

On the Mechanism of Latex Particles Formation in Polymerization in Heterogeneous Monomer-Water System

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Abstract: Investigations show that in monomer water heterogeneous systems polymerization, located in the interface, can disperse the system. Following polymerization in the density gradient field it is shown that in such systems latex particles are nucleated from monomer microdroplets, containing a certain amount of polymer molecules. It could be considered that, independently of the nature of the monomer itself, polymerization in monomer water statistic heterogeneous systems modulate emulsion polymerization process.

Key words: Polymerization, static system, density gradient, turbidity, emulsion.

1. Introduction

EP (emulsion polymerization) in heterogeneous monomer water systems is the main method of synthesis of latices. A classical example is EP in micellar styrene water emulsion where polymerization is initiated efficiently by a water soluble initiator [1, 2]. In the initial stage of EP micelles begin to disappear [3]. At the same time monomer microdroplets begin to appear in the system. These microdroplets transfer to particles containing a polymer molecule and the growing radical. These droplets are then called PMP (polymer monomer particles). After 5%-10% of monomer conversion micellar emulsion is transformed to a dispersion consisting of two sets of particles of the monomer droplets and PMP, the diameter of which reaches 20-50 nm. After the disappearance of the micelles PMP number does not change, and their diameter will grow steadily and at 60% monomer conversion it reaches around 100 nm.

Schematically micellar monomer water emulsion

before and after the disappearance of the micelles is shown in Figs. 1a and 1b.

The fact of the disappearance of the micelles and the constancy of PMP after their disappearance become the basis for the creation of micellar model of EP [3], according to which the PMP originate in the aqueous phase when primary or oligomeric radicals falling into the micelles.

Other mechanisms of PMP initiation are also suggested by chemists. According to them polymer molecules are formed in the aqueous phase as nuclei of the new phase [4-6]. Further, the polymer molecules associated and dissolving monomer converted into PMP. Such a homogeneous nucleation mechanism of particulate matter is considered to be more likely in the EP polar monomers (for example, vinyl acetate). Disappearance of micelles in this case is explained by adsorption of molecules of emulsifier from the aqueous phase to the surface of dispersed particles. However, it is easy to show that the growth of the chain polymerization of styrene in the aqueous phase is up to a maximum of 3 or 4 monomer units. These surface active oligomers with sulfate ion end groups are accumulated in the water phase, and that

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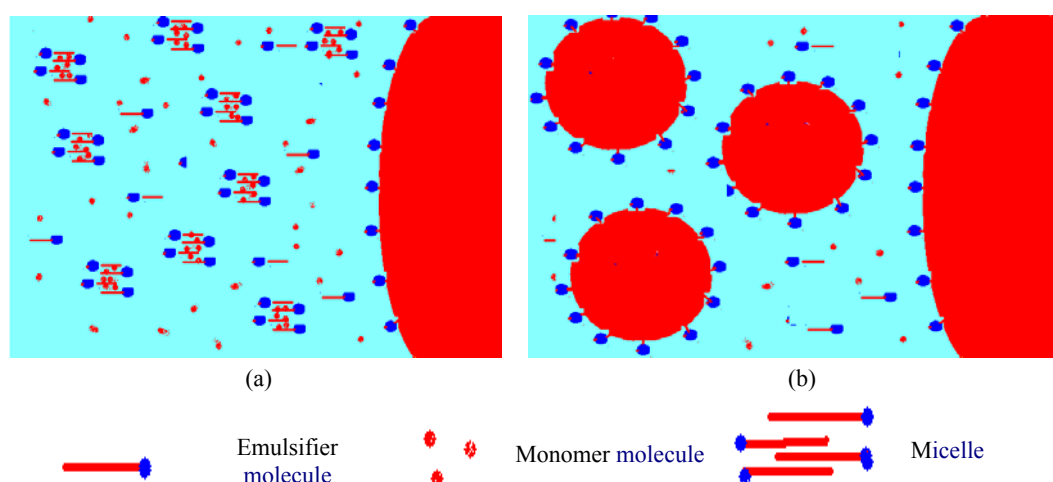


Fig. 1 Micellar emulsion before the polymerization starts (a) and after 5-10% of monomer conversion (b).

soon lead to the emergence of new micelles, rather than the disappearance of the existing ones.

According to the theory of micelle formation micelles in water appear when the concentration of dissolved molecular emulsifier is what is called the CMC (critical micelle concentration). At CMC chemical potentials of molecules of the emulsifier in water μ_w and micelles μ_m microns are aligned and the system equilibrium is established:

$$\mu_w = \mu_m \quad (1)$$

Thermodynamic prerequisite for the disappearance of micelles in the emulsion is to decrease the chemical potential of the molecules of the emulsifier in water:

$$\mu_w < \mu_m \quad (2)$$

Lowering the concentration of emulsifier in water and disturbance of equilibrium conditions (1) can occur in the system when a new interface is formed and when the adsorption of the emulsifier from the aqueous phase on that surface takes place.

Both micellar and homogeneous models do not take into account the heterogeneity of EP system and require a sophisticated phase boundary, which has bulk properties. Polymerization in this zone of the heterogeneous system may significantly influence both the kinetics of EP, and the process of dispersed particles forming.

Based on the theory of the formation of a new phase

and the theory of heterogeneous systems the authors can conclude that the polymerization reaction at the interface layer is able to disperse large droplets of the monomer (with diameters of tens of micrometers). According to the theory of heterogeneous systems, new surface interface can be created by elastic deformation of the interface, transferring a certain amount of substances from one phase to another and creating at the interface protuberances or depressions. New surface can also be obtained by dividing each of the phases into small particles. If both phases are liquid ones, the minimum unit of work to create a surface with all the above methods is the same, it is determined only by the temperature and the chemical potential of the contacting phases. It follows that if the released heat of polymerization is able to transfer a certain amount of the monomer from the interface to the volume of water, it can be assumed that the polymerization reaction can also deform the interface and fragment the system. Fragmentation of the system will inevitably lead to the disappearance of the micelles.

Previously, by numerical calculations the authors have shown that the heat of polymerization is more than sufficient for the nucleation of the monomer in water microdroplets, by creating supersaturation of the monomer in the boundary layer of the aqueous

phase [7]. In order to assess the driving forces in the calculation used the value of the surface tension (γ) at the interface between the monomer water. For the styrene-water system:

$$\gamma = 33 \text{ mJ/m}^2 \quad (3)$$

The area occupied by the molecule at the interface is equal to 1/4 of the surface [8], therefore, the surface free energy per molecule of styrene is equal to:

$$E = \gamma / 4\pi r^2 \approx 4 \times 10^{-18} \text{ mJ} = 4 \times 10^{-14} \text{ erg} \quad (4)$$

where, r —radius of styrene molecules $\approx 2 \times 10^{-10} \text{ m}$.

For the styrene molecule to leave the interface surface and to diffuse into the aqueous phase an energy, three times the $4 \times 10^{-14} \text{ erg}$ (its remaining portion is 3/4 the area associated with the styrene molecule adjacent molecules in the bulk monomer phase) is required. When radical polymerization evolved heat of reaction is approximately equal to 20 kcal/mol, or about $1.4 \times 10^{-12} \text{ erg}$ per one molecule. Thus, in the emulsion at each occurrence of polymerization active centre at the monomer-water interface, about 10 monomer molecules leave the surface and can get into saturated monomer aqueous phase. In water non-polar hydrocarbons molecules tend to the association and supersaturation is necessary for the emergence of sustainable small droplets. Therefore, the polymerization reaction at the interface will certainly lead to the ingress of new monomer molecules in water and the formation of stable microdroplets.

The possible formation of monomer microdroplets in EP due to the monomer-water interfacial polymerization can be concluded flows from the equation relating the interfacial surface tension with temperature:

$$\gamma = \gamma_0(1-T/T_c)^n \quad (5)$$

where, n —constant depending on the nature of the substance (for organic liquids $n \approx 1.22$, T —the critical temperature of the liquid in which there is a mixture of phases). Therefore, in each act of the reaction heat release in certain areas of the phase boundary γ strongly decreases partial mixing of fluids. Obviously,

the presence of surfactant in water, this process will be irreversible, leading to the formation of stable monomer microdroplets.

2. Experimental Sections and Discussion

To confirm experimentally that the initial stage of formation PMP can occur at the monomer-water interface, this process must be investigated under conditions when monomer polymerization in the aqueous phase is not accompanied by polymer allocation or precepitation. The authors have also to exclude, where possible, other factors causing dispersion of monomer in water, primarily mechanical stirring.

If on the aqueous solution of potassium persulfate in the tube layer carefully styrene and then thermostat the system, after a certain time, the authors can watch the turbidity of the system, which subsequently converted into a stable latex [7, 9]. Such a system is essentially a model of monomer droplets in the aqueous phase of the monomer-water emulsion.

Considering the fact that the dependence of interfacial surface energy and solubility in water of the monomer particle radius affected only at very low values of the latter, research results obtained in this system can be extended to emulsion systems where the monomer is in a highly dispersed state.

The static monomer-water system allows to be observed and studied the physical and chemical processes occurring as at the interface, as well as in separate bulk phases.

Fig. 2 shows a schematic latex formation in a static system styrene-water in the absence of an emulsifier.

To determine the nature of the system introduced in the disperse particles, it is taken into account to the fact that after the lamination the aqueous monomer phase, the diffusion process begins in the system, the density of the aqueous phase drops upwards. The diffusion rate of dispersed particles is much less than the rate of diffusion of the molecules. A density gradient along the height of the aqueous phase and

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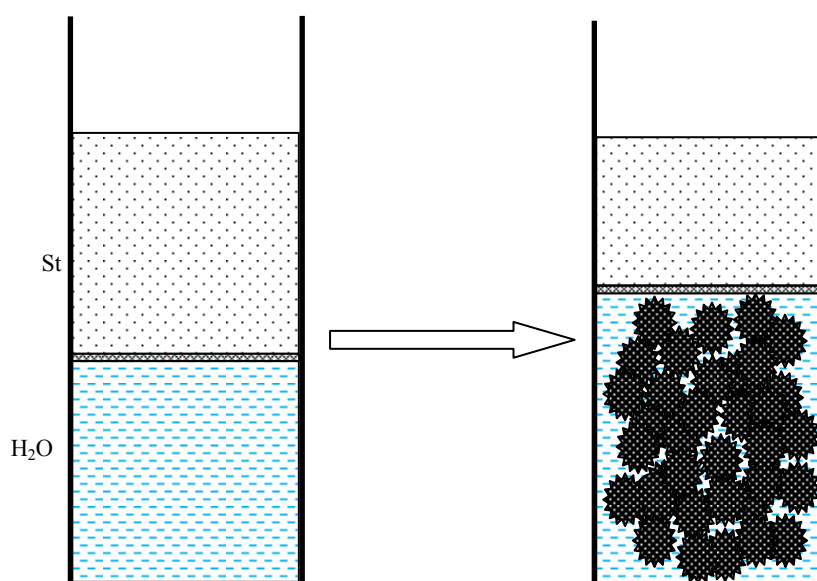


Fig. 2 Schematic representation of the conversion of the monomer-water static system in the latex.

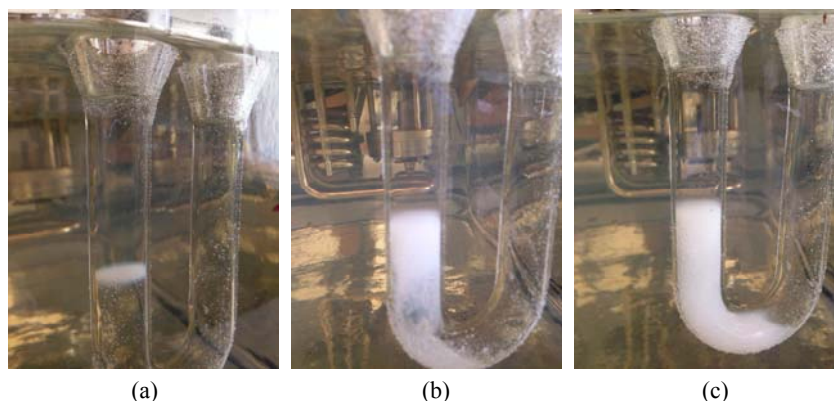


Fig. 3 Topological picture of turbidity of the aqueous phase in the solution of vinyl acetate in ethanol—0.4% aqueous solution of potassium persulfate in different time intervals of observation (a-30 min, b-90 min, c-120 min).

accumulation of particles can be localized in the zone of the aqueous phase below of which the medium density is higher than the density of dispersed particles. In this way, by measuring the density of the aqueous phase the authors can estimate the density of dispersed particles. To carry out such experiments styrene and vinyl acetate were used as monomers. The density gradient is created by introducing liquid alcohol (methanol, ethanol) to the monomer phase.

Polymerization was conducted in a thermostatic tube. Temperature of experiments was 60 °C. Static monomer system—0.4% aqueous solution of potassium persulfate was set by gently layering an aqueous monomer solution in ethanol. Volumes of

monomer, ethanol and aqueous phases were 2, 5 and 30 mL, respectively.

The polymerization of vinyl acetate was carried out in U-shaped flasks, which made it possible to take samples for analysis from the aqueous phase, without disturbing the stationary mass transfer process and particle formation at the interface.

Topological picture of turbidity of the aqueous phase is shown in Fig. 3. The same pattern was also obtained in the styrene-water system [10]. Fig. 3 clearly shows the dynamics of the process: the dispersed particles, created during the polymerization process are initially localized in a narrow zone of water phase near the monomer-water interface, then

gradually sink deep into the aqueous phase.

Density of different zones of the aqueous phase at the time of occurrence of turbidity is illustrated in Fig. 4. Comparing densities in different zones of the aqueous phase with the values of the density of polystyrene and polyvinyl acetate (1.06 and 1.15 g/cm^3 , respectively), the authors can notice that in the initial stages of formation the density of the dispersed particles is much less than the density of polymers, and, therefore, they are the monomer microdroplets containing a certain amount of

polymeric molecules.

Topology turbidity of the aqueous phase in the density gradient is reproduced in a three-phase static system monomer-water-crystal of potassium sulfate or persulfate. This experiment schematically depicted in Fig. 5.

It becomes obvious that the dispersion of the monomer-water heterogeneous system under the action of the elementary acts of polymerization occurring at the interface is a specificity of the heterophase radical polymerization.

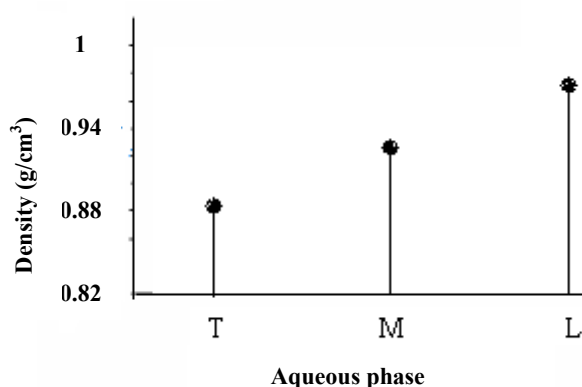


Fig. 4 Density different zones of the aqueous phase in a static system monomer (vinyl acetate, styrene)—aqueous solution of potassium persulfate at the time of occurrence of dispersed particles (T-top, M-mean L-lower zone of the aqueous phase).

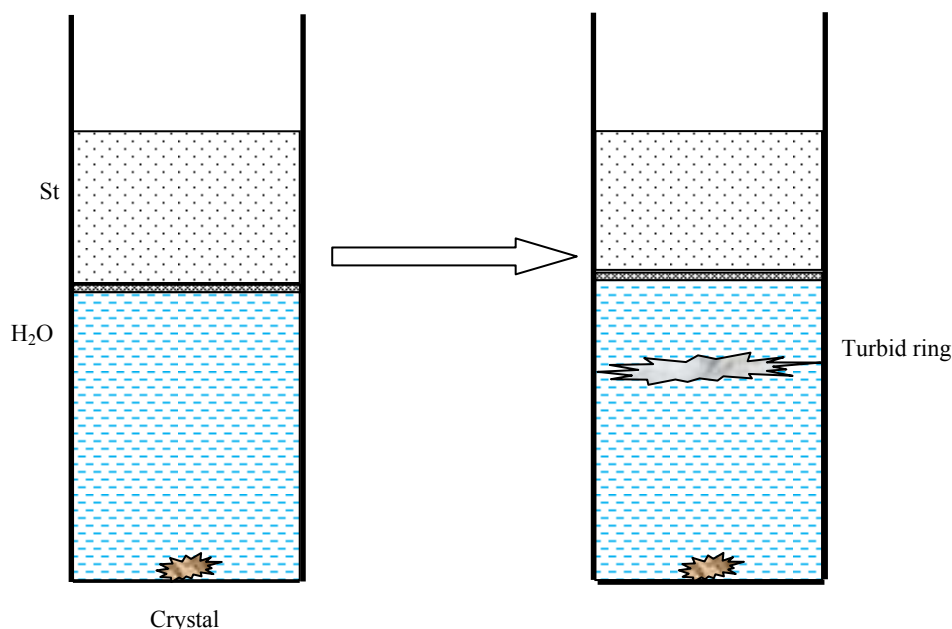


Fig. 5 Topology turbidity due to the polymerization of styrene in the three phase system monomer-water-crystal of potassium persulfate.

3. Conclusions

One of the possible mechanisms for the latex particles generation in the emulsion polymerization is represented as a process of dispersing monomer (without the dispersing agents) and nucleation of polymer monomer particles which takes place at the monomer–water interface in the boundary zone of the aqueous phase. Energy to produce work needed to disperse the monomer comes from the heat of elementary acts in polymerization occurring at the interface of the monomer droplet-water.

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