GENERATION OF LATEX PARTICLES AND PHASE FORMATION IN A HETEROGENEOUS STATIC MONOMER−WATER SYSTEM

© 2025   **A. A. Hovhannisyan*, G. K. Grigoryan, A. G. Nadaryan, and N. H. Grigoryan**

Scientific and Technological Center for Organic and Pharmaceutical Chemistry of the National Academy of Sciences of Armenia, Erevan, Armenia

*e-mail: hovarnos@gmail.com

Abstract. The aim of this work is to find new ways to synthesize latexes (polymer suspensions) with a given size and surface structure of particles. The need for such latexes is not large-scale, but their development and production are extremely important for the development of high technologies. Monodisperse latexes are especially valuable in immunological diagnostics of a wide range of diseases. The article presents the results of studies of the nucleation of latex particles in a heterogeneous monomer−water system. The results of these studies made it possible to find conditions for the reproducible synthesis of monodisperse polystyrene latexes. In order to change the surface structure of latex particles, cetyl alcohol was dissolved in the initial monomer phase (styrene). The article presents the results of electron microscopic studies of the synthesized latexes. Nano crystals of this alcohol are clearly visible on the surface of the latex particles. It is suggested that, in deep monomer conversions, the process of crystallization of cetyl alcohol begins in polymer-monomer particles.

Keywords: *polymerization, latex, cetyl alcohol, styrene, phase formation, crystallization, interface*

INTRODUCTION

The mechanism of nucleation and formation of latex particles during emulsion polymerization has been studied by many authors. According to the Harkins theory [1], in micellar emulsions latex particles are formed from micelles in the form of polymer-monomer particles (PMPs). In [2, 3] it is assumed that PMPs are also formed as a result of homogeneous association of oligomers in the aqueous phase.

Latexes are also synthesized without emulsifiers, in monomer−water dispersions. The aim of such works is to synthesize monodisperse latexes with a specific chemical structure of the surface of dispersed particles. Such synthesis is often possible by selection of monomers and co-monomers [4−6]. In [7], the results of a systematic study of polymerization processes and polymer disperse phase formation in emulsifier-free monomer−water systems are presented. The authors showed that the choice of conditions for heterophase polymerization largely determines the colloidal parameters of the final suspension. This work also shows ways to modify the surface structure of emulsifier-free polymer suspensions.

The mechanism of latex particle formation, without emulsifier (in the absence of micelles) has been studied in [8, 9, 10]. In [8], measurements of optical density in different zones of the aqueous phase during polymerization led the author to the conclusion that as a result of polymerization in the monomer−water interface, the monomer is dispersed into small droplets containing polymer molecules. The stability of such polymer-monomer particles, according to the author, is due to the ionic end groups of the polymer molecules. The authors [9, 10] came to the same conclusion after using atypical experimental methods (conductivity measurement, optical microscopy, and polymerization without stirring) to study emulsion polymerization of styrene.

In [11] it is assumed that in emulsifier-free systems PMPs are also formed by the mechanism of homogeneous association of oligomers in the aqueous phase. In [12], the possibility of PMP generation by penetration of a growing radical into the volume of monomer droplets is also considered.

In micellar emulsions, the generation of latex particles can occur simultaneously by different mechanisms [12]. Obviously, for this reason, the size

distribution of latex particles narrows in the absence of micelles.

It becomes obvious that one of the ways to synthesize monodisperse latexes may be to find a polymerization method in which only one mechanism of latex particle formation is active. This is what the experimental part of this work is aimed at.

Mass transfer occurring during the polymerization reaction at the monomer–water interface was confirmed experimentally during styrene polymerization in microfluidics, which allowed the use of infrared thermospectroscopy for simultaneous IR transmittance and thermoemission imaging measurements [13]. In this experiment, intense heat and concentration fluxes in the contact layer of laminar flows of styrene and toluene containing an initiator were recorded in the contact zone of the two fluids. Styrene and toluene are unlimitedly soluble in each other, and mass transfer does not change the homogeneity of the system, but in the two-phase system styrene–water solution of the initiator, mass transfer from the monomer phase to the aqueous phase can lead to saturation of the aqueous phase with the monomer [14–15]. In water, nonpolar hydrocarbon molecules tend to associate [16], and a small supersaturation is sufficient for the nucleation of styrene microdroplets in the aqueous phase.

Diffusion in liquids is a slow process, and it can be assumed that microdroplets of monomers can exist in a static system until they transform into PMP, the stability of which is ensured by ionic end groups of growing radicals and polymers.

The formation of monomer microdroplets also follows from the strong dependence of the interfacial surface tension of liquids on temperature. It can be assumed that mixing of liquids and dispersion of the system occurs as a result of a local increase in the temperature of the monomer–water interfacial layer during polymerization reactions there.

Supersaturation and phase formation can also occur in PMP if the monomer phase includes substances that do not participate in polymerization reactions. Depending on the nature of the substances and polymerization conditions, nuclei of a new phase may appear both during polymerization and during evacuation of residual monomer from latex. Phase formation in PMP can also occur when the latex storage temperature changes. Depending on the structure of the impurity molecules, crystals can grow on the surface of latex particles. Obviously, the crystals must be insoluble in water. The experimental part of the paper presents the first results of studying the formation phases in PMP. The studies were carried out during styrene polymerization in a static heterogeneous monomer–water system in the presence of cetyl alcohol (CA).

The choice of CA was conditioned by the fact that this alcohol is insoluble in water, is not an emulsifier and crystallizes from solutions of organic solvents. The low density and melting point of this alcohol were also taken into account. All these qualities of CA allowed us to hopefully detect nanoscale CA crystals on the surface of styrene latex particles.

RESULTS AND DISCUSSION

1. Starting substances and methods of research

Starting materials: styrene (Aldrich) was purified from stabilizer by distillation under vacuum, potassium persulfate (Sigma Aldrich), cetyl alcohol, azoisobutyric acid dinitrile — reagent grade products, water — double distillate.

Electron microscopic photographs were obtained using a Prism3 scanning electron microscope (Czech Republic), NMR spectra were obtained using a Mercury 300 spectrometer (Varian). The size and Z-potential of latex particles were determined using a Liteizer 500 device.
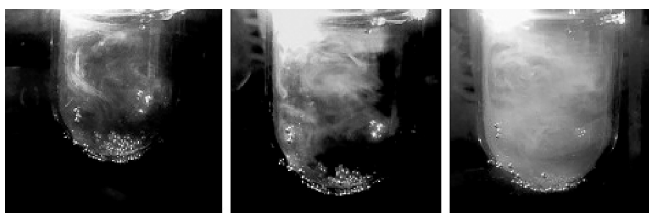
2. Polymerization and phase formation in static and semi-static monomer–water systems

Polymerization was carried out in temperature-controlled tubes in which the monomer phase (styrene or a solution of CA in styrene) was gently applied to the surface of an aqueous solution of potassium persulfate (PP). The experimental temperature was 50 °C, the volume of monomer phase was 2 mL, the volume of aqueous phase was 30 mL, and the concentration of potassium persulfate in water was 0.4%. The dry residue of the aqueous phase was determined by gravimetry, the viscosity of the monomer phase was determined by viscometry.

In the static system, polymerization is accompanied by turbidity (change in optical density) of the aqueous phase, which indicates the formation of a dispersed phase in the system. The turbidity of the aqueous phase was determined using a SF-24 spectrophotometer at a wavelength of 540 nm. The experiments were carried out simultaneously in six test tubes. One sample was taken from each tube for analysis.

As noted above, in the static system polymerization is accompanied by a turbidity of the aqueous phase, which is recorded by the spectrometer after a certain period of time from the beginning of polymerization. In our experiments, this period lasted 90 min and did not depend on the concentration of CA (from 0 to 6%). This result indicates the inertness of CA in the process of "emulsification" of the system. A photograph of the initial stage of aqueous phase turbidity is presented in Fig. 1.

As can be seen in Fig. 1, turbidity begins at the monomer–water interface and gradually deepens into the aqueous phase. This pattern is particularly clear when an inert salt (potassium sulfate) is dissolved in water [8], or ethanol in styrene [17]. Potassium sulfate increases the density of the aqueous phase, while ethanol decreases the density of dispersed particles. In both cases, the residence time of dispersed particles in the zone of their formation increases.

Fig. 1. The picture of turbidity change in the aqueous phase at the initial stage of polymerization.

The concentration of latexes synthesized in the static system does not exceed 2%. The time to reach this concentration is approximately 24 hours. The viscosity of the monomer phase does not change during this time.

The dynamics of aqueous phase turbidity changed dramatically when polymerization was carried out in a semi-static system in which only the aqueous phase was stirred. A photograph of this experiment is shown in Fig. 2. In the first test tube, the polymerization was carried out under semi-static conditions, while in the second test tube, the static condition was maintained. In the semi-static system, the aqueous phase remained transparent in throughout the entire stirring time (more than 240 min). In all probability, this is the amount of time required to reach supersaturation in the entire volume of the aqueous phase in this experiment. Turbidity in this test tube only began to be observed after the mechanical stirrer was suspended. In the control tube, the results of the previous experiment were reproduced (Fig. 1).
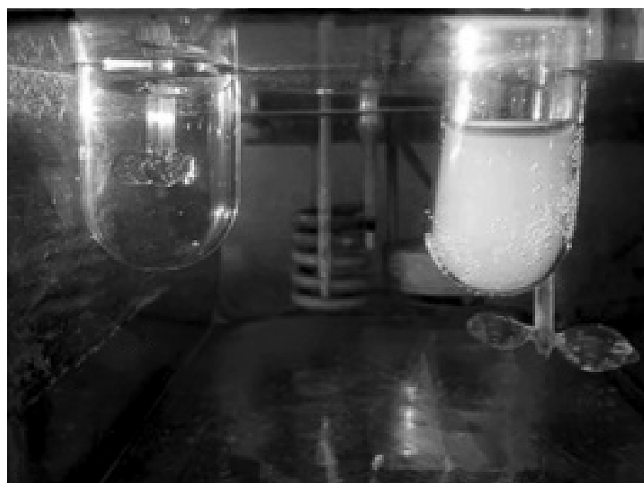
In a semi-static system, local supersaturation of the aqueous phase is impossible, and the results of this simple experiment can be considered to confirm the assumption that in a static system the driving force for the nucleation of monomer microdroplets is the supersaturation of the monomer−water interface layer by styrene molecules.

An electron microscopic photograph of latex synthesized in a semi-static system is shown in Fig. 3. The sample was taken after complete turbidity of the aqueous phase. As can be seen from the figures, the latex synthesized in the semi-static system has a rather narrow particle diameter distribution. This result is well reproducible.
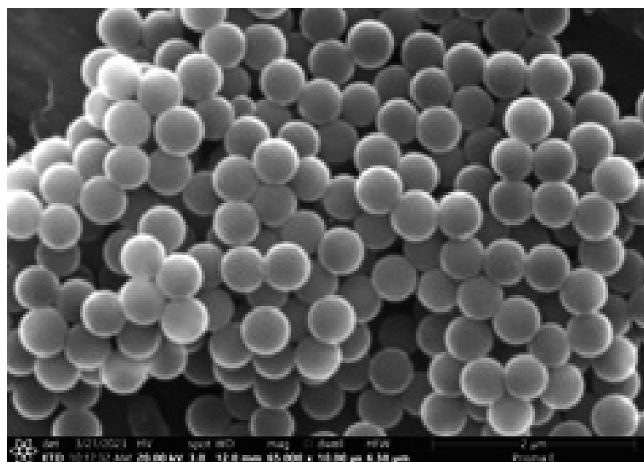
The synthesized latexes are stable (Z-potential of particles is equal to -67.3 mV), have a fairly narrow distribution of particles in diameter, which allows their use in immunodiagnostics, as well as for other applied purposes. The particle diameter distribution is shown in Fig. 4.

3. Phase formation in a polymer-monomer particle

Initially, phase formation in PMP was investigated by polymerization of styrene in a block. The CA content in styrene was 6%. The polymerization was initiated by
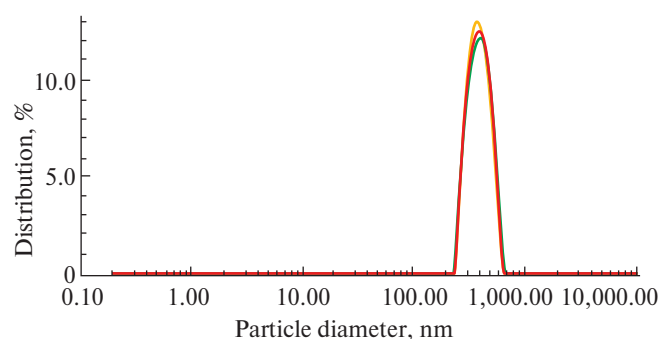

Fig. 2. Photographs of tubes in which polymerization was carried out in semi-static (tube 1) and static (tube 2) mode.

Fig. 3. Electron microscopic photograph of polystyrene latex synthesized in a semi-static monomer−water system.

azoisobutyric acid dinitrile. Crystallization began to be observed in the viscous polymer-monomer mixture when the temperature of the system was slowly lowered to 5°C. (Fig. 5). The 1H NMR spectrum of the crystalline

Fig. 4. Particle diameter distribution of latex synthesized in a semi-static styrene−water potassium persulfate solution system.
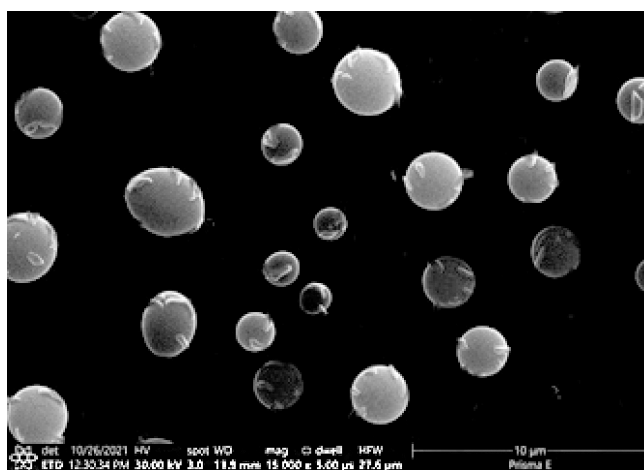
Fig. 5. Appearance of CA crystals in styrene block copolymer when the temperature is lowered to 5°C.

Fig. 6. Crystallization of CA in styrene when the solution temperature is lowered to 5°C. The concentration of CA in styrene is 6%.

Fig. 8. Electron microscopic photograph of diluted polystyrene latex synthesized in the presence of 2% CA in styrene.

particles was identical to that of the CA. The nucleation and growth of the CA crystal was also observed when the temperature of the solution of this alcohol in styrene was lowered (Fig. 6).

Electron microscopic photographs of latex particles synthesized in a static heterogeneous styrene−water PP solution system in the presence of CA are shown in Fig. 7. The needle-like crystals and the "growth cone" on the PMP surface are clearly visible in these photographs. These photos also show very small spherical particles, the composition of which is not very clear yet.

Structural formations on the surface of latex particles are also detected at low concentrations of CA in styrene. Fig. 8 shows electron microscopic photograph of polystyrene latex synthesized at 2% CA in styrene.

CONCLUSION

The results of this work allowed us to make a final conclusion that in the static heterogeneous monomer−water system the interface is one of the generation zones of latex particles, which allowed us to find conditions for reproducible synthesis of monodisperse polystyrene latexes.

The paper reveals the conditions for the synthesis of latex particles in the heterogeneous monomer−water system carrying nanoscale crystals of organic substances on their surface.

FUNDING

ETHICS DECLARATION

There are no human or animal studies in this paper.

CONFLICT OF INTERESTS

The authors of this paper declare that they have no conflict of interests.

Fig. 7. Electron microscopic photographs of polystyrene latex synthesized in the presence of 6% CA in styrene.

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