

# On Problems of Synthesis of Mono-dispersed Latexes in the Static Heterogeneous Monomer-Water System

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## Abstract

Static mode of polymerization in a heterogeneous monomer-water system can be considered as one of the most promising methods for the synthesis of monodisperse lattices. Since any mixing systems (mechanical, ultrasound, creating convection currents, etc.) expands uncontrollably the particle size distribution. In a static heterogeneous monomer-water system, the nucleation of latex particles in the form of micro drops of monomer in the aqueous phase is represented as the formation of a new phase from supersaturated solutions. The driving force of this process is super saturation, which is set and maintained by the polymerization reaction proceeding at the monomer-water phase boundary. However, in addition to the nucleation of microdroplets, other phase formation processes can occur in the aqueous phase, due to its saturation with products of radical reactions. The likelihood of these processes is discussed in this article.

**Keywords:** Polymerization; Latex; Styrene

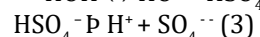
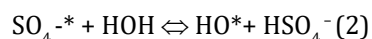
## Introduction

Potassium persulfate is the main initiator of polymerization in a heterogeneous monomer water system [1-3]. The initiation of polymerization proceeds in the aqueous phase:

$K_2S_2O_8 \leftrightarrow 2K^+ + 2SO_4^{\cdot-}$  - thermal decomposition of persulfate and the formation of sulfate ion radicals ( $SO_4^{\cdot-}$ )

$SO_4^{\cdot-} + M \rightarrow SO_4M^*$  (1) - initiation of monomer radicals ( $M^*$ )

Monomers that are used in heterogeneous monomer-water systems have low solubility in water (styrene, chloroprene, vinyl acetate) and therefore, sulfate-ion radicals can also react with water molecules and initiate polymerization according to the following scheme:



Where  $HO^*$  is the hydroxyl radical

During the polymerization, the aqueous phase will be saturated with the products of the reaction of quadratic termination of radicals and phase formation in the system will begin,

In a saturated solution of styrene in water the products of radical reaction are oligomers, consisting of few monomeric units, and one or two ionic end groups. Phase formation in this system can occur by a simple mechanism of crystallization from solutions. Obviously, the process of aggregation of longer polymer molecules can also proceed by a simple mechanism if this aggregation process is limited by the density of the surface charge induced only by sulfate end groups of the molecules. With large size macromolecules in the form of coils in water, the potential barrier phase transition can also be caused by a decrease in the entropy of

the system due to deformation of coils when they collide [4]. However, this additive component of the potential barrier will change only the value of maximal supersaturation in water. The kinetics of aggregation and the final size of the dispersed particles will still be determined by the charge density on the surface of the particles.

Thus, the supersaturated concentration in studied systems, after which they may overcome the potential barrier, and the aggregation of the oligomers starts, is determined by the number and nature of monomer units in their molecule. In fact, the rate of supersaturation achievement, in these cases, is equal to the rate of formation of oligomers in the water, i.e. to the initiation rate (quadratic termination) of radicals. The detection of the occurrence of radical reactions in an aqueous phase is very important for the development of the synthesis of monodisperse latexes, which are a valuable material in high technology. Based on these systems, it is possible to obtain modern medicines and mini-technologies are being created to produce thin films. Using polymer particles, transmission and

other physicochemical properties of biological membranes and films are investigated. Dispersed polymer systems are now accepted in hormone and pulsotherapy for transporting drugs to the internal affected organs. The development of modern supramolecular chemistry is largely associated with the study of dispersed polymer systems. These studies have identified the ability to store Nano system information.

### Experimental Part

A photograph and schemes of unit of polymerized are shown in Figure 1 and 2. In these installations, the monomer is layered on the aqueous phase in thermo stated tubes. The parameters of the aqueous phase are measured by instruments whose electrodes are immersed in the aqueous phase (figure 2). During the polymerization, samples are taken from the tubes to determine the dry residue of the latexes. Samples are taken using pipettes. In this work, we studied the polymerization of styrene in a heterogeneous static system of monomer - aqueous solution of potassium persulfate.



Figure 1: Photograph of unit of polymerized.

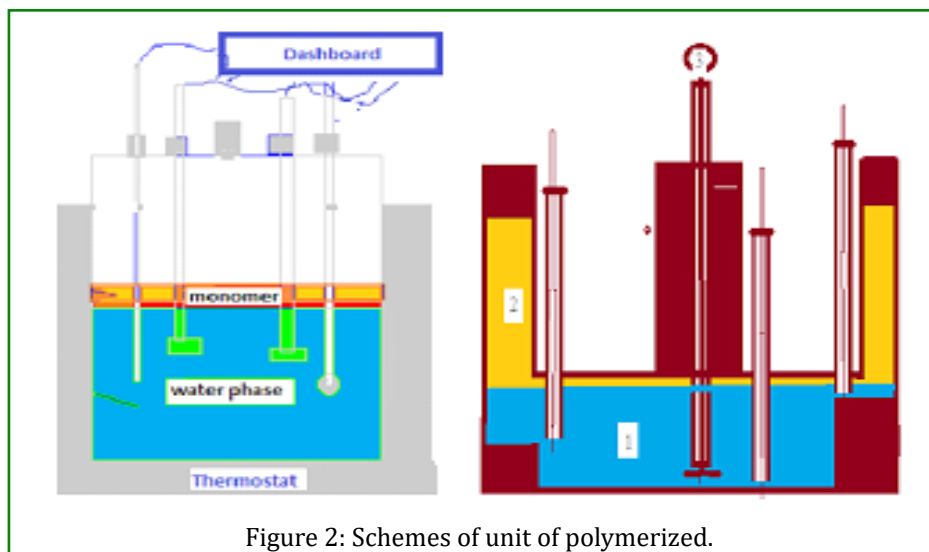


Figure 2: Schemes of unit of polymerized.

According to reactions 2 and 3, the pH of the aqueous phase in the course of polymerization should fall, and to detect these reactions, the pH of the aqueous phase in the course of polymerization was measured. The results of continuous measurement of pH of an aqueous solution of potassium

persulfate are shown in figure 3. An analogous picture is also observed during the polymerization of styrene, chloroprene and vinyl acetate in a two-phase static system monomer - aqueous solution of potassium persulfate.

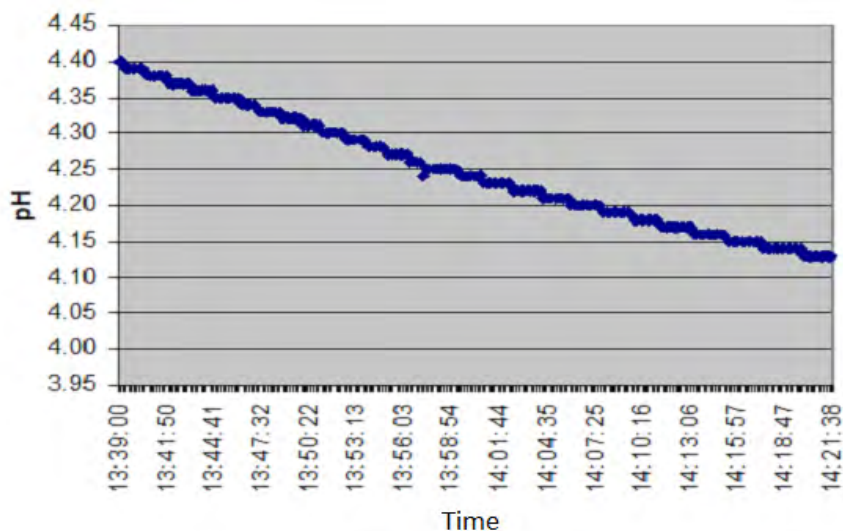


Figure 3: The change in pH aqueous solution of potassium persulfate over time. The initial conditions of pH 4.4, T 60°C:

The latex particles were investigated by electron microscopy. On figure 4 shows the latex particles obtained during after 6 hours and on figure 5 after 48 hours of polymerization. The appearance of fine particles in Figure 5. The electron density of which differs significantly from the electron density of large particles is obviously associated with the supersaturation of the aqueous phase with styrene oligomers and their aggregation.



Figure 4: Electron microscopic photograph of polystyrene latex obtained after 6 hours withstanding of static system.

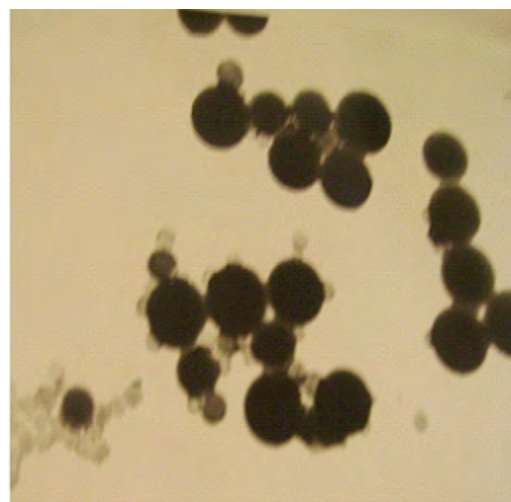


Figure 5: Electron microscopic photograph of polystyrene latex obtained after 48 hours withstanding of static system.

## Conclusions

It was shown that during polymerization in a static heterogeneous monomer-water system, phase formation

occurs both at the interface and in the aqueous phase. However, the nucleation of dispersed particles in the aqueous phase begins at the deep stages of polymerization. From the obtained results it follows that monodisperse latexes can be obtained upon completion of polymerization at an early stage of monomer conversion.

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