to study the elementary reactions of emulsion polymerization and use the results for the synthesis of polymers with properties fundamentally different from those obtained in homogeneous systems. In their study of initiation reaction in emulsion polymerization of styrene, it was suggested that the adsorption layer of PMP has concentrating and orienting effect on the initiator molecule.

2.2. The mechanism of homogeneous nucleation

According to the hypothesis of the formation mechanism of PMP for homogeneous nucleation [27, 35-42], the formation of particles or macromolecules derived from the radicals who have reached the critical length (j_c), where they lose solubility and precipitate in the aqueous phase. Further growth of the polymer particles dropped in the water is treated differently. Some authors believe that these particles grow by diffusion of monomer from the monomer droplets, i.e. as well as in the case of micellar mechanism, other authors suggest that there exist their limited flocculation and, consequently, the formation of PMPs.

First who suggested the formation of the PMP precipitated from an aqueous solution of polymer molecules was Khomikovsky in 1948 in his study of emulsion polymerization of methyl methacrylate and vinylcyanide [43]. He found that the dependence of the rate of polymerization of the two monomers on the emulsifier concentration is different: the rate of vinylcyanide polymerization decreases with increasing concentration of emulsifier and the rate of MMA polymerization increases, the concentration of emulsifier in these experiments being above the critical micelle concentration (CMC). Khomikovsky explained the results in such a way that vinylcyanide polymerization, initiated by potassium persulfate, begins in water.

Upon reaching the length of polymer chain when oligomers became insoluble in water they precipitate in the aqueous phase to form particles that are stabilized by the adsorption emulsifier molecules on their surface. Initiation of polymerization transforms them to PMP. Here, the polymerization proceeds similarly to that in PMP formed from micelles during polymerization of monomers poor soluble in water.

Later on, these ideas found their development in the investigations of Priest [35], Roe [36], Fitch and Tsai [39, 40], Yeliseyeva [37, 38], Christiansen [44], Ugelstad [27], Pepard [45] Wilkinson [46-48], Oganesyan [49-51], Tauer [52-57], etc.

A quantitative description of the processes of polymerization of the monomers, partially soluble in water, was given by Fitch and Barrett [58].

Fitch proposed the theory called the theory of homogeneous nucleation. Quantitative analysis of this theory was based on the process of self-exhaustion of oligomeric radicals that have reached a critical degree of polymerization.

Considering the theory of Fitch, Barrett has identified two possible distribution of radicals between the aqueous phase and particles:

1. The equilibrium distribution of radicals between the particle and the volume of the aqueous phase, the radical capture rate here is proportional to the volume of the particle.
2. The equilibrium distribution of radicals between the surface of the particle and the aqueous phase, the radical capture rate in this case is proportional to the square of the particle surface.

He showed that the second case is realized more likely, explanation being that small particles are more effective for the capture of oligomeric radicals than larger particles.

The number of particles, according to the theory of Barrett, depends mainly on the distribution coefficient of oligomeric radicals between the surface and volume of the particles and the aqueous phase.

As the number of particles increases during polymerization, the rate of radical absorption by particles increases, as long as all the newly formed radicals will not be absorbed by the particles without having to reach a critical length.

Two variants of the flow of polymerization in the absence of coagulation of particles were considered:

a. a short nucleation time (due to a high rate of initiator decomposition), here all the particles start to grow almost simultaneously at the same average rate, and reach finally approximately the same size. The result of this reaction is the large number of particles of small diameter and narrow particle size distribution.

b. a long time of nucleation (due to a slow initiation), the particles are formed longer, which leads to a broader particle size distribution.

The rate of flocculation of the particles can be controlled by varying the concentration of emulsifier, which is adsorbed on the surface of primary particles and prevents flocculation due to the formation of the electric double layer or due to steric stabilization factor.

In the absence of emulsifier or at its very low concentration and a high rate of initiation,a rapid increase in the number of particles due to the high rate of decomposition of the initiator and the formation of free radicals is noticed during the first stage of polymerization.

Further, due to flocculation, the number of particles drops sharply at the end of the nucleation, particles reach a certain stability by increasing the density of the surface electric charge. If the period of the particles nucleation is short, then, the polymer suspension is characterized by a narrow particle size distribution, on the contrary, the distribution is broad if this period is long.

Ugelstadt and Hansen [27] consider that EP model with partially water soluble monomers should take into account the different stages of the diffusion of oligomeric radicals, as well as the reaction of oligomeric radicals with monomer in the particles.

Using the basic assumption of Fitch that the oligomeric radicals have to reach a certain critical degree of polymerization at which they spontaneously precipitate from the aqueous phase, Ugelstadt and Hansen examined the effect of diffusion of oligomeric radicals in the formation of PMP on the number of particles formed by the mechanism of homogeneous nucleation.

The main provisions of the model are similar to those observed in the Fitch theory and are as follows:

1. Oligomeric radicals spontaneously precipitate when a critical degree of polymerization is reached;
2. Absorption of oligomeric radicals by particles depends on the molecular weight of the radicals;
3. There is a desorption of monomeric radicals from particles;
4. The role of the emulsifier (at a concentration below CMC) is to stabilize the primary particles.

According to this model, in the absence of emulsifier radicals which are formed by the decay of the initiator can:

- add monomer dissolved in the aqueous phase;
- be captured by existing polymer-monomeric particles or adsorbed on the surface of the PMP;
- recombine in the aqueous phase with the other radicals;
- associates to form micelles with other types of radicals dissolved;
- precipitate when the oligomeric radicals critical chain length (j_c).

The tendency of dissolved oligomeric radicals to the association is small because of their low concentrations (<10^{-7} mol/l).

Termination of oligomeric radicals in the aqueous phase may, or may not lead to the formation of new particles. Loss due to recombination leads to a doubling of the chain length of oligomeric radicals, but in this case oligomeric product contains two ionic end groups, resulting in a critical chain length required will increase. Therefore it is not clear whether the loss be oligomeric product from the solution.

According to Fitch model, Ugelstadt determined the number of PMPs in the reaction system is determined by a limited coagulation process of the primary particles.

To explain the influence of emulsifier on the nature of the stabilization process of PMPs Yeliseyeva et al. [12, 13] proposed to use the emulsifier adsorption isotherms at PMPs as a main characteristic.

These authors believe that in EP the rate of emulsifier adsorption on the surface of PMP is a function of adsorption energy, which, in turn, depends on the nature of the emulsifier, and the nature of the surface of the PMP. Later, in the publications of Yeliseyeva et al. adsorption of emulsifier on the particle surface was considered as the main factor determining the kinetics of EP of polar monomers.

Because of the high flow rate of the polymerization process it is difficult experimentally to determine the number of particles during their formation.

Published data show that existing models of EP, based on ideas about the formation mechanism of PMPs homogeneous nucleation satisfactorily describe only the polymerization with a low content of monomer in the initial system (5-10% wt.) in the absence of an emulsifier, or at very low (below the CMC) concentrations.

2.3. Aggregative nucleation mechanism

Along with the micellar and homogeneous mechanisms, aggregative nucleation of particles in EP is widely recognized. It is carefully designed by Lichti [59-61] and Feeney [62-64] on the basis of the study of the size distribution of polystyrene latex particles stabilized with sodium dodecyl sulfate. According to them, precursor particles are formed as a result of the growth of oligomeric radicals in the surfactant micelles. Precursor particles are highly unstable and aggregate, reducing the interfacial tension at the oil / water boundary. Thus, there are germs of the particles.

The rate of nucleation time is extremely high, the authors explain this fact as a result of coagulative (aggregative) nucleation. To describe aggregate nucleation a mathematical model has been used which is a combination of the kinetic theory of coagulation, and Muller-Smoluchowski theory of DLVO (Derjaguin, Landau, Verwey and Overbeek) [65], which determines the strength of the electrostatic repulsion opposing the dispersion forces of attraction as the main factor responsible for the stability of the colloidal particles.

A further development of the mechanism of nucleation of aggregate particles is reflected in the publications of Tauer, Kuhn et al. [52-57, 66]. This theory is indeed a combination of ideas proposed by Fitch et al. [39-41] and Oganesyan [51] with the difference that the authors consider the surface energy of the particles as an adjustable parameter of the model.

The basic assumption of aggregative mechanism is the formation of water-soluble oligomers of PMP with a certain chain length. The proposed mechanism can be regarded as a refinement of the mechanism of homogeneous nucleation of particles and act as an independent theory. This mechanism is similar to the mechanism of homogeneous nucleation, but in this case the particles are not dropped from the aqueous phase oligomeric radicals that have reached a critical chain length, and from particles formed by aggregation of several water-soluble oligomeric radicals which are called clusters [66].

This theory is based on the results of a study of the polymerization of styrene, methyl methacrylate, and vinyl acetate in the absence of surfactant [58]. Selected monomers suitable for this model as well studied in the literature are presented all the necessary constants and experimental data on the critical value (j_c) the chain length of oligomeric radicals, in which they precipitate in the aqueous phase, in addition, these monomers differ significantly in their solubility in water [22, 67-70].

As part of this mechanism depends significantly on the over-saturation of the oligomeric chain length (j), which in turn depends on the polymerization conditions. The higher values of j_c, the lower the solubility of oligomers and the lower concentration required to achieve saturation and the phase formation.

For different monomers nucleation occurs at different times and for different values of j: the higher solubility of the monomer in water, the higher the j_c and the longer time required for the appearance of the particles. For the three monomers selected above the calculated j_c agree well with the experimental values.

The theory of Hansen and Ugelstad of homogeneous nucleation of particles is based on several assumptions whose validity has not yet been proved. As a main place of particle formation the authors consider a saturated aqueous solution of monomer and initiator and do not take into account the processes occurring at the monomer/water interface.

The formation of the polystyrene suspension during emulsifier-free polymerization initiated by potassium persulfate and the detection of styrene oligomers with the 8-9 degree of polymerization in the aqueous phase are considered as an experimental proof of this theory [27].

Identifying the formation of particles according to the homogeneous nucleation process that takes place in a perfectly pure supersaturated solutions, these authors did not find the original monomer/water system emulsifier micelles or microdroplets of monomer.

In these studies it is assumed that ion-radicals falls out of solution as a new phase at attaching a certain number of monomer molecules (up to 10). However, the size of oligomeric radicals is widely debated by many authors.

Detailed studies of physico-chemical processes occurring at the interface as well as in separate bulk phases in monomer-water solution of potassium persulfate static systems were performed and described by Oganesyan et al. [49-51].

The authors studied the polymerization of styrene in static conditions in the absence of an emulsifier, using potassium persulfate as initiator at 50°C in temperature-controlled reactors. The system was kept in the oven for 2 hrs where decomposition of initiator and initiation of polymerization took place, the aqueous phase became turbid. After standing for more than two days, the aqueous phase transformed into stable latex. These studies were carried out at a volume ratio styrene/water equal to 1:7.

The authors explained these results via the formation of particles at the droplets of the monomer / water interface.

To confirm this conclusion, the authors have found conditions which allow to extend the residence time of particles at the interface and to enable them to build-out there. They increased the density of the aqueous phase by increasing the concentration of initiator. The experiments require a high purity and it was necessary to exclude the influence of possible impurities on the stability of the system under study and eventual variations in temperature. Experiments were carried out in batch reactors, which are attached to the cover of the crystallization apparatus designed for growing crystals under isothermal conditions and having an electronic device to provide a constant temperature with high accuracy.

Crystals of potassium persulfate are grown up in the crystallization apparatus. They are used to initiate polymerization at concentrations in the range of 0.5 - 3% by weight. Aqueous solutions of potassium persulfate and styrene separately thermostated at a temperature of 50°C, and carefully layered on the aqueous phase styrene. Painting turbidity of the aqueous phase was dependent on initiator concentration (>2%), turbidity appeared at high concentrations of initiator in the narrow boundary layer from the aqueous phase, and then distributed throughout the volume. For the remaining initiator concentrations area of the initial turbidity of water phase was extended.

Authors believe that the formation of monomer droplets in static conditions is necessary to find the source of energy to perform work on the dispersion of the monomer, which is determined by temperature and chemical potential of the contacting phases. It is believed that if the heat of polymerization is able to transfer a certain amount of monomer in the aqueous phase, then the polymerization reaction at the interface can deform the surface of the interface and disperse system. Further, they assume that at an initial equilibrium state of the system the transfer of certain amount of monomer in the monomer-rich aqueous phase is equivalent to supersaturation of water molecules of the monomer, and nucleation of monomer droplets in the aqueous phase near the interface can be expected.

2.4. Mechanism of particle formation from microdroplets of monomer

According to the representations of micellar [1-7] and homogeneous [27, 35-40] theories of particles nucleation, the monomer droplets play the role of a reservoir from which the monomer in the polymerization process goes into growing PMP by the diffusion through the aqueous phase. Subsequent studies performed by Pravednikov, Gritskova, Taubman, Nikitina, Ugelstad and co-workers have shown that the monomer droplets may be involved in the formation of PMPs if their size may be reduced to the size of the order of 1 micron or less [28, 49-51, 71-111].

Droplet size of emulsions obtained by emulsification of the monomer in the aqueous solution with stirring may be evaluated by the equation:

$$D \approx \left(\frac{\sigma_{12}}{d_{wp}} \right)^{3/5} E^{-2/5} \qquad (2)$$

where σ_{12} is interfacial tension, d_{wp} is the density of the dispersion medium, and E is the energy expended to move a unit mass of the medium [80].

The dispersion of the monomer depends on the power consumed for mixing of the reactor design, the type of the mixer and mixing rate. The presence of the surfactant in the system has a significant influence on the dispersion of the monomer emulsion : adsorption of surfactant at the interface alters the interfacial tension, which facilitates the process of fragmentation and prevents the coalescence of droplets of the monomer when they collide. On the other hand, the irregular distribution of surfactant between monomer and aqueous phases in the initial system provokes transfer of surfactant across the interface, which can lead to the destruction of the border and microemulsification. Thus, in addition to fragmentation and coalescence processes that determine the size of the emulsion droplets in the presence of surfactants, microemulsification may take place. Assignment of microemulsification as a separate factor influencing the formation and composition of the initial emulsion system relates to the fact that the size of droplets produced here is significantly less than those determined by the direct effect of mechanical agitation (less than 0.2 microns). Therefore, the investigation of microemulsification goes beyond traditional ideas about the formation of disperse systems under mixing.

A significant attention in the literature was devoted to the investigation of the properties of microemulsions (ME) and conditions of their formation [81-94], however, the thermodynamic equilibrium of lyophilic systems [81, 82] was mainly considered.

Rebinder was one of the pioneers who studied and later developed the process of spontaneous microemulsification [89, 90]. According to his ideas, this process results in the formation of lyophilic colloidal phase corresponding to such a state when an increase of free energy in the formation of the colloidal phase is close to the energy of thermal motion. This process is accompanied by an increase in entropy of the system due to the formation of a large number of colloidal particles. Entropy factor will compensate for the increase in free energy associated with an increase in the interface area.

In contrary to the real (true) spontaneous emulsification when dispersion occurs in the total volume of the dispersed phase with the formation of thermodynamically stable lyophilic system [79, 95-100], in this case the dispersion may occur in one or both phases simultaneously with interfacial surface tension, far from the critical (σ_{min}), as a result of hydrodynamic instability of the interfacial layer, and leading to mass transfer of one phase to another. As a result, only part of the dispersed phase the in the layer adjacent to the interface can be involved in emulsification [91-94].

The mechanism of interphase mass transfer of surfactant with microemulsification remains open. Various hypotheses are put forward, including those which are based on interfacial instability in the development of interfacial turbulence caused by Marangoni effect. Besides, local fluctuations of the interfacial tension, which lead to the movement of the surface layers of liquid, which, in turn, can increase the interfacial tension gradients in the presence of phase transfer surfactant may be also took into consideration [101].

Thermodynamically stable ME are translucent, lyophilic systems containing spherical aggregates whose size is in the range of 10 to 20 nm. The formation and the type of microemulsion depend on the ratio of the components in the system and the interaction between the surfactant molecules, hydrocarbon and water, the length of the alkyl chain in the molecules of surfactant and co-surfactant (if the later exists), as well as on the nature of the hydrocarbon [111-116].

It should be noted that microemulsions formed as a result of surfactant phase transfer are only kinetically stable and significantly different from those traditionally considered as thermodynamically stable ME. Again we note that the size of monomer microdroplets exceeds the characteristic size of the emulsifier micelles, but is much smaller than droplet size which can be obtained with the corresponding value of interfacial tension by mechanical fragmentation of the monomer.

Mass transfer at the interface caused by the diffusion of surfactant, soluble in both phases, provided greater solubility of the surfactant in one phase, without stirring, bringing with him through the phase boundary, and enjoys a certain amount of the solvent (monomer) that is emulsified in the other phase.

The intensity of microemulsification is slowed over time and can be completely terminated with prolonged contact of phases. This is explained by the fact that the interface formed a dense layer of ME, retarding the process of mass transfer. Microemulsification observed in systems with sufficiently high values of interfacial tension σ_{12} (about 1-10 mN / m). The increase in interfacial surface at high values of σ_{12} can not be explained by thermodynamic factors, because the corresponding increase in free energy can not be offset by an increase in entropy of microdroplets. This means that the stability of such a dispersed system has a kinetic rather than thermodynamic in nature.

In this case, when the surface energy of the droplets is much higher than KT, the formation of droplets can not be explained only by thermal fluctuations. Note that the ratio of the surface energy of a KT scan, depending on the size of droplets can be large, even for low values of σ_{12}. So for a drop having a diameter D = 100 nm and σ_{12} = 10^{-2} mN / m, for this ratio, we obtain

$$\frac{\pi D^2 \sigma_{12}}{KT} \approx 75 \qquad (3)$$

This process is a kind of "quasi-spontaneous" emulsification, and once again we recall that in contrast to the spontaneous emulsification of the true droplets can form various degrees of dispersity, from colloidal particles to the droplets, significantly exceeding the size, for example, microscopic investigation of emulsion obtained in a glass capillary at the interface of 10% aqueous solution of sodium butylnaphthalenesulfonate / xylene, clearly showed that the formation of direct and inverse emulsions. Unstable inverse emulsion of water in coarse xylene - the diameter of water droplets is in the range 1-5 microns. The emulsion is xylene in the aqueous phase (direct emulsion) is visually observable in the form of a milky-white layer below the interface and is extremely stable and formed droplets whose size is beyond the interval of an optical microscope. Therefore, the determination of the dispersion ultra ME is carried out by electron microscopy [79]. The diameters of the particles according to electron microscopy were in 20-40 nm intervals.

There is a proportional relationship which was noticed between the resulting number of ME microdroplets and the quantity of surfactant have passed through the interface. The effectiveness of microemulsification is associated not only with surfactant phase transfer caused by initial non-equilibrium distribution of surfactants between the phases. Parameters determining the condition of interfacial instabilities are also: a sign of the derivative $d\sigma_{12}/dG$ (G - surface concentration of surfactant), the relationship of diffusion coefficients D_1/D_2 and coefficients of the kinetic viscosity γ_1/γ_2 in different phases [77]. It should be noted that the surface concentration of surfactant uniquely determines the surface tension only in the absence of local gradients of G, leading to a surface instability. Dynamic surface tension measured in the presence of interfacial instability, depends on the distribution of local values of G, and may be substantially lower than the equilibrium value. Numerous experimental determination of σ_{12} under non-equilibrium conditions confirms this fact.

Interphacial transfer causing the destruction of the interface can also lead to the fragmentation of large monomer droplets, whose dimensions are determined mainly by conditions of mechanical stirring. By analogy with the effect of interphase mass transfer direction that depends on the surfactant distribution coefficient on the rate of microemulsification, we can assume that the fragmentation of large droplets of the monomer will depend on the way the surfactant is introduced to the system:

- surfactant is dissolved initially in aqueous phase (traditional way);
- surfactant is dissolved initially in monomer;
- surfactant is formed on the interface layer (when acid and alkaline components of surfactant are dissolved in monomer and aqueous phase respectively)

Investigation of polymerization of vinyl and diene monomers in the presence of a nonionic emulsifier, performed in [79, 95, 100] led the authors to conclude that monomer microemulsification is the first stage of PMP formation in EP.

When free radicals are injected into the microdroplets of monomer, they become PMP. Polymer-monomer particles are microdroplets of polymer solution in monomer, on the surface of which the polymer sedimentate, forming a polymer film. This film is the site of fixation of polymer radicals and, therefore, it is the place of formation of high molecular mass polymer.

Monomer to the reaction site (surface layer) of a particle diffuses as from inside this particle as from the outside monomer droplets, if later are present in the system and if the monomer concentration in microdroplets reached critical values lower than monomer/polymer equilibrium concentration. The authors believe that, along with the diffusion of monomer through the water, the transfer of the monomer can be carried out through direct contact of PMP with a monomer droplets.

Thermodynamic substantiation of formation of monomer microdroplets was investigated by Oganesyan [49, 51, 109]. In his study of the static monomer/water system the author tried to find the source of energy needed to perform work on the formation of droplets. His analysis came from the following considerations: the minimum work necessary to create a unit of the interface (the specific surface free energy) is the interfacial tension. New surface can be created by elastic deformation of the interface, the transfer of some amount of a substance from one phase to another and the creation of the surface bumps or depressions, as well as the division of each of the phases in small particles. If both phases are liquid, the minimum work to create a unit surface area for all modes is the same because it is defined only by temperature and chemical potential of the contacting phases [79]. If the released heat of polymerization at the interface is able to transfer a certain amount of monomer in the aqueous phase, it can be assumed that the polymerization reaction can also deform the interface and disperse system. If we start from an initial equilibrium state of the system, the transfer of certain amount of monomer in the monomer-rich aqueous phase of water is equivalent to supersaturation with respect to monomer and nucleation can be expected in the monomer droplets in the aqueous phase in the vicinity of the interface.

Oganesyan et al. [49-51] believe that the formation of droplets of the monomer due to polymerization at the interface monomer - water, can also be explained on the basis of their dependence on the specific surface energy, γ, and temperature.

$$\gamma = \gamma_0 \, (1 - T / T_c)^n \tag{4}$$

where n is a constant depending on the nature of the substance (for organic liquids it is equal to 11/9 [51]). T_c is the critical temperature (at $T = T_c$ there is a mixture of phases). From equation (4) it follows that with increasing T, γ strongly decreases. Thus, for every act of the reaction heat release in certain areas of the interface performs a partial mixing of fluids, and if stabilizing agents, such as surfactants or oligomeric growing radicals, are present in the system this process will lead to the formation of microdroplets of the monomer.

2.5. Mixed mechanism of PMP nucleation

In [34, 35, 117, 118] Hansen and Ugelstad proposed to consider all three mechanisms of nucleation of PMP (micellar, homogeneous, and from microdroplets) when investigating EP at a concentration of emulsifier above CMC, assuming that the micelles containing solubilized monomer and monomer microdroplets compete with one another in the capture of oligomeric radicals from the aqueous medium. This causes that the rate of formation is the sum of the rate of the particle nucleation by all three mechanisms.

$$\frac{dN_p}{dt} = \rho_i (P_m + P_h + P_d) \tag{5}$$

where P_m and P_d - the probability of absorption of oligomeric radicals by solubilized micelles and microdroplets of monomer respectively, and P_h is the probability of homogeneous nucleation in the aqueous phase. The sum of all probabilities is equal to unity:

$$P_m + P_h + P_d + P_{p0} + P_{p1} = 1 \tag{6}$$

where P_{p1} and P_{p0} are the probability of capture of oligomeric radicals by PMP containing one and zero free radical.

On the basis of this model, several extreme cases have been investigated, such as

a. homogeneous nucleation of particles, taking into account the possible absorption of oligomeric radicals by particles and nuclei of small flocculation [34];
b. the limited flocculation of particles and nuclei, and small micellar nucleation PMP microdrop [34 , 35];
c. competing homogeneous and micellar nucleation, with the possibility of desorption and reabsorption of free radicals with little flocculation of particles [117];
d. homogeneous nucleation of microdrop and low flocculation of particles [118].

Song and Poeleyn suggested a scheme (Figure 2) of particles nucleation at the initiation of EP monomer and potassium persulfate developed general kinetic model that takes into account all the mentioned above three possible mechanisms of particle nucleation [119-120].
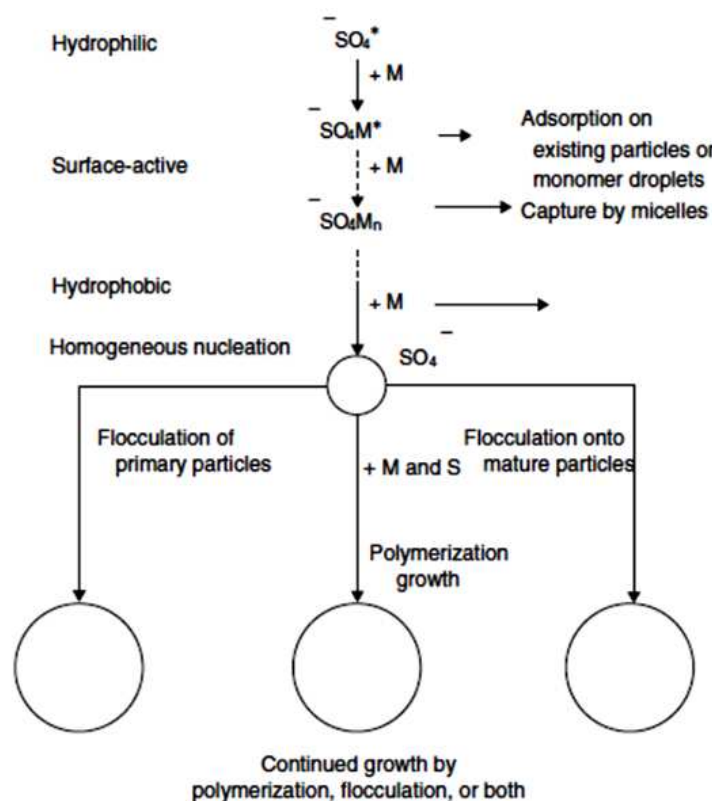
Figure 2. Paths for the formation of particle nuclei starting from persulfate initiator radicals generated
in the continuous aqueous phase. The symbols M and S represent monomer and surfactant species,
respectively (from Principles and applications of emulsion polymerization / by Chorng-Shyan Chern.
John Wiley & Sons, Inc., Hoboken, New Jersey 2008) [121].

These published data suggest that current theoretical ideas on the mechanism of PMP
varied. This complicates the establishment of methods of synthesis of polymeric suspensions
with regulated properties and makes it relevant and important research aimed at solving
this problem.

3. Model of styrene emulsion polymerization. The effect of the initial dispersion of the system on the polymerization rate and size distribution of polymer–monomer particles

The models of latex particle nucleation described in the literature were generalized in [122].
These models are the "collision process" [123, 124], "diffusion process" [27, 29],
"diffusion/propagational" model (Maxwell et al. [125]), "collision/empirical" model
(Dougherty [126] and Penlidis et al. [127]), "surface coverage" model (Yeliseyeva and
Zuikov [128]), and "colloidal" model (Penboss et al. [129]).

The authors of [74] assume that the original monomer emulsion contains, in addition to
surfactant micelles, monomer microdroplets with a size of 50–150 nm that are formed owing
to fragmentation of monomer droplets in the initiation of polymerization and owing to the
mass transfer of the emulsifier at the monomer/water interface. It was shown that the ratio

of the number of micelles and microemulsion droplets in the system depends on both the type of surfactant and the method of introducing it into the system [101]. The number of microdroplets affects the pattern of the particle size distribution and the molecular mass distribution of the polymer. According to the authors of [101], PMPs are formed from both micelles and microemulsion droplets.

The simulation of emulsion polymerization of styrene is the subject of many publications, in which the authors discuss the dependence of the kinetics of the process on the emulsifier and initiator concentration [130], the particle size distribution [127, 131-134], and the molecular mass distribution [135-139] and perform a complete simulation of the kinetic characteristics of the process [24, 38, 130, 140-145]. However, all these studies are based on the Harkins–Yurzhenko qualitative theory and disregard the participation of microdroplets in the formation of PMPs.

In this study, we attempt to develop a mathematical model of emulsion polymerization for a partially water-soluble monomer (styrene) that takes into consideration that the original emulsion contains microdroplets that participate in the formation of PMPs.

The calculations are performed with disregard for homogeneous nucleation, polymerization in emulsion macrodroplets, and radical desorption from PMPs. In our opinion, these assumptions are fully justified for the polymerization of partially water-soluble monomers, such as styrene, and in the presence of a fairly high amount of emulsifier.

Let us introduce the following notations: The concentration of PMPs with volume ν with volume fraction of the monomer in them containing i growing radicals at time t is $f_i(\nu, \phi, t)$, the total concentration of PMPs in the system is expressed through $f(\nu, \phi, t)$ as , and their average diameter

$$\overline{D} = \frac{\sum_i \int D f_i(v,\phi,t)dv}{\sum_i \int f_i(v,\phi,t)dv} \tag{7}$$

To determine the effect of the dispersion state of the original emulsion system on the characteristics of emulsion polymerization, we performed a model calculation of the polymerization rate and the PMP size distribution in systems with different initial states.

Consider two limiting cases:

i. A system that contains, in addition to the aqueous phase and monomer emulsion droplets, microdroplets of the same size (here micelles can be regarded also as a limiting case of microdroplets). With this aim in view, we calculate the dependence of the polymerization rate and the PMP size distribution on the diameter of microdroplets.

ii. A system that contains the aqueous phase, monomer emulsion droplets, and micelles and microdroplets of the same size. In this case, we estimate the effect of the ratio between the number and size of micelles and microemulsion droplets on the polymerization rate and the PMP size distribution.

3.1. A monodisperse system consisting of monomer microdroplets

Consider an emulsion system that contains emulsion droplets dispersed in the aqueous phase and microdroplets of diameter D_0 (accordingly, of volume V_0), the concentration of which is M_0 particles per cubic centimeter. Monomer microdroplets will be present in the system if $M_0 V_0 < (1+r)^{-1}$, where r is the volume ratio of the aqueous and monomer phases. We assume that the monomer diffusion from droplets towards PMPs through the aqueous phase does not limit the process of emulsion polymerization.

If the emulsifier concentration in the system is high, that is, much higher than the critical concentration of micelle formation (it is this case that will be discussed below), we can disregard the fraction of a surfactant adsorbed on droplets. In this case, M_0 and D_0 are related as follows:

$$\pi M_0 D_0^2 = a_{m(D_0)} S_E N_A$$

where S_E is the emulsifier concentration in the system (mol•cm⁻³), a_m is the area occupied by one surfactant molecule on the microdroplet surface, and N_A is Avogadro's number.

In the absence of PMP coalescence and radical desorption from particles, the system of equations for the PMP distribution function $f_i(v)$ for volume v; the volume fraction of the monomer in them, ϕ ; and number i of growing radicals has the form

$$
\begin{aligned}
\frac{\partial f_i}{\partial t} + i\frac{\partial}{\partial v}(f_i \theta_v) + i\frac{\partial}{\partial \phi}(f_i \theta_\phi) = \\
= j(v)(f_{i-1} - f_i) + \frac{k_t}{2v}\Big[(i+1)(i+2)f_{i+2} - i(i-1)f_i\Big] + M(t)\delta(v-V_0)j(v)\delta(\phi-1)
\end{aligned}
\tag{8}
$$

In Eq. (8), the first term in the right-hand side describes the arrival of a radical to a particle from the aqueous phase, the second term defines the change in the number of radicals during termination, and the last term describes the formation of new particles after the entry of a radical into a microdroplet. In the left-hand side of Eq. (8), θ_v and θ_ϕ define, respectively, the volume growth rate and the rate of change in the volume fraction of the monomer for a PMP that contains one radical. These rates can vary with the particle size. In addition, $j(v)$ is the diffusion flux of radicals towards particles; k_t is the chain termination rate constant; and $\delta(v-V_0)$ is the generalized Dirac function,

$$
\delta(x) = \begin{cases} 0, & x \neq 0 \\ \infty, & x = 0 \end{cases}
$$

From the balance for the emulsifier, we derive the time dependence of the microdroplet concentration:

$$
\frac{\pi M(t) D_0^2}{a_{m(D_0)}} + \sum_i \iint dv\, d\phi\, \frac{f_i v^{2/3}\sqrt[3]{36\pi}}{a_{m(v)}} = S_E N_A
\tag{9}
$$

Depending on the time of PMP formation, the volume fraction of the monomer, ϕ, of some particles will be higher than equilibrium volume fraction ϕ_M, which is determined from the thermodynamic equilibrium; for some particles, $\phi = \phi_M$. We divide f_i into two parts: PMPs with $\phi > \phi_M$ ($Y_i(\phi,t)$) and particles with $\phi = \phi_M$ ($X_i(v,t)$); that is,

$$f_i(v,\phi,t) = X_i(v,t)\delta(\phi - \phi_M) + Y_i(\phi,t)\delta(v - V_0)$$

The total concentration of PMPs in the system is

$$N = \sum_i \left(\int_{\phi_M}^{1} Y_i d\phi + \int_{V_0}^{\infty} X_i dv \right) \tag{10}$$

The polymerization rate W is expressed in terms of the functions X_i and Y_i according to the equation

$$W = \frac{k_p}{v_M} \sum_i i \left(\int_{\phi_M}^{1} Y_i \phi d\phi + \phi_M \int_{V_0}^{\infty} X_i dv \right) \tag{11}$$

Equations (12)–(14) completely describe the first and second stages of emulsion polymerization. To calculate the distribution function f_i, we introduce dimensionless variables and parameters:

$$X_i = \frac{M_0}{V_0} \tilde{X}_i \quad v = V_0 y \quad \gamma = \frac{k_p M_0}{V_0 \rho}$$

$$Y_i = M_0 \tilde{Y}_i \quad t = M_0 x / \rho \quad \kappa = \frac{M_0 \theta_v}{V_0 \rho} \equiv \frac{d_M}{d_P} \cdot \frac{\phi_M}{1 - \phi_M} \cdot \gamma$$

$$M = M_0 \xi \quad \lambda = \frac{k_t M_0}{2 V_0 \rho}$$

If $\lambda \gg 1$, then all $\tilde{X}_i$ and $\tilde{Y}_i$ at $i \geq 2$ are equal to zero (i.e., the approximation of fast termination is valid for the system), and the system with an infinite number of equations will transform into a system of equations for f_i with $i = 0$ and 1. The appropriateness of the approximation of fast termination, other things being equal, is determined by the value of termination constant k_t. If we take the termination constant value for in bulk polymerization as k_t, then, for typical values of the initiation rate $\rho = 10^{11}$–10^{13} cm^{-3} s^{-1} and the emulsifier concentration $S_E \approx 10^{-4}$ mol/cm^3, the value of λ will be $\lambda \approx 10^{10}$ for particles with a size of $D_0 = 10$ nm and $\lambda \approx 10^3$ for particles with $D_0 = 150$ nm. The termination constant for the emulsion polymerization in particles with a volume fraction of the monomer of $\phi = \phi_M = 0.5$ is two to four orders of magnitude lower than that for bulk polymerization; therefore, the value of λ will be lower as well. Nevertheless, at the first stage of emulsion polymerization, the

approximation of fast termination is valid for small particles owing to $\lambda \gg 1$ that is due to the low value of D_0; for large particles (up to $D_0 \approx 300\text{–}500$ nm), for which $\phi > \phi_M$ throughout the first stage, the approximation of fast termination is appropriate because of the high value of the termination constant. However, note that, at the second stage of emulsion polymerization, when the volume fraction of the polymer is high in large PMPs, the approximation of fast termination may be inapplicable to these large particles.

In the approximation of fast termination we obtain the following system

$$\begin{cases} \dfrac{\partial \tilde{X}_0}{\partial x} = J(y)(\tilde{X}_1 - \tilde{X}_0) \\[2mm] \dfrac{\partial \tilde{X}_1}{\partial x} + \kappa \dfrac{\partial \tilde{X}_1}{\partial y} = J(y)(\tilde{X}_0 - \tilde{X}_1) + \gamma \phi_M \tilde{Y}_1(\phi_M)\delta(y-1) \end{cases} \qquad (12)$$

$$\begin{cases} \dfrac{\partial \tilde{Y}_0}{\partial x} = J(1)(\tilde{Y}_1 - \tilde{Y}_0) \\[2mm] \dfrac{\partial \tilde{X}_1}{\partial x} - \gamma \dfrac{\partial (\tilde{Y}_1 \phi)}{\partial \phi} = J(1)(\tilde{Y}_0 - \tilde{Y}_1) + J(1)\xi\delta(\phi-1) - \gamma \phi_M \tilde{Y}_1(\phi - \phi_M) \end{cases}$$

where κ is the dimensionless parameter in equations

3.1.1. A system containing small microdroplets.

The criterion of a small size of microdroplets is short time t_M of settling of the equilibrium volume fraction of the

Monomer ϕ_M in PMPs relative to the duration of the first stage t_1; that is, $t_M < t_1$.

Figure 3 shows the PMP size distribution by the end of the first stage and the time dependence of microdroplet concentration in the system. It is evident that the PMP concentration increases almost linearly with time nearly to the end the first stage ($t < t_1$), and the microdroplet concentration decreases also almost linearly; only near the end of the first stage, a sharp decrease in the microdroplet concentration down to zero occurs.

These results are derived under the assumption that the time of settling of the equilibrium volume fraction of the monomer, ϕ_M, in a PMP is much shorter than the duration of the first stage. Using the expression for the dependence of the first-stage duration on parameters of the system, we find that the above calculations are valid for systems whose parameters satisfy the inequality

$$t_M = \frac{V_0}{k_p}\ln\frac{1}{\phi_M} \ll \frac{M_0}{\rho}\kappa^{-2/5} \approx t_1 \qquad (13)$$

or, since $\phi_M \approx 0.5$ and $d_P/d_M \approx 1$, this inequality is equivalent to inequality $\kappa \gg 1$.

Thus, if inequality (13) is fulfilled (the system consists of small microdroplets), then the PMP concentration will depend only on the initiator and emulsifier concentrations and will not depend on the size of microdroplets.
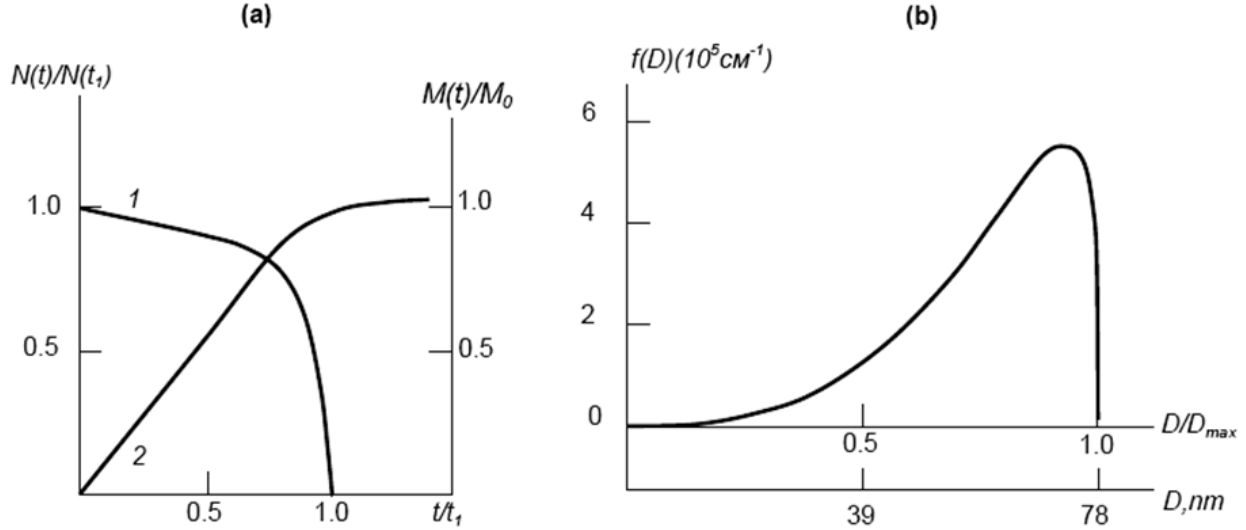

Figure 3. (a) Time dependences of the concentrations of (*1*) microdroplets and (*2*) PMPs and (b) PMP size distribution by the end of the first stage: $D_{\max} = D_0(1 + \theta t_1 / V_0)$, and t_1 is the time of exhaustion of microdroplets.

3.1.2. A system containing large microdroplets

If the original emulsion system contains microdroplets with a large diameter ($\kappa \leq 1$), throughout the first stage (at certain sizes, including a part or the entire second stage), the volume fraction of the monomer in PMPs formed from these microdroplets will be higher than equilibrium, $\phi > \phi_M$. In this case, PMPs will not absorb the monomer from emulsion droplets and, consequently, change their volume. Thus, the surfactant adsorbed on the surface of microdroplets is not consumed for the stabilization of PMPs, and the finite number of PMPs will be equal to the number of microdroplets in the original system.

In this system, the concentration of PMPs with $\phi = \phi_M$ is zero, $X_i = 0$, and the polymerization process is described by equations for functions $Y_i(\phi, t)$, which, in the approximation of fast termination, in dimensionless variables, have the form

$$\begin{cases} \dfrac{\partial \tilde{Y}_0}{\partial x} = \tilde{Y}_1 - \tilde{Y}_0 \\ \dfrac{\partial \tilde{Y}_1}{\partial x} - \gamma \dfrac{\partial}{\partial \phi}(\phi \tilde{Y}_1) = \tilde{Y}_0 - \tilde{Y}_1 + \xi \delta(\phi - 1) \end{cases} \tag{14}$$

Let us use $n_0(x) = \int \tilde{Y}_0 d\phi$ and $n_1(x) = \int \tilde{Y}_1 d\phi$ to denote the fractions of dead and alive PMPs in the system, respectively (relative to the total number of PMPs and microdroplets equal to M_0); $W_0 = \int \phi \tilde{Y}_0 d\phi$ and $W_1 = \int \phi \tilde{Y}_1 d\phi$. The PMP concentration in the system and the polymerization rate are expressed in terms of functions n_0, n_1, W_0, W_1.

For the time dependence of conversion, from the condition of balance for the monomer, we
have

$$p(t) = \frac{d_P}{d_M} \frac{M_0 V_0}{(r+1)^{-1}} \big((n_0 + n_1) - (W_0 + W_1) \big) \tag{15}$$

Figure 4 shows the time dependence of conversion for the original system of large
microdroplets, which is calculated through formula (15), and, for comparison, the time
dependence of conversion for the original system of small microdroplets. It is evident that,
in the approximation of fast termination, the polymerization occurs faster in the system with
small microdroplets.
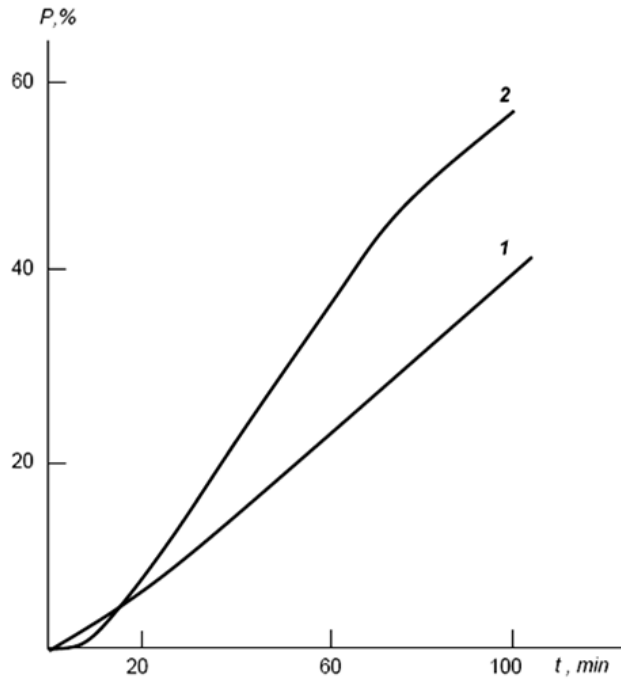
Figure 4. Time dependence of monomer conversion in systems with microdroplets of different sizes:
$D0 = (1)$ 150 and (2) 10 nm, $a_m = 0.4$ nm^2, $S_E = 2 \bullet 10^{-4}$ mol cm^{-3}, and $\varrho = 10^{12}$ cm^{-3} s^{-1}.

Figure 5 shows the calculated dependence of the final concentration of PMPs in the system on
the size of microdroplets for the case in which the rate of radical entry into particles is
proportional to their surface. The characteristic size of microdroplets, D_C, starting from which
the PMP concentration decreases, is determined by the value of parameter $\kappa = 1$; therefore, it
depends not only on D_0 but also on the initiation rate and the emulsifier concentration. For
typical values of concentrations of the components, this size is $D_C \approx 40$–60 nm.

To determine the effect of microdroplet size on the PMP size distribution through solution
of system of equations (12)–(13), we calculated also the PMP size distribution by the end of
the first stage for different values of D_0 and changes in the distributions during
polymerization. Figure 6 represents the PMP diameter distribution by the end of the first
stage; Fig. 6 depicts a change in the distribution during polymerization, it shows that the
PMP size distribution becomes narrower as the size of microdroplets increases.
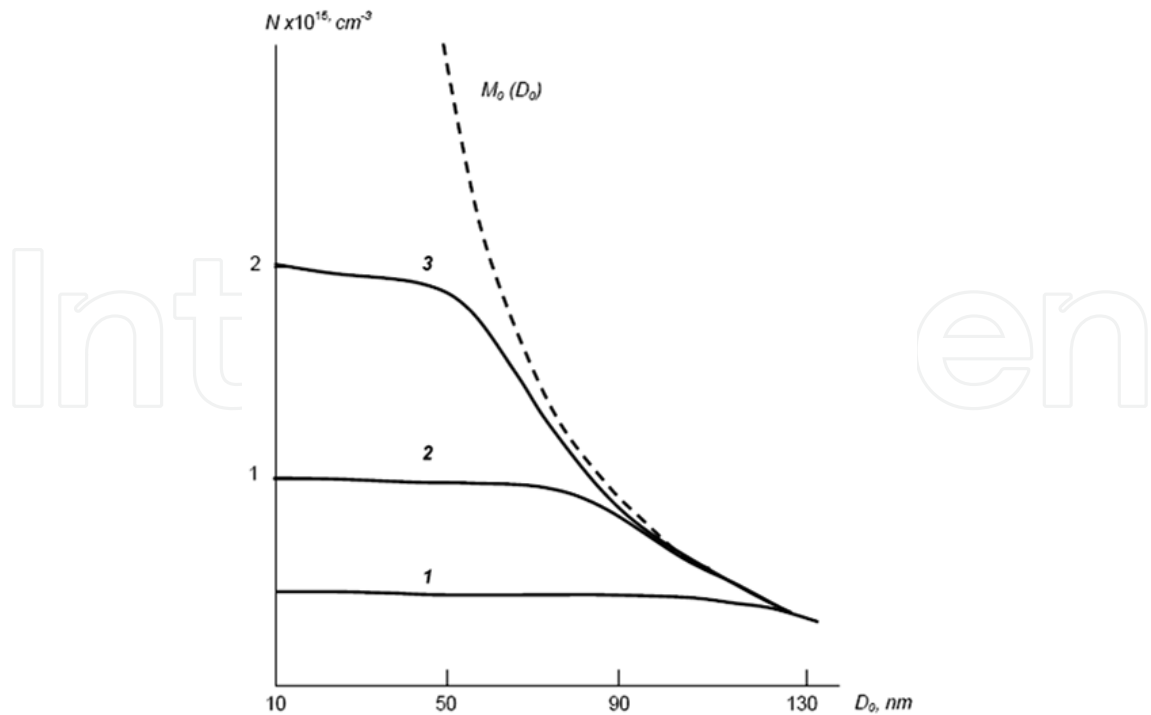
Figure 5. Dependence of PMP concentration in the system on the initial size of microdroplets: $\varrho = 10^{11}$ *(1)*, 10^{12} *(2)* and 5×10^{12} cm^{-3} s^{-1} *(3)*, $a_m = 0.4$ nm^2, $S_E = 2 \cdot 10^{-4}$ mol cm^{-3}.
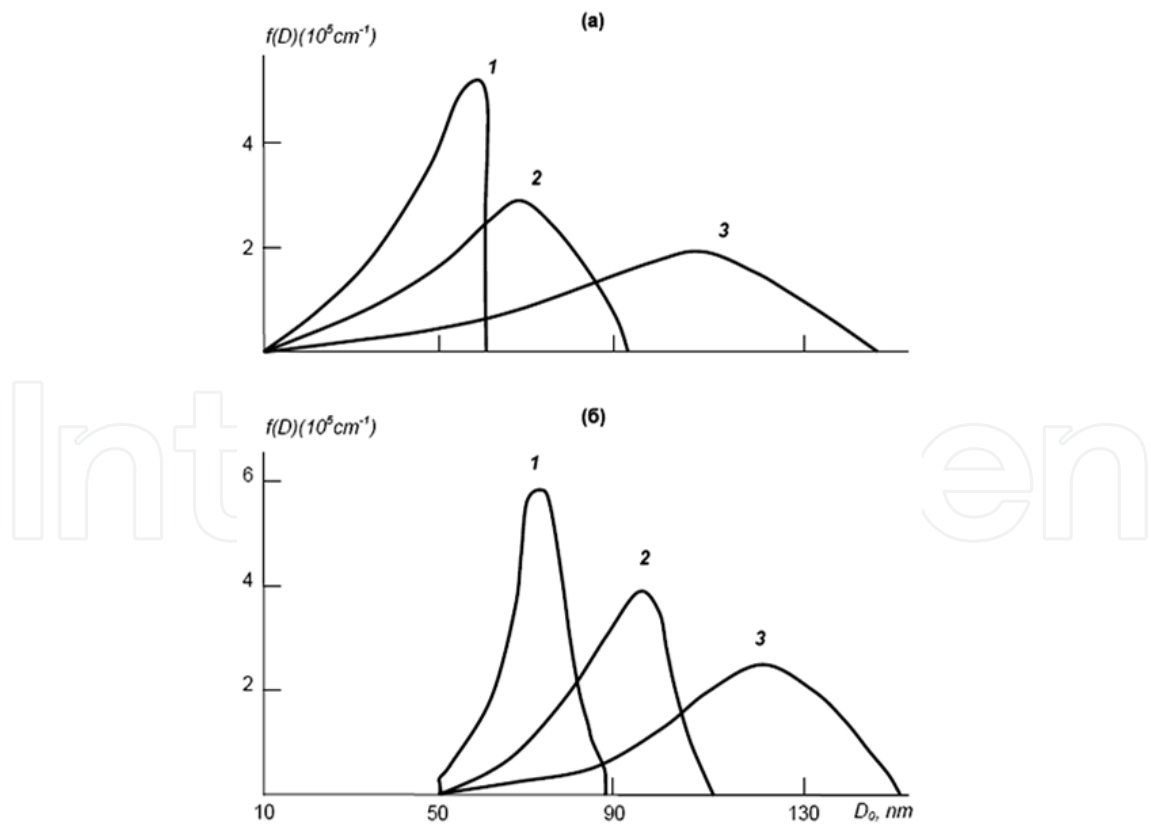

Figure 6. Change in the PMP diameter distribution during polymerization at conversions $P = (1)$ 5, *(2)* 15, and *(3)* 50%. Initial microdroplet size of (a) 10 and (b) 50 nm, $a_m = 0.4$ nm^2, $S_E = 2 \cdot 10^{-4}$ mol cm^{-3}, and $\varrho = 10^{12}$ cm^{-3} s^{-1}.

3.2. A bidisperse system of microdroplets

To determine the mechanisms of polymerization in the case of comparable rates of PMP formation from micelles and microemulsion droplets, we study a bidisperse system that contains M_0 microemulsion droplets with diameter D_0 and μ_0 micelles with diameter d_0 and calculate the polymerization process in this system.

Depending on the method of introducing the emulsifier into the system, the formation of new droplets of the microemulsion can occur during polymerization; however, owing to the absence of experimental data on the rate of microemulsification in these systems and its dependence on the concentration of the free emulsifier and its distribution between phases, we restrict ourselves to the discussion of a system with a fixed number of microemulsion droplets. Consideration for the finite rate of formation of the microemulsion will only lead to a change in the duration of the stage of PMP formation and slightly affect other characteristics of the process.

To describe the rate of polymerization and the concentration of PMPs in the system under discussion, we introduce parameter Γ that characterizes the fraction of the surfactant adsorbed on the microemulsion surface:

$$\Gamma = \frac{\pi M_0 D_0^2}{N_A S_E a_m(D_0)} \tag{16}$$

where M_0, D_0, μ_0, and d_0 are related as follows

$$\frac{\pi M_0 D_0^2}{a_m(D_0)} + \frac{\pi \mu_0 d_0^2}{a_m(d_0)} = S_E N_A$$

We shall divide all PMPs in the system into two types: PMPs formed from micelles (with subscript μ) and PMPs formed from the microemulsion droplets (with subscript M):

$$f_i(v,\phi,t) = f_{\mu,i}\delta(\phi - \phi_M) + f_{M,i}(v,\phi,t)$$

Here, we take into account that, in PMPs formed from micelles, the equilibrium volume fraction of the monomer, ϕ_M, is settled almost immediately. By time t, the volume fraction of the monomer of a portion of the PMPs formed from microemulsion droplets will be equal to ϕ_M and that of another portion will be higher than ϕ_M; that is, $f_{M,i}$ can be represented as the sum

$$f_{M,i} = X_i(v,t)\delta(\phi - \phi_M) + Y_i(\phi,t)\delta(v - V_0)$$

the total number of PMPs formed from the microemulsion droplets, N_M, is equal to the initial number of droplets, M_0, and the number of PMPs formed from micelles, N_μ, is $N_\mu = \mu\kappa^{-2/5}$ at $\kappa \gg 1$. The total number of PMPs per unit volume of the system by the end of the first stage is

$$N = N_\mu + N_M = \mu_0 \kappa^{-2/5} + M_0 = N_\mu^0 \left[1 - \Gamma\left(1 - \frac{d_0}{D_0}\kappa^{-2/5}\right) \right] \qquad (17)$$

where

$$N_\mu^0 = \frac{S_E a_m N_A}{\pi d_0^2} \kappa^{-2/5}$$

is the total number of PMPs formed in the system if it contained only micelles. Since for large particles, for which the above formulas are valid, $M_0 \theta / V_0 \varrho < 1$, then the total number of PMPs is less than N_μ^0.

The PMP size distribution is the sum of two distributions: the distribution corresponding to PMPs formed from micelles and the distribution corresponding to PMPs formed from microemulsion droplets. The index of diameter polydispersity by the end of the first stage is derived through calculation of the average diameter and the square of the average diameter of PMPs:

$$\begin{cases} \bar{D} = \frac{3}{4}d_0\kappa^{1/5}\dfrac{1 + \dfrac{4}{3}\dfrac{M_0 D}{\mu_0 d}\kappa^{1/5}}{1 + \dfrac{M_0}{\mu_0}\kappa^{2/5}} \\[4mm] \overline{D^2} = \frac{3}{5}d_0^2\kappa^{2/5}\dfrac{1 + \dfrac{5}{3}\dfrac{M_0}{\mu_0}\left(\dfrac{D_0}{d_0}\right)^2}{1 + \dfrac{M_0}{\mu_0}\kappa^{2/5}} \\[4mm] K_D = \left(\dfrac{\overline{D^2}}{\bar{D}^2}\right)^{1/2} = \dfrac{\left(1 + \dfrac{5}{3}\dfrac{\Gamma}{1-\Gamma}\right)\left(1 + \dfrac{\Gamma}{1-\Gamma}\left(\dfrac{d_0}{D_0}\right)^2\kappa^{2/5}\right)}{\left(1 + \dfrac{4}{3}\dfrac{\Gamma}{1-\Gamma}\dfrac{d_0}{D_0}\kappa^{1/5}\right)^2} \end{cases} \qquad (18)$$

Figure 7 shows the dependence of K_D on Γ for $\kappa = 10^4$. It is evident that index K_D by the end of the first stage depends on the d_0/D_0 ratio and has maximum.

Figure 8 shows the dependence of the finite number of PMPs formed in the system on parameter Γ at different values of d_0/D_0. It is evident that, during an insignificant difference between the sizes of the two fractions, the PMP concentration hardly changes at all; however, when the size of large microdroplets is five (or more) times larger than the size of small microdroplets (solubilized micelles), the PMP concentration sharply decreases with an increase in Γ. Figure 9 depicts the size distributions of PMPs by the end of the first stage for various values of Γ and d_0/D_0. It is evident that the distribution is bimodal. Figure 10 shows

that the PMP size distribution by the end of the first stage is bimodal in the general case. The peak relating to a smaller diameter corresponds to PMPs formed from micelles; that relating to a larger diameter corresponds to PMPs formed from microemulsion droplets. The transition from the bimodal size distribution of PMPs to the unimodal size distribution of PMPs by the end of the first stage occurs at a ratio of the initial sizes of micelles and microemulsion droplets of $d_0/D_0 \approx \kappa^{-1/5}$.
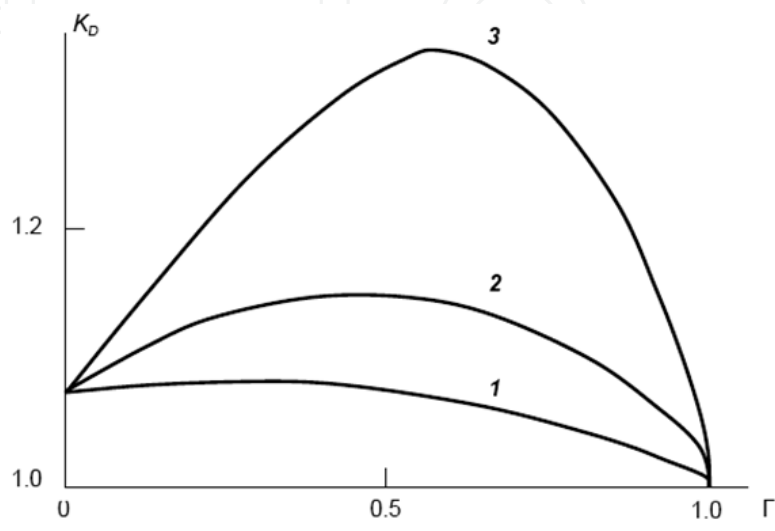

Figure 7. Dependence of the polydispersity index of the PMP size distribution on the amount of the surfactant adsorbed on the microemulsion surface (parameter Γ): $a_m = 0.4$ nm^2, $S_E = 2 \cdot 10^{-4}$ mol cm^{-3}, and $\varrho = 10^{12}$ cm^{-3} s^{-1}. $d_0 = 10$ nm; $D_0 = $ (1) 80, (2) 100, and (3) 150 nm.
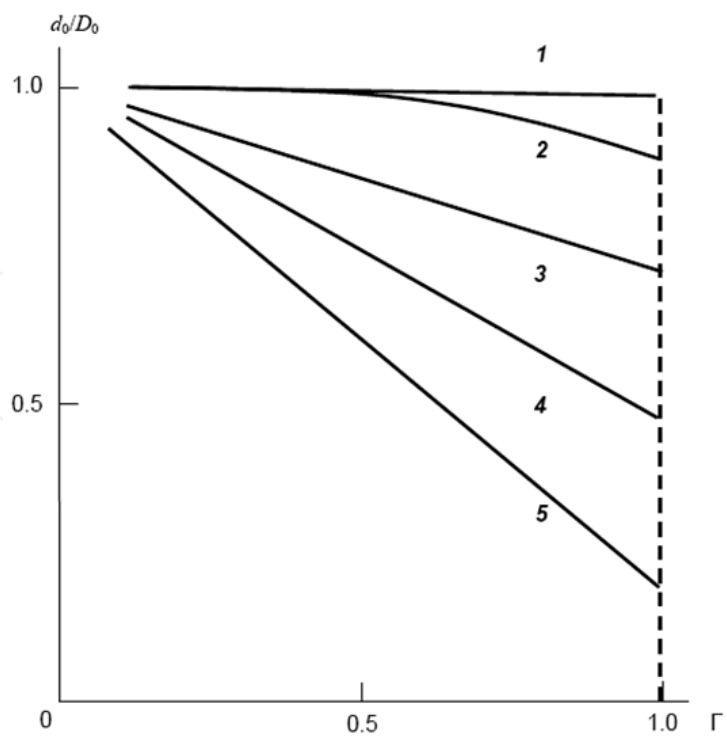

Figure 8. Dependence of PMP concentration on parameter Γ: $d_0 = 10$ nm; $D_0 = 20$ (1), 50 (2), 80 (3), 100 (4) and (5) 150 nm
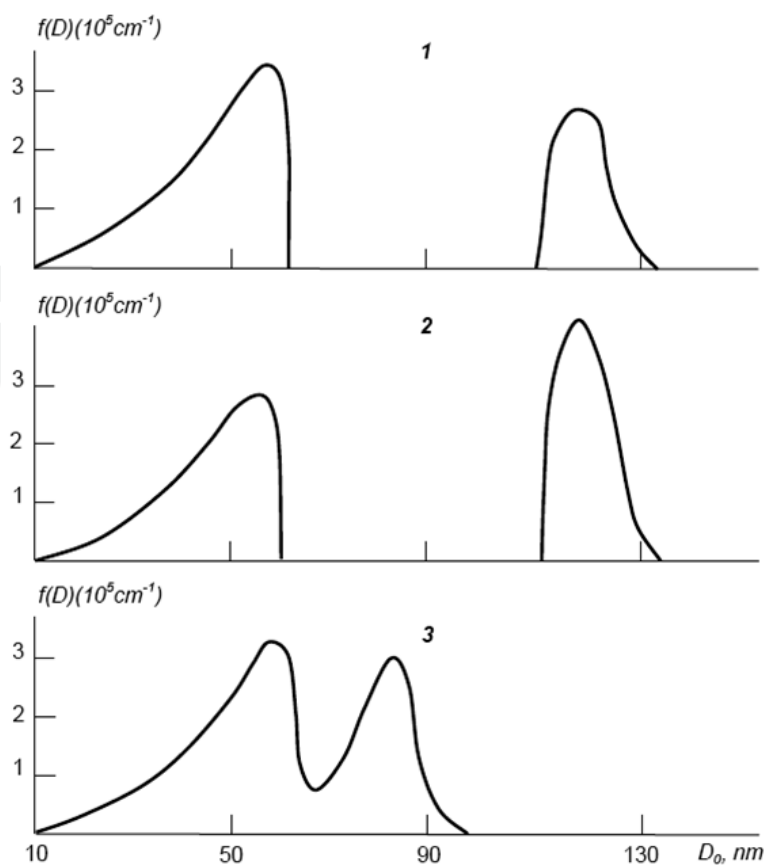
Figure 9. PMP size distribution in systems with simultaneous PMP formation from micelles and microemulsion droplets. The end of the first stage. Here, $d_0 = 10$ nm, $D_0 = $ (*1, 2*) 100 and (*3*) 50 nm, and $\Gamma = $ (*1*) 0.25 and (*2, 3*) 0.5.

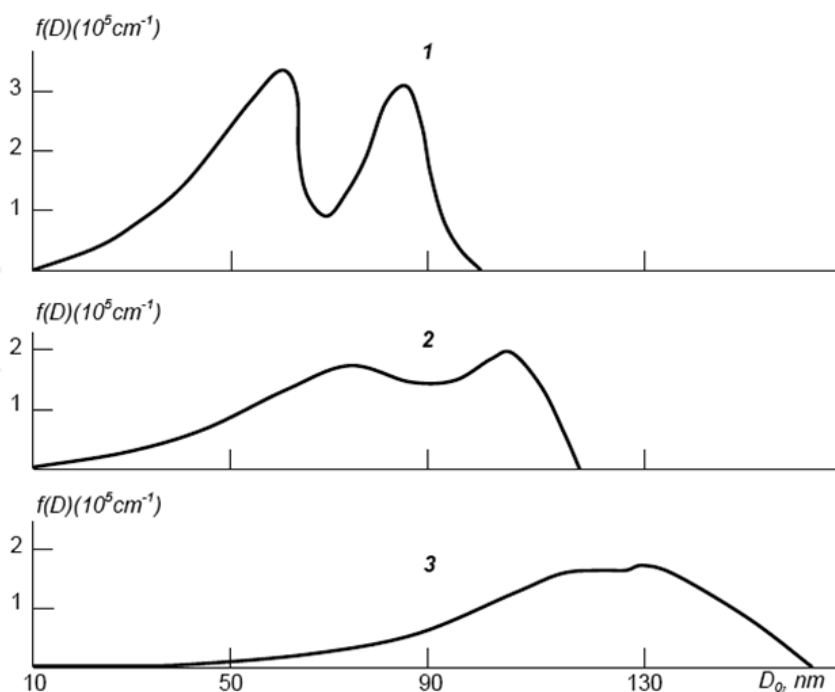**Figure 10.** Change in the PMP diameter distribution during polymerization: $d_0 = 10$ nm, $D_0 = 50$ nm, and $\Gamma = 0.5$. Monomer conversion: (*1*) 3, (*2*) 15, and (*3*) 50%.

So a mathematical model of emulsion polymerization of poor soluble monomers has been developed. It takes into account the basic physio-chemical characteristics of the system and enables simultaneous calculating important parameters of the system such as polymerization rate, the time dependence of conversion, the concentration and size distribution of PMPs and molecular mass distribution of polymer[105]. The models predicts that with increasing microdroplet size D_0 above the critical value $D_C \sim$ 40–60 nm, the PMP concentration and the polymerization rate will decrease; at $D_0 < D_C$, both the polymerization rate and the PMP concentration do not depend on D_0. The PMP distribution becomes narrower with an increase in D_0. In the case of simultaneous formation of PMPs from micelles and monomer microdroplets, the PMP size distribution is broad or, under certain conditions, even bimodal.

Analysis of experimental data shows that monomer microdroplets play an important role which should not be ignored neither in studying mechanism of polymer-monomer particles nucleation in emulsion polymerization nor in modeling this complicated process.

Author details

M. Khaddazh[*]
Kurnakov Institute of General and Inorganic Chemistry Russian Academy of Sciences, Moscow, Russia

I. A. Gritskova
Lomonosov State University of Fine Chemical Technologies, Moscow, Russia

G. I. Litvinenko
Karpov Institute of Physical Chemistry, Moscow, Russia

4. References

[1] Harkins W D (1947) Theory of the Mechanism of the Emulsion Polymerization. J.Amer.Chem.Soc. 69: 1428-1444.

[2] Harkins W D (1950) General Theory of Mechanism of the Emulsion Polymerization. J. Polym. Sci. 5: 217-251.

[3] Yurjenko A I (1946) Physico-chemical investigation of hydrocarbons polymerization in emulsions (in Russian). J.Obschei Himii 16: 1171-1188.

[4] Yurjenko A I, Kolechkova M S (1947) Physico-chemical investigation of hydrocarbons polymerization in emulsions (in Russian). J.Obschei Himii17: 354-357.

[5] Smith W V, Ewart R M (1948) Kinetics of Emulsion. J.Chem.Phys.16: 592-599.

[6] Smith W V (1948) The Kinetics of Styrene Emulsion Polymerization. J.Am.Chem.Soc.70: 3695-3702.

[*] Corresponding Author

[7] Smith W V (1949) Chain initiation in Styrene Emulsion Polymerization. J.Am.Chem.Soc.70: 4077-4082.

[8] Khomikovsky P M (1958) Kinetics and topochemical particularities of emulsion polymerization (in Russian). Uspehi Himii 27: 1025-1055.

[9] Khomikovsky P M (1959) Elementary reactions in emulsion polymerization (in Russian). Uspehi Himii 287: 545-575.

[10] Sheinker A P, Medvedev S S (1956).Rubber Chem.Technol. 29**:** 121

[11] Berezhnoi G D, Khomikovsky P M Medvedev S S (1960) Kinetics of emulsion polymerization(in Russian). Vysokomol.Soed. 2: 5-17.

[12] Yeliseeva V I, Aslamazova T R (1991) (in Russian). Uspehi Himii. 2: 398

[13] Yeliseeva V I, Zharkova N G, Lukyanovich V M (1968) (in Russian). Dokl. AN SSSR 178: 1113-1116.

[14] Medvedev S S (1968) Emulsion polymerization. Kinetics, Mechanism and Transformation of Macromolecules (in Russian). Ed. KorshakV V. Moscow.

[15] Bovey F A, Kolthoff I M, Medalsa A J, Meehan E I (1955) Emulsion Polymerization. New York – London. Interscience Publ. 455.

[16] Qiu J, Charleux B, Matyjaszewski K (2001) Controlled/living radical polymerization in aqueous media: homogeneous and heterogeneous systems. Prog.Polym.Sci. Elsevier. 2083-2134

[17] Gardon J L (1968) Emulsion polymerization. I Recalculation and extension of the Smith-Ewart theory. J.Polym.Sci. Chem. 6: 623-641.

[18] Gardon J L (1968) Emulsion polymerization. II Review of experimental data in the context of the revised Smith-Ewart theory. J.Polym.Sci. Chem. 6: 643-664.

[19] Gardon J L (1968) Emulsion polymerization. Ⅲ Theoretical prediction of the effects of slow termination rate within latex particles.J.Polym.Sci.Chem. 6: P. 665-685.

[20] Gardon J L (1968) Emulsion polymerization. IV Experimental verification of the theory based of latex particles. J.Polym.Sci. Chem. 6: 687-710.

[21] Gardon J L (1968) Emulsion polymerization. V. Lowest theoretical limits of the ratio k_t/k_p J.Polym.Sci. Chem. 6: 2853-2857.

[22] Gardon J L (1968) Emulsion polymerization. . VI. Concentration of monomer in latex particles J.Polym.Sci. Chem. 6: 2859-2879.

[23] Gardon J L (1977) Emulsion Polymerization.– In: Polym/ Process. New York. 143-197.

[24] Harada M., Nomura M, Kojima H, Eguchi W, Nagata S (1972) Rate of emulsion polymerization of styrene. J.Appl.Polym.Sci. 16: 811-833.

[25] Stockmayer W H (1957) Note on the kinetics of emulsion polymerization. J.Polym.Sci. 24: 313 – 317.

[26] O'Toole J T (1965) Kinetics of emulsion polymerization. J.Appl.Polym.Sci. 9:1291 – 1297.

[27] Hansen F K, Ugelstad J (1978) Particle nucleation in emulsion polymerization. I. A theory for homogeneous nucleation. J.Polym.Sci.Polym.Chem. 16: 1953.

[28] Hansen F K, Ugelstad J (1979) Particle nucleation in emulsion polymerization. IV. Nucleation in monomer droplets. J.Polym.Sci.Polym.Chem. 17: 3069-3078.

[29] Hansen F K, Ugelstad J (1982) Particle formation mechanism. In: Piirma I, editor. Emulsion polymerization. New York: Academic Press. 51-92.

[30] Kuchanov S I. (1975) Digest of Chemistry and Technology of High-Molecular Compounds Moscow. 7: 167.

[31] Kuchanov S I. (1978) Methods of Kinetic Calculations in Polymer Chemistry (in Russian). Moscow-Leningrad. Himiya. 368.

[32] Pismen L M, Kuchanov S I (1971) Qualitative theory of emulsion polymerization (in Russian). Vysokomol.Soed. A. 13: 1055-1065.

[33] Pavlyuchenko V N, Ivanchev S S (1981) Emulsion polymerization of non-polar monomers (Development of representation about kinetics and topochemistry) (in Russian). Uspehi Himii. 50: 715-745.

[34] Ivanchev S S, Pavlyuchenko V N, Rozhkova D A (1973) Surfactants as alkamons as components of redox initiating systems in emulsion polymerization of styrene (in Russian). DAN SSSR. 211: 885-888

[35] Priest W J (1952) Particle growth in the aqueous polymerization of vinyl acetate. 56: 1077–1083.

[36] Roe C P (1968) Surface chemistry aspects of emulsion polymerization. Ind.Eng.Chem. 60: 20 – 33.

[37] Yeliseyeva V I (1977) New Theory of Emulsion Polymerization. Sunthesis and Modification of Latexes (in Russian). Moscow, Himiya 3-9.

[38] Yeliseyeva V I, Ivanchev S S, Kuchanov S.I, Lebedev A I (1977) Emulsion Polymerization and its Applications in Industry (in Russian). Moscow, Himiya. 240.

[39] Fitch R M (1971) Homogeneous nucleation of polymer colloids. IV. The role of soluble oligomeric radicals. Polymer colloids, Plenum Press. New York.103 – 116.

[40] Fitch R M The homogeneous nucleation of polymer colloids. Br.Polym.J. -1973. - 5. – P. 467 – 483.

[41] Fitch R M (1973) Particle formation in polymer colloids. III. Prediction of the number of particles by a homogeneous nucleation theory. In: Fitch RM, editor. Polymer colloids. New York: Plenum Press.

[42] Fitch R M, Tsai C H (1970) Polymer colloids: particle formation in nonmicellar systems theory. J.Polym.Sci., Polym.Chem. B. 8: 703-710.

[43] Khomikovsky P M (1948) About mechanism of emulsion polymerization of vinyl acetate and methyl methacrylate in water and in soap solutions (in Russian). DAN SSSR. 60: 615-618.

[44] Christiansen J A, Nielsen A E (1952) The interplay between nucleus formation and crystal growth. Z. Electrochem. 56: 465-467.

[45] Pepard B (1974) Particle nucleation phenomena in emulsion polymerization of polystyrene. University Microfilms, – Ann Arbor.

[46] Goodal A R, Wilkinson M C, Hearn J (1975) Formation of anomalous particles during the emulsifier-free polymerization f styrene. J.Coll.Interface Sci. 53: 327.

[47] Cox R.A. , Wilkinson M C, Greasy J M (1977) Study of the anomalous particles formed during the surfactant-free emulsion polymerization of styrene. J.Polym.Sci., Polym.Chem.Ed. 15: 2311.

[48] Goodal A R, Wilkinson M C, Hearn J (1977) Mechanism of emulsion polymerization of styrene in soap-free systems. J.Polym.Sci., Polym.Chem.Ed. 15: 2193.

[49] Oganesyan A, Gukasyan A, Bayagyan V, Matsoyan S (1985) The generation place of growing radicals and their behavior in styrene – sodium persulate aqueous system (in Russian). Armenian Chem.J. 38: 331-333.

[50] Oganesyan A, Airapetyan K, Gukasyan A, Kinoyan (1986) About the chemistry of initiation reaction of monomer radicals in sodium persulate aqueous solution saturated with styrene (in Russian). DAN Armenian SSR. 82: 134-136.

[51] Oganesyan A (1986) Оганесян, А.А. Radical polymerization and phase formation in heterogeneous monomer/water systems. Dr. Sc. Thesis. Moscow. MITHT. 201.

[52] Tauer K , Kuhn I (1996) Modeling Particle Formation in Emulsion Polymerization: An Approach by Means of the Classical Nucleation Theory. Macromolecules. 28: 2236 - 2239.

[53] Tauer K (1998) Comment on the Development of Particle Surface Charge Density during Surfactant-Free Emulsion Polymerization with Ionic Initiators. Macromolecules. 31: 9390 - 9391.

[54] Tauer K , Kuhn I, Schellenberg C (1999) Tauer, K. A comprehensive experimental study of surfactant-free emulsion polymerization of styrene. Colloid Polym.Sci. 277: 607. – 626.

[55] Tauer K, Oz N (2004) Interfacial Energy Promotes Radical Heterophase Polymerization. Macromolecules. 37: 5880 - 5888.

[56] Tauer K , Schellenberg C, Zimmermann A (2000) Nucleation in heterophase polymerizations. Macromol. Symp. 150: 1-12.

[57] Kozempel S , Tauer K, Rother G (2005) Aqueous heterophase polymerization of styrene — a study by means of multi-angle laser light scattering. Polymer. 46: 1169 – 1179.

[58] Barrett K E (1975) Dispersion polymerization in organicmedia. Wiley-Interscience: Bristol.

[59] Lichti G, Hawkett B S, Gilbert R G, Napper D H, Sangster D F (1981) Styrene emulsion polymerization: particle-size distributions. J.Polym.Sci.Chem. 19: 925-938.

[60] Lichti G, Gilbert R G, Napper D H (1977) The growth of polymer colloids. J.Polym.Sci.Polym.Chem.Ed. 15: 1957-1971.

[61] Lichti G, Gilbert R G, Napper D H (1983) Mechanisms of latex particle formation and growth in the emulsion polymerization of styrene using the surfactant sodium dodecyl sulfate. J.Polym.Sci.Polym.Chem.Ed. 21: 269-291.

[62] Feeney P J, Napper D H, Gilbert R G (1984) Coagulative nucleation and particle size distributions in emulsion polymerization. Macromolecules. 17: 2520-2529.

[63] Feeney P J, Napper D H, Gilbert R G (1987) Surfactant-free emulsion polymerization: predictions of the coagulative nucleation theory.Macromolecules. 20: 2922-2930.

[64] Feeney P J, Napper D H, Gilbert R G (1985) Surfactant-free emulsion polymerization: predictions of the coagulative nucleation theory. J.Colloid Interface Sci. 107: 159-173.

[65] Deryagin B V, Churaev N V, Muller V M (1987) Surface Forces (in Russian). Moscow.Nauka.

[66] Adamson A W (1990) In Physical Chemistry of surfaces . J. Wileyand Sons. Inc. New York.

[67] Nielsen, A. E. Kinetics of Precipitation // Pergamon Press:Oxford. U.K.- 1964.

[68] Elias H G (1972) In Mdmmolekiile. Huthig & WepfVerlag:Basel,Heidelberg.

[69] Gunderl F, Wolf B A (1989) In Polymer Handbook. Wiley-Interscience. New York,.

[70] Barton A F M (1990) In CRC H of Polymer-Liquid Interaction Parameters and Solubility Parameters. CRCPRESS Inc. - Boca Raton.

[71] Hansen F K, Ofstad E B, Ugelstad J (1975) Emulsification of styrene with mixtures of anionic emulsifier and long chain fatty alkohols. Emulsion polymerization with initiation in monomer droplets. Theory and Practic of Emulsion Technology. Ed.by Smith London, Acad. Press. 13-25.

[72] El-Aasser M S, Lack C D, Chou Y T, Min T I, Vanderhoff J W, Fowkes F J (1984) Interfacial aspects of microemulsion polymers. Coll.S. 12: 79 - 97.

[73] El-Aasser M S, Miller C M (1997) Preparation of Latexes Using Microemulsions, in Polymeric Dispersions — Principles and Applications , J. M. Asua (Ed.). Kluwer, Dordrecht. 109–126.

[74] Gritskova I A, Sedakova L I, Muradyan G S, Pravednikov A N (1978) About topochemistry of emulsion polymerization (in Russian). DAN SSSR. 238: 607-610.

[75] Pravednikov A N, Gritskova I A, Muradyan G S, Margolin D N, Vassilev L A, Sedakova L I (1981) A new method of latex dispersion investigation (in Russian). Kolloid.J. 41: 595 - 597.

[76] Pravednikov A N, Simakova G A, Gritskova I A, Prokopov N I (1985) The formation of surfactant at the interface in emulsion polymerization (in Russian). Kolloid.J. 47: 192 - 194.

[77] Simakova G A, Kaminsky V A, Gritskova I A, Pravednikov A N (1984) Microemulsification in emulsion polymerization (in Russian). DAN SSSR. 276: 151 - 153.

[78] Gritskova I A (1979) Emulsion polymerization of monomers slightly soluble in water (in Russian). Dr. Sc. Thesis. Moscow. MITHT 304 C.

[79] Gritskova I, Marchenko S, Zaitsev S (2002) Polymer surfactant interfacial layer of polystyrene particles modeling by monolayer techniques. Coll.S. 198-200: 501-508.

[80] Hinze J O (1955) Fundamentals of the hydrodynamic mechanism of splitting in dispersion processes. Amer.Inst.Chem. Eng. J. 1: 289-295.

[81] Micellization, Solubilization, and Microemulsions/ Ed. by K.L. Mittal. N.Y.; L.: Plenum Press, 1977. 597.

[82] Yentov V M, Kaminsky V A, Lapiga Ye Ya (1976) Calculation of coalescence rate of emulsion in turbulent flow (in Russian). Izv. AN SSSR. Ser.Mech.Zhidk.Gas. 3: 47-55.

[83] Hicke H F, Rehark J (1976) On the formation of water/oil microemulsion. Helv.Chim.Acta. 59: 2883-2891.

[84] Rose S, Nishioka G (1975) Foaminees of binary and ternary solutions. J.Phys.Chem. 79: 1561-1565.

[85] Gierbacia W, Rosano H L (1973) Microemulsion formation and stabilization. J. Colloid Interface Sci. n 44: 242-248.

[86] Smith G D, Donelan C R, Barden R E (1977) Oil-continuous microemulsions composed of hexane, water and 2-propanol. J. Colloid Interface Sci. 60: 488-496.

[87] Bourrel M, Grasia A, Schecher R S (1979) The relation of emulsion stability to phase behavior and interfacial tension of surfactant systems. J. Colloid Interface Sci. 72: 161-163.

[88] Hall A C (1980) Interfacial tension and phase behavior in systems of petroleum sulfonate n-alkane. Coll.S. 1: 209-228.

[89] Rebinder P A (1946) About theory of emulsions (in Russian). Koll.J. 8: 157-174.

[90] Rebinder P A, Taubman A B (1961) Notes on the question about aggregative stability of disperse systems (in Russian). Koll.J. 23: 359-361.

[91] Simakova G A, Chalykh A Ye, Vasenin R M, Nikitina S A, Taubman A B (1969) Investigation of nonionic surfactants in water and xylene (in Russian). Koll.J. 31: 893-896.

[92] Chalykh A Ye (1987) Diffusion in Polymer Systems (in Russian). Moscow:Himiya. 312.

[93] Taubman A B, Nikitina S A (1962) Structural mechanical properties of surfactant surface layers and stabilization mechanism of concentrated emulsions (in Russian). Koll.J. 24: 633-635.

[94] Taubman A B, Nikitina S A (1965) Role of quasi-spontaneous emulsification in stabilation of emulsions (in Russian). Koll.J. 27: 291 - 295.

[95] Dudukin V V, Medvedev S S, Gritskova I A (1967) Styrene polymerization in the presence of nonionic surfactant polyoxyethylene polypropylene glycol (in Russian). DAN SSSR. 172: 1125 - 1127.

[96] Ishkov A, Cherkasov V, Prokopov N, Gritskova I (1996) Synthesis of polymer suspensions for immuno-chemical studies. J.Appl.Polym.Sci. 61: 1465-1471

[97] Gritskova I, Adebayu G, Krasheninnikova I, Kaminsky V (1998) The synthesis of polymer suspensions with narrow size distribution for immunochemistry. Coll.Polym.Sci. 276: 1068-1077.

[98] Lovell P A, El - Aasser M S (Eds.) (1997) Emulsion Polymerization and Emulsion Polymers. John Wiley & Sons , West Sussex , 1997 .

[99] Haward R N (1949) Polymerization in a system of discrete particles. J.Polym.Sci. 4: 273 – 287.

[100] Zhachenkov S V, Litvinenko G I, Kaminsky V A, Ilmenev P Ye, Pavlov A V, Guryanova V V, Gritskova I A, Pravednikov A N (1985) Particularities of styrene emulsion polymerization with various methods of initial emulsion preparation (in Russian). Vysokomol.Soed. 27: 1249 - 1253.

[101] Kaminsky V A, Gritskova I A (1996) Interface phenomena and formation of particles in emulsion polymerization. J.Phys.Khim. 70: 1516-1520.

[102] Gan L M, Lee K C, Chew C H, Ng S C (1995) Effects of Surfactant Concentration on Polymerizations of Methyl Methacrylate and Styrene in Emulsions and Microemulsions. Langmuir. 11: 449 - 454.

[103] Prokopov N I, Gritskova I A, Kiryutina O P, Khaddazh M, Tauer K, Kozempel S (2010) The mechanism of surfactant-free emulsion polymerization of styrene. Polym.Sci. Ser. B. 52: 339-345.

[104] Khaddazh M, Litvinenko G I, Gritskova I A (2011) A Theoretical Study of the Emulsion Polymerization of Styrene: The Effect of the Initial Dispersion of the System on the Polymerization Rate and Size Distribution of Polymer–Monomer Particles. Polym.Sci. Ser. B. 53: 209-222.

[105] Khaddazh M, Litvinenko G I, Gritskova I A (2011) A Theoretical Study of the Emulsion Polymerization of Styrene: The Effect of the Initial Dispersion of the System on the molecular-mass distribution of polystyrene. Polym.Sci. Ser. B. 53: 283-291.

[106] Gritskova I A, Zhachenkov S V, Tsar'kova M S, Levachev S M, Simakova G A, Khaddazh M, Prokopov N I (2011) Styrene polymerization in the presence of different initiators and properties of polymer suspensions. Polym.Sci. Ser. B. 53: 568-577.

[107] Khaddazh M, Zhachenkov S V, Gritskova I A (2011) The influence of method of preparation on kinetic characteristics of styrene emulsion polymerization (in Russian). Vestnik MITHT. 6: 97-101.

[108] Zhachenkov S V, Gritskova I A, Levachev S M, Khaddazh M, (2011) Particularities of styrene heterogeneous polymerization under statistic conditions in the presence of emulsifiers and co-surfactants. Vestnik MITHT. 6: 85-88.

[109] Oganesyan A A, Melkonyan L G, Gritskova I A, Bagdasaryan R V (1971) Dependence of rate of initiator-free chloroprene emulsion polymerization on the concentration of emulsifier (in Russian). Armenian Khim.J. 3: 284-288.

[110] Oganesyan A A, Melkonyan L G, Gritskova I A, Bagdasaryan R V (1971) About mechanism and Topochemical particularities of chloroprene emulsion polymerization (in Russian). Armenian Khim.J. 3: 660-667.

[111] Gilbert R G, Napper D H (1983) The direct determination of kinetic parameters in emulsion polymerization system. J.Macromol.Sci.Rev.Macromol.Chem.Phys. 23: 127-186.

[112] Candau F (1987) in Encyclopedia of Polymer Science and Engineering. Mark F, Bikales N M, Overberger C G, Mengers G (Eds.). Wiley Interscience New York. 718-724 .

[113] Chern C S (2002) in Encyclopedia of Polymer Science and Technology.. Kroschwitz J I (Ed.), John Wiley & Sons. New York.

[114] Guo J S, Sudol E D, Vanderhoff J W, El Aasser M S (1992) Kinetics and Mechanism of Styrene Microemulsion Polymerization /in Polymer Latexes: Preparation, Characterization, and Applications, Daniels E S, Sudol E D and El-Aasser M S (Editors), ACS Symposium Series. 492: 99-113.

[115] Tang P L, Sudol E D, Adams M E, Silebi C A, El Aasser M S (1992) Miniemulsion Polymerization / P.L. Tang, E.D. Sudol, M.S. El Aasser /in Polymer Latexes: Preparation, Characterization, and Applications, Daniels E S, Sudol E D and El-Aasser M S (Editors), ACS Symposium Series. 492: 72-98.

[116] Guo J S, El Aasser M S, Vanderhoff J W (1989) Microemulsion Polymerization of Styrene. J.Polym.Sci.:Part A: Polym.Chem. 27: 691-710.

[117] Hansen F K, Ugelstad J (1978) Particle nucleation in emulsion polymerization. II. Nucleation in Emul-sifier-free Systems Investigated by Seed Polymeriza-tion. J.Polym.Sci.Polym.Chem. 16: 3033-3046.

[118] Hansen F K, Ugelstad J (1978) Particle nucleation in emulsion polymerization. III. Investigation of Nucleation in Systems with Anionic Emul-sifier by Seeded and Unseeded Polymer-ization. J.Polym.Sci.Polym.Chem. 16: 3047-3068.

[119] Song Z, Poehlein G W (1989) Particle nucleation in emulsifier-free aqueous-phase polymerization : Stage 1. J. Coll.Interf.Sci. 78: 486-500.

[120] Song Z, Poehlein G W (1990) Kinetics of emulsifier free emulsion polymerization of styrene. J.Polym.Sci. 28: 2359-2392.

[121] Chern C S (2008) Principles and applications of emulsion polymerization. John Wiley & Sons, Inc., Hoboken, New Jersey. 252.

[122] Gao J., Pendilis A (2002) Mathematical modeling and computer simulator/database for emulsion polymerizations. Prog. Polym.Sci. 27: 403-535.

[123] Fitch R M, Tsai C H (1971) Particle formation in polymer colloids. III. Prediction of the number of particles by a homogeneous nucleation theory. In: Fitch RM, editor. Polymer colloids. New York: Plenum Press, 73-102

[124] Fitch R M, Tsai C H (1971) Homogeneous nucleation of polymer colloids. IV. The role of soluble oligomeric radicals. In: Fitch R M, editor. Polymer colloids. New York: Plenum Press. 103-116.

[125] Maxwell I A, Morrisson B R, Napper D H, Gilber R G (1991) Entry of free radicals into latex particles in emulsion polymerization. Macromolecules.;24:1629.

[126] Dougherty E P (1986) The SCOPE dynamic model for emulsion polymerization I. Theory. J.Appl.Polym.Sci. 32: 3051 -3078.

[127] Penlidis A, MacGregor J F, Hamielec A E. (1986) Mathematical modeling of emulsion polymerization reactors: a population balance approach and its applications. ACS Symp Ser. 313: 219—240.

[128] Yeliseyeva V I, Zuikov AV (1982) Interfacial phenomena in of polar monomers. In:Priima I, GardonJL, editors. Emulsion polymerization. ACS Symp Ser. 24: 62-81

[129] Penboss I A, Napper D H,. Gilbert R G (1983) Styrene emulsion polymerization. J.Chem.Soc.Faraday Trans. 79: 1257-1271.

[130] Bataille P, Gonzalez A (1984) Emulsion polymerization of styrene. III. Effect of Ti(III) and Cl(I) on the polymerization of styrene initiated by potassium persulfate. J.Polym.Sci.Chem.Ed. 22: I409-1417.

[131] Penlidis, A. Mathematical modeling of emulsion polymerization reactors: a population balance approach and its applications / A. Penlidis, J.F. MacGregor, A.E. Hamielec // ACS Symp. Ser. – 1986. – 313. – P. 219-240.

[132] Sudol E D, El-Aasser M S, Vanderhoff J W (1986) Kinetics of successive seeding of monodisperse polystyrene latexes. I. Initiation via potassium persulfate. J.Polym.Sci.Chem.Ed. 24: 3499-3513.

[133] Sudol E D, El-Aasser M S, Vanderhoff J W (1986) Kinetics of successive seeding of monodisperse polystyrene latexes. II. Azo initiators with and without inhibitors. J.Polym.Sci.Chem.Ed. 24: 3515-3527.

[134] Giannetti E (1993) Nucleation mechanisms and particle size distributions of polymer colloids. AIChE J. 39: 1210—1227.

[135] James Jr. H L, Piirma I (1975) Molecular weight development in styrene and methyl methacrylate emulsion polymerization. Polym.Prepr. 16: 198-204.

[136] Piirma I, Kamath V R, Morton M (1975) The kinetics of styrene emulsion polymerization. Polym.Prepr. 16: 187-191.

[137] Miller C M, Clay P A, Gilbert R G, El-Aasser M S (1997) An experimental investigation on the evolution of the molecular weight distribution in styrene emulsion polymerization. J.Polym.Sci.Chem.Ed. 35: 989-1006.

[138] Said Z F M. (1991) Molecular-weight distributions in the thermally initiated emulsion polymerization. Makromol.Chem. 192: 405-414

[139] Salazar A, Gugliotta L M, Vega J R, Meira G R (1998) Molecular weight control in a starved emulsion polymerization of styrene. Ind.Eng.Chem.Res. 37: 3582-3591.

[140] Morbidclli M, Storti G, Carra S (1983) Role of micellar equilibria on modeling of batch emulsion polymerization reactors. J.Appl.Polym.Sci. 28: 901-919.

[141] Bataille F., Bataille P, Fortin R (1988) Emulsion polymerization of styrene. IV. Effect of Co(II), Ni(II), and Pb(ll) on the polymerization of styrene initiated by potassium persulfate. J.Polym.Sci.Chem.Ed. 26: 1471-1477.

[142] Thickett S C, Gilbert R G (2006) Mechanism of radical entry in electrosterically stabilized emulsion polymerization systems. Macromolecules. 39: 6495.

[143] Kusters J M H, Napper D H, Gilbert R G, German A L (1992) Kinetics of particle growth in emulsion polymerization systems with surface-active initiators. Macromolecules. 25: 7043-7050.

[144] Anderson C D, Sudol E D, El-Aasser M S (2003) Elucidation of the miniemulsion stabilization mechanism and polymerization kinetics. J.Appl.Polym.Sci. 90: 3987-3993.

[145] Min KW, Ray W H (1974) On the mathematical modeling of emulsion polymerization reactors. J.Macromol.Sci,Rev.Macromol. C11: 177-255.