Competitive Topological Models of Emulsion Polymerization

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Abstract

The main components of the emulsion polymerization (EP) are the monomer, water, emulsifier and initiator. Usually molecules of the emulsifier do not participate in the elementary acts of polymerization. The final product of EP is polymer particles in water (latex). The performance properties of latexes are determined by the parameters of the colloidal system and the physic mechanical parameters of the polymer material. These parameters, in addition to the nature of the monomer, are determined by the mechanism of nucleation and formation of dispersed particles of polymers. This article discusses the existing models for the generation of latex particles, which are proposed on the basis of topological studies of EP by various authors.

Keywords: Polymerization; Emulsion; Micelles; Latex

Abbreviations: EP: Emulsion Polymerization; PMP: Polymer-Monomer Particles; CMC: Critical Micelle Concentration.

Introduction

Harkins topological model

Harkins investigated the topology of the generation and formation of latex particles in monomer-water micellar emulsions [1,2]. According to Harkins [3], micelles swollen with a monomer in a micellar emulsion begin to disappear in the initial stage of polymerization, and monomeric micro droplets containing molecules of the polymer and a growing radical, appear in the aqueous phase. Such liquid micro particles are called polymer-monomer particles (PMP). After 5-10% conversion, the micellar emulsion turns into a dispersion consisting of two sets of particles: large monomer droplets with diameter about 1μm and PMPs.

The fact of the disappearance of the micelles is a basic aspect for creating micellar model of EP, according to which the PMPs are nucleated when an active center of polymerization in micelles is formed. According to this model, the monomer droplets are not involved in the polymerization reactions, as evidenced by the EP flowing in soap solutions with no monomer droplets in the system but in contact with monomer vapor [1]. It is assumed that, depending on the solubility of the monomer in water, monomer radical's nucleation can begin in water or directly in the micelles. The formation of PMPs completes at 2-15% conversion of the monomer, and then polymerization occurs only in the PMPs, the number of which is constant, and their size increases continuously. As a result, the latex with particle sizes in the range of -200 nm is obtained. After the disappearance of micelles, polymerization proceeds at a constant rate until about 60% monomer conversion, and this period is considered to be the stationary period of EP.

The model of homogeneous nucleation

According to this model, in the initial stage of EP initiation of monomer molecules takes place in the aqueous phase and the oligomers formed are then associated in coils [3-

9]. According to Hansen FK & Ugelstad J [9], a homogeneous latex particle generation mechanism is supported in emulsifiers' free monomer-water systems. The absence of micelles in primary monomer-water system allowed the authors Hansen FK & Ugelstad J [9] to identify the formation of latex particles with a homogeneous nucleation process that takes place in perfectly pure supersaturated solutions. The process of homogeneous nucleation in pure salt solutions is presented as a chemical polymerization reaction in which the elementary act of polymer chain accession of monomer molecules is reversible [10,11]. A similar scheme describing the nucleation of particles during EP, but without the reversibility of elementary acts, is presented in [9].

The authors Hansen FK & Ugelstad J [9] assume that the sulfate ion-radical ($SO_4^{-\bullet}$) having attached to a certain number of molecules of styrene (up to 10) precipitates in water as a nucleus of the new phase. However, this assumption is not consistent with the fundamental concepts of new phase formation, according to which the minimum radius of the nucleus, in which it can exist and continue to grow in a supersaturated solution, is determined by the following equation:

$$\Delta\mu = 2v\gamma/r \quad (1)$$

Where γ - specific free surface energy of the interphase, v-specific volume of the molecules in the bud, $\Delta\mu$ - difference between the chemical potentials of the molecules in the mother medium and in the bud.

For a growing radical, the equation 1 is not applicable and the possibility of the nucleation of the polymer phase is determined by the state of the oligomers formed in the medium. Oligomers with one sulfate ionic group and a few monomeric units, most likely differ in their surface-active properties, and ascribing to an oligomer consisting 5 monomer units the characteristics of a nucleation seed, and the status of molecular solute for that with 4 monomer units, one is considered to be extremely doubtful. The modern theory of nucleation [11] allows describing the surface and bulking phase concepts for associates consisting several molecules, besides, it proves that the packing density of the molecules in the associate corresponds to their density in the macro particle.

Since polymerization is thermodynamically favorable process, $\Delta\mu$ is positive at any monomer concentration in water. But in this case the precipitation of the polymer phase in the water phase as a result of growth of one active center can take place when the kinetics of radical reactions allows chain propagation until the transformation of the macroradical into a coil. In addition,

it is necessary to take into account the fact that the polymer is soluble in its monomer, therefore in the course of growth, the macro radical loses its water solubility, becoming soluble in the monomer phase, and thus the precipitation of the growing radical in the aqueous phase seems to be equivalent to its dissolving in monomer droplets. Both micellar and homogeneous models of EP do not consider the existence of a highly developed boundary monomer layer near the interface. However, in highly dispersed water-monomer systems processes that occur at the interface can significantly affect the kinetics of chemical reactions and the formation mechanism of PMP. These issues are to be discussed in the following chapters.

Topology of PMP generation in monomer-water static system

If in thermostatic tubes, when styrene is layered accurately at the top of an aqueous solution of $K_2S_2O_4$, one can observe, under static conditions, at 50° C and after about 1.5-2 hours, the appearance of turbidity in an aqueous phase. As a result, the aqueous phase is converted into stable latex (Figure 1).
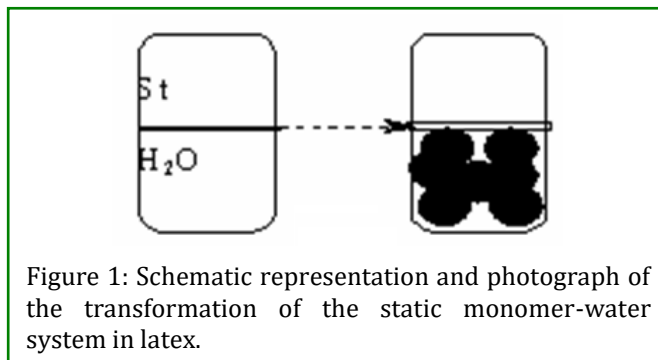

Figure 1: Schematic representation and photograph of the transformation of the static monomer-water system in latex.

Preliminarily, it could be assumed that in a static system styrene diffuses into the aqueous phase and the formation of particles takes place in this phase by homogeneous nucleation mechanism. By carrying out direct observation of generation of particles in separate zones of styrene-water system it has been suggested that by increasing the density of the aqueous phase a longer extending of the residence time of the particles in the zone of their generation can be achieved [12-14]. One way to increase aqueous phase density, without increasing the number of components in the system, is to increase the concentration of potassium per sulfate in water, which reduces the probability of generation of particles in the water phase volume (that aspect reduces statistical ratio of long growing radicals in water). In the tube, where the per sulfate concentration was 2%, the specific turbidity pattern of the aqueous phase was observed [13]. First turbidity has appeared as a narrow boundary layer from

the aqueous phase side at the interface, and then, intensifies within the entire front and extending downwards (Figure 2).
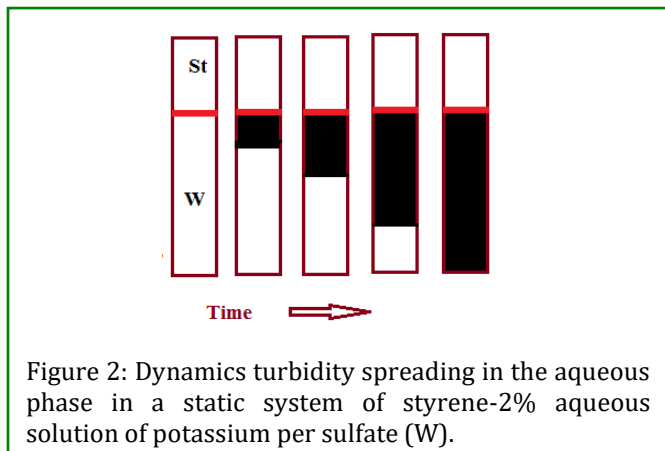

Figure 2: Dynamics turbidity spreading in the aqueous phase in a static system of styrene-2% aqueous solution of potassium per sulfate (W).

The density of 2% aqueous solution of $K_2S_2O_8$ at 50° C is 1.014 g/cm^3, which is much less than the density of polystyrene (1.05 g/cm^3), gives grounds to assume that dispersed particles are generated in the form of a PMP. In another series of experiments methanol was dissolved in styrene to create a significant density gradient in the aqueous phase [14]. The dynamics of turbidity of the aqueous phase was photographed. The results are shown in Figure 3. These pictures show clearly the dynamics of the process of accumulation of particles in the system: first, they are localized in a narrow zone of water phase near the monomer-water interface, and then they gradually plunge into the deep of the aqueous phase. Similar images were obtained during polymerization of vinyl acetate (Figure 4).

Figure 3: Dynamics of latex formation in static system styrene - aqueous solution of potassium per sulfate in the presence of methanol.

Figure 4: Dynamics of latex in static system vinyl acetate - aqueous solution of potassium persulfate in the presence of methanol.

Summarizing the results of the described experiments we can come into conclusion that the monomer-water interface is one of the particle nucleation areas in the polymerization in static heterogeneous systems. The possibility of formation of micro droplets due to monomer polymerization at the water-monomer interface follows

from dependence of interfacial tension γ on temperature [15].

$$\gamma = \gamma_0 (1 - T/T_c)^n \quad (2)$$

Where n - constant depending on the nature of the compound (for organic liquids n=11/9) [15],
γ0-initial interfacial tension,

Tc-critical temperature of the liquid (when T=Tc a mixing of phases is observed).

As follows from 2, temperature increase leads to a significant decrease of γ. Thus, at each act of reaction due to heat release the partial mixing of liquids takes place at certain areas in the interface. In the presence of stabilizing substances this process will be irrevocable and will lead to the formation of micro droplets of monomer.

According to the theory of heterogeneous systems, new surface interface can be created by elastic deformation of the interface, transfer 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. This conclusion was confirmed by an experiment conducted in [16]. The authors used the technology of thermal spectroscopic imaging, which was used to measure the vibrational spectroscopy and heat of radical polymerization of styrene in a microfluidic. They measured the heat release and diffusion of styrene molecules at the interface of two liquids and observed the appearance of concentration flows in the system.

The heat of reaction released during radical polymerization is approximately 1.4 • 10–12 erg / molecule. In the monomer-water system, this heat is sufficient for the monomer molecules to leave the interface and enter the aqueous phase. In water, non-polar hydrocarbon molecules tend to be associated, and a little oversaturation is required to form stable microdroplets. The origin of the micro droplets of the monomer in the aqueous phase leads to the disappearance of micelles in micellar emulsions. According to the thermodynamic theory of micelle formation, micelles in water occur when the concentration of dissolved emulsifier molecules is higher than the critical micelle concentration (CMC). At CMC chemical potentials of molecules of emulsifier in water μ_w and micelles μ_m are aligned, and the system equilibrium is established:

$$\mu_w = \mu_m \text{ (3)}$$

A necessary condition for the disappearance of micelles is the decrease in the concentration of emulsifier in water and the violation of the equilibrium condition 3. Obviously, this condition will arise when the emulsifier molecules are adsorbed from the aqueous phase on the surfaces of incipient dispersed particles.

Conclusion

Formation of PMPs can proceed by three different mechanisms during emulsion polymerization. It is obvious that the probability of each of them depends on the nature of the monomer and the composition of the emulsion. We can choose such components and polymerization conditions under which PMPs will be generated only at the interface of the monomer-water phase and in order to synthesize latexes with narrow particle distribution. Such latexes are used in different areas of high technology and are very valuable.

Figure 5 shows latexes that were synthesized in a static system of styrene - water and chloroprene - water without the use of emulsifiers.

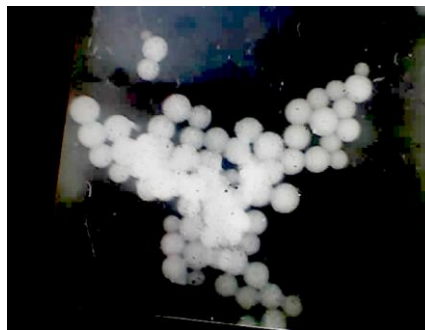Figure 5.1: Electron photographs of polychloroprene latex.

Figure 5.2: Electron microscopic photograph of polystyrene latex.

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