
MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

The Influence of Leucanol on the Aggregative Stability of Synthetic Latexes

V. N. Beresnev^a, I. I. Kraynik^a, I. V. Baranets^a, and L. V. Agibalova^a

*Scientific Research Institute of Synthetic Rubber named after Academician S.V. Lebedev, St. Petersburg, 198035 Russia
e-mail: tomorrow2004@inbox.ru*

Received April 16, 2018

Abstract—On the example of model systems (polystyrene latexes and copolymers of styrene with polar monomers, acrylonitrile and ethoxyethyl acrylate), the effect of sodium naphthyl formaldehyde sulfonate on the aggregative stability of synthetic latexes was analyzed. Upon reaching the limit conversion, these latexes during storage spontaneously transfer to a solid gel having a periodic colloidal crystal-like structure. It is shown that the gelation process obeys the Smoluchowski law for coagulation. An increase in the molecular weight of the polymer and in the size of the latex particles during the formation of the gel was recorded. The introduction of a NF dispersing agent neutralizes the gel effect, stabilizes the system, prevents gelation and leads to a slight increase in the molecular weight of the polymer and the degree of polydispersity of the polymers obtained. It has been suggested that stable macroradicals accumulating from the gel-effect stage and remaining in the system after completion of polymerization can be one of the reasons for the loss of aggregative stability of latexes, and incorporating the dispersing agent into the adsorption layer of polymer-monomer particles leads to the recombination of these radicals within the particle and the stabilization of latexes in the polymerization process.

Keywords: nonionic emulsifiers, latex coagulation, aggregative stability, acrylonitrile, stable free radicals

DOI: 10.1134/S107042721807011X

Rubbers of emulsion polymerization occupy the first place in the structure of the world industry of synthetic rubbers. At present, their annual production is more than 4 million tons per year in the world and 400 thousand tons per year in Russia.

An important problem in the industry of emulsion rubbers and latexes is the preservation of the stability of the latexes obtained during the synthesis, during thermal exposure, and during storage. In the existing formulations for the synthesis of emulsion rubbers, when a transition from a biologically undegradable emulsifier of nekal, sodium dibutyl-naphthalenesulphonate, to alkyl derivatives with an ion-forming sulphonic or carboxyl group, a leucanol—sulfated product of formaldehyde and naphthalene sulfonic acid condensation, in an amount of 3–10% by weight with respect to the emulsifier is introduced to improve the stability of latexes in the synthesis and thermal stages during the distillation of monomers.

The greatest demand for the use of this dispersing agent was manifested in the production of butadiene-nitrile and chloroprene rubbers. This dispersing agent is also used in the synthesis of thermoplastic acrylate rubbers produced at the pilot plant FSUE “NIISK” (SKBNK5, SKBNVP, SKBEVP). However, this dispersing agent is not biodegradable in wastewater produced by the separation of rubber from latex [1]. The task of replacing leucanol with a biodegradable analogue or excluding its entry into wastewater is important and relevant for the modern synthetic rubber industry.

In order to stabilize industrial latexes obtained in the production of emulsion butadiene–styrene and butadiene–nitrile rubbers, as well as latexes of thermoplastic acrylate rubbers, anionic surfactants are mainly used. In this case, the stability of latex particles is ensured by ionization of the adsorption layer of polymer-monomer particles. Violation of it requires overcoming electrostatic and hydration protection of the adsorption layer. When

stabilizing polymer-monomer particles with nonionic surfactants, the main stabilizing factor is only the hydration of the surfactant in the adsorption layer.

Long-term attempts to replace leucanol, including polymer biodegradable compounds, combining the properties of surfactants and polyelectrolytes, did not lead to positive results [2]. The lack of understanding of the true role of this dispersing agent in the stabilization of latex systems, in addition to the fact of the increase in the electrokinetic potential of particles attributed to it, is the reason for the complexity of its replacement by an equivalent component of the formulation.

One of the important issues of emulsion polymerization is the effect of live free macroradicals on the polymerization process. Radicals of small size can emerge from the polymer-monomer adsorption layer and recombine in the liquid phase [3–5], and can be sorbed back by interacting with the adsorption layer [6–8]. Earlier, Beresnev [9] showed that macroradicals can remain inside the polymer-monomer particle and be one of the reasons for the loss of stability leading to gel formation of the entire volume of latex (systems on nonionic surfactants). Such gelation in latex systems on anionic surfactant: sodium lauryl sulfate, with the formation of gel-like structures is particularly pronounced in the preparation of copolymers with polar monomers [10].

The slowing down of the gelation was observed when polystyrene latex was added to nonionic surfactants when a high degree of conversion of monomers ($\geq 95\%$) of stable nitric acids was reached, the lifetime of the latex up to the instant of gelation correlated with a decrease in its content to the minimum limiting concentration in the system. The concentration of stable free radicals was determined from the change in the intensity of the electron paramagnetic resonance spectrum.

Introduction of more active free radicals [diphenylpicrylhydrazine (DPPH)] into the system ensured the stability of the system at lower molar concentrations than the nitric acid radicals. The same action is caused also by the inhibitors of radical polymerization (dimethyldithiocarbamate Na at $\text{pH} \geq 7.5$), as well as by an increase in the degree of saturation of the adsorption layer at the additional introduction of an emulsifier. Therewith the stabilization of polymer-monomer particles (PMP) prevents the coalescence of latex particles at collision.

The aim of the work is to determine the factors affecting the stability of synthetic latexes and the mechanism of

action of the non-biodegradable leucanol dispersing agent entering the formulation of emulsion polymerization.

EXPERIMENTAL

As a model system, latexes were synthesized on nonionic emulsifiers. This made it possible to exclude the influence of the electrostatic factor on the stability of latexes. Styrene SDMFK of the premium grade, ethoxyethyl acrylate (EEA), and acrylonitrile (AN) were used. Polystyrene latexes and copolymers of styrene with AN and EEA were produced in amounts of 10, 20, 25, 50% by weight of styrene. Also, the dispersing agent NF Leucanol produced by JSC Polyplast-Novomoskovsk was introduced into the emulsifiers. Nonionic surfactants: compounds based on oxyethylated alcohols—Sintanol ALM-10, and on the basis of octylphenol—OP-14, were used as emulsifiers. Distilled water was used as a dispersion medium; an oxidation–reduction system consisting of pinane hydroperoxide, rongalite, and iron-trilon complex was as the initiating system. The polymerization was carried out in a four-neck flask with a jacket under a nitrogen atmosphere at a temperature of $+5^\circ\text{C}$, which ensured the polymerization in the micellar phase. The constant temperature was maintained by means of a LOIP-530 thermostat by feeding a cooling mixture of water and ethylene glycol (70 : 30) into the jacket of the reactor. Immediately before the synthesis, a vacuum distillation of styrene and ethoxyethyl acrylate was carried out to be freed from the homopolymer and the inhibitor. Before the start of the polymerization, the reactor was evacuated and purged with nitrogen twice. The emulsification time was 1.5 h. The polymerization formulation is shown in Table 1.

The pH of the emulsion before the introduction of the initiator was maintained at 7.5 ± 0.1 . The pH was measured using a HI 2020 instrument from HANNA Instruments.

The conversion of the monomers was determined from the content of the dry residue in samples taken during the course of the polymerization.

The latex stability measure was taken to be the lifetime of the latex, i.e., the time from the end of the polymerization to the complete formation of a solid gel in the volume of the latex.

The degree of saturation of adsorption layers of synthesized latexes was determined by the method of adsorption titration by Maron on the du Noüy tensiometer.

Table 1. The polymerization formulation

Function	Component	State Standard GOST, TU	Weight, wt %
Monomer	Styrene Ethoxyethyl acrylate Nitrileacrylate	GOST 10003–90 TU 2478-435-05842324–2013 GOST 11097–86	100
Dispersion medium	Distilled water		250
Emulsifier	Syntanol ALM-10 OP-14	TU 2483-064-0515207–99 GOST 8433–81	10
Initiator	Pinane hydroperoxide, 50 wt %	TU 38.40386–92	0.4
Red-Ox system	Trilon B Rongalite FeSO ₄ · 7H ₂ O	GOST 10652–73 GOST 939859 GOST 4148–78	0.15 0.25 0.3
Dispersing agent	Leucanol	GOST 6848–79	0.5

Samples for chromatography were obtained by isolating the polymer with ethyl alcohol from latex with further drying under vacuum at $T = 30\text{--}40^\circ\text{C}$. They were then dissolved in tetrahydrofuran with a solution concentration of 2 mg mL^{-1} . Chromatograms of the samples were obtained on a gel chromatograph from Waters, USA of the Breeze system equipped with two detectors: refractometric and ultraviolet ($\lambda = 100\text{--}700\text{ nm}$). A set consisting of three columns with spiragel: 1HR, 2HR, 4HR, dividing the sample in the molecular weight range 100–5000, 500–20 000, 5000–600 000 Da, respectively, was applied. Tetrahydrofuran of chemically pure grade was used as the solvent, at $T = 35^\circ\text{C}$, the solution concentration was $0.2\text{ g}/100\text{ cm}^3$. The device was calibrated to the narrow standards of polystyrene (firm Waters).

Measurement of the hydrodynamic dimensions of latex particles was carried out by molecular light scattering using a Coulter N 4 submicrometer particle size analyzer (Coultronics, France), working on the principle of a correlometer.

Investigation of the morphology of latexes and formed gel structures was carried out with the help of an analytical complex based on the Leica DM-2500 optical microscope, the Leica DFC-420C high-resolution color digital camera, and a specialized computer station. Capturing, archiving, and quantitative image processing are performed using the program Leica Las. Samples of latexes, their mixtures with water and gels were studied

in the form of thin layers between the slide and cover glass of Menzel in the bright field, phase contrast, crossed Nicole, and differential-interference contrast modes in order to obtain the most complete information about the materials under study.

RESULTS AND DISCUSSION

The final concentration of the polymer in the latex was $c \geq 28\%$ by weight with a monomer conversion of 95% or more. The kinetic curves of polymerization of styrene, including those with leucanol introduced into the emulsifier, and of styrene with AN and EEA are shown in Fig. 1. With the addition of polar monomers, the rate of polymerization sharply increases (Fig. 2). The addition of 0.5% by weight of leucanol dispersing agent to the polymerization formulation of the monomer leads to a slowing of the polymerization rate. During the synthesis, at a conversion degree of 30–45% or more, a gel effect was observed, an increase in the polymerization rate was due to the diffusion difficulty of the chain termination stage. The polymerization rate at the gel effect stage increases with the content of the polar monomer in the styrene–EEA–AN series. The gel effect is clearly pronounced when copolymerizing styrene with a high-polar AN. When leucanol is added in an amount of 0.5–1% by weight per monomer to the polymerization formulation, the gel effect is minimized, the acceleration of the polymerization process at a conversion degree of

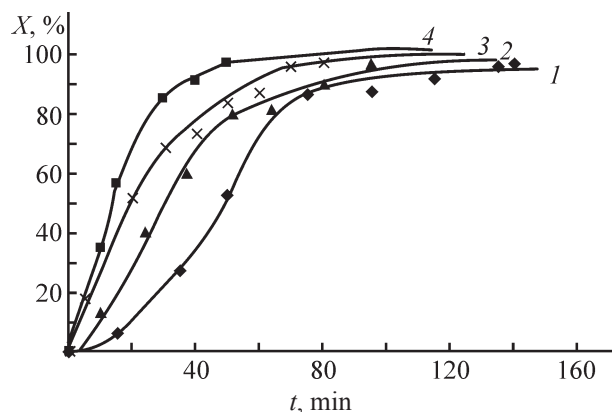


Fig. 1. Kinetics of polymerization of styrene and a mixture of styrene with AN and EEA in the presence of the emulsifier Sintanol ALM-10. (X) Conversion, (t) time. (1) Polystyrene, (2) copolymer of styrene (80% by weight) and ethoxyethyl acrylate (20% by weight), (3) copolymer of styrene (80% by weight), and HAA (20% by weight) with 0.5% by weight added to leucanol monomer, (4) copolymer of styrene (80% by weight) and AN (20% by weight); the same for Fig. 2.

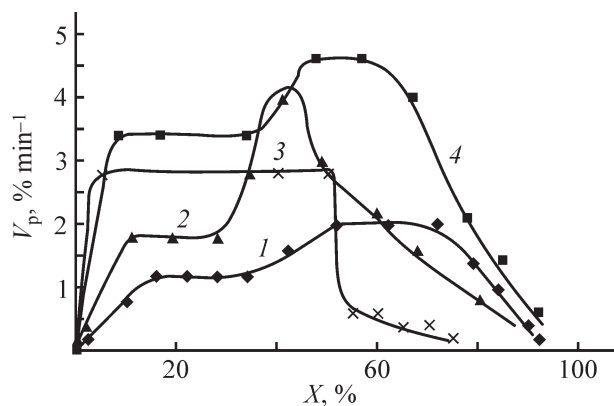


Fig. 2. Polymerization rate V_p of styrene and a mixture of styrene with AN and EEA vs. degree of conversion X in the presence of the emulsifier Syntanol ALM-10.

$45 \pm 5\%$ is practically not observed. When the conversion reaches 50% or more, the polymerization rate gradually decreases down to its completion with a conversion of 95–97%.

When OP-14 derivatives are used in the formulation of the nonionic surfactant during the synthesis of emulsion polystyrene, when the conversion reaches 95%, the resulting latexes prove to be unstable, the viscosity of the system changes dramatically, and a highly viscous gel is formed. The loss of stability is observed in 20–25 min after the end of the synthesis. At the end of a certain induction period, a sharp spontaneous structuring of the

latex in the volume occurs, leading to a slowdown of the mixer. At the same time, gel formation and the formation of a solid gel are not accompanied by a noticeable thermal effect. As the speed of mixing increases, the intensity of the collision of particles increases, which leads to destabilization of the system.

When passing from the nonionic surfactant derivatives of octylphenol to the saturated fatty alcohols (C_{10} – C_{12}), the polystyrene latex lifetime increases from 20–25 min to 15–30 h with an emulsifier content in the polymerization formulation in an amount of 10 wt. parts per 100 parts of monomer. Therewith the emulsifiers have a different hydrophilic–hydrophobic balance (8.2 for OP-14 and 9.8 for Sintanol ALM-10) and a critical micelle concentration (10^{-3} mol^{-1} for OP-14 and $4.5 \times 10^{-3} \text{ mol}^{-1}$ for Syntanol ALM-10). Syntanol ALM-10 has a higher solubility in water and a higher critical concentration of micelle formation.

Table 2. Effect of styrene–AN copolymer composition on the lifetime of latex

Latex concentration, %	Latex lifetime, h, at the concentration of AN in the polymer, %				
	0	10	20	25	50
28	14	0.7	0.4	0.3	0.1
20	20	1	0.7	0.5	0.3
15	40	1.5	1.3	1	0.5
10	60	2.5	2	1.5	1
5	–	–	–	–	–
$\tan \alpha$	0.5271	0.0204	0.0179	0.0135	0.01

Table 3. Effect styrene–EEA copolymer composition on the lifetime of latex

Latex concentration, %	Latex lifetime, h, at the concentration of EEA in the polymer, %				
	0	10	20	25	50
28	14	20	25	30	45
20	20	30	35	45	65
15	40	45	53	60	100
10	60	65	75	110	130
5	–	–	–	–	–
$\tan \alpha$	0.5271	0.531	0.5569	0.8994	1.85

Theory of the polar AN monomer leads to a sharp decrease in aggregative stability. When using Syntanol ALM-10 for the styrene–AN copolymer (10–50 wt % AN) as an emulsifier, the latex is unstable in 15–20 min after achieving a monomer conversion of $95 \pm 2\%$. For copolymers of styrene with ethoxyethyl acrylate, an increase in the lifetime is observed with both systems with AN and with pure polystyrene latexes. The latex is stable for $\tau \geq 40$ h. This can be explained by the hydration of the EEA units in the polymer chain due to the formation of hydrogen bonds with oxyethylated units, similar to the hydration of emulsifier molecules of polymer-monomer particles.

The obtained data indicate a correlation between the lifetime of the latex and the slope α to the abscissa axis of the obtained dependences of the lifetime on the concentration of latex (Tables 2, 3).

From the data on the change in the lifetime of the latex upon dilution of the system, it can be seen that the gela-

tion rate, determined by the particle collision intensity, is inversely proportional to the square of the number of particles per unit volume. The lifetime of the latex is inversely proportional to the square of its concentration, and, thus, the rate of gelation obeys Smoluchowski's law for coagulation (Figs. 3, 4). It should be noted that there is a minimum limiting concentration of latex in the solution, in our case 5–7% by weight, at which no system destabilization occurs.

The slope of the dependencies to the abscissa axis can serve as a characteristic reflecting the effect of the copolymer structure on the aggregative stability of synthetic latexes (Fig. 5). Introduction AN sharply destabilizes the system, whereas the introduction of EEA increases the aggregative stability of latex, presumably it is due to surface hydration of the EEA polymer chain links on account of the formation of hydrogen bonds with oxyethylene polymer links.

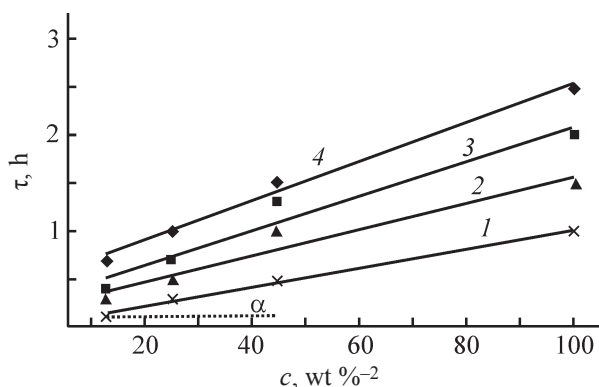


Fig. 3. Lifetime τ of copolymers of styrene with AN on nonionic surfactant Syntanol ALM-10 vs. the concentration of latex. Concentration of AN (wt %): (1) 50, (2) 25, (3) 20, (4) 10.

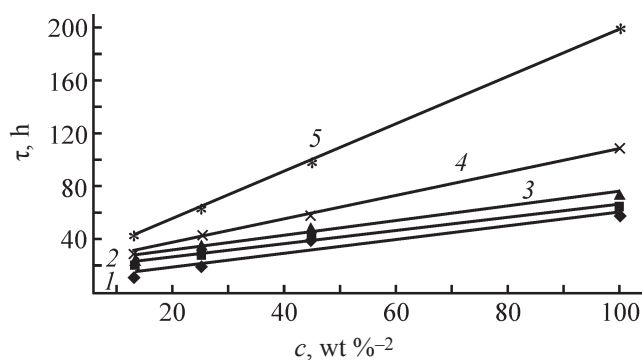


Fig. 4. Lifetime τ of copolymers of (1) polystyrene latex and (2–5) copolymers of styrene with EEA on nonionic surfactant Syntanol ALM-10 vs. the concentration of latex c . EEA concentration (wt %): (2) 10, (3) 20, (4) 25, (5) 50.

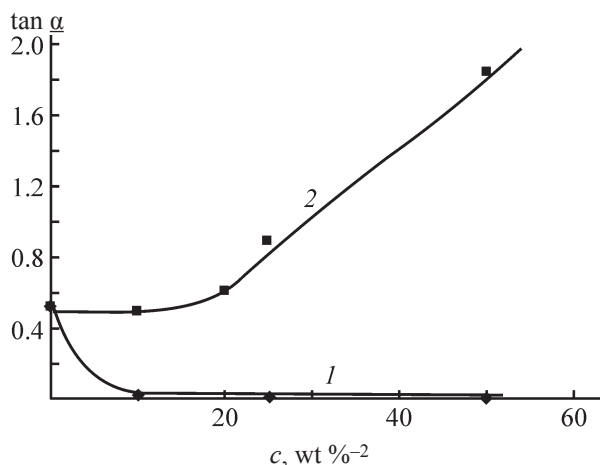


Fig. 5. Effect of the monomer phase composition on the stability of polystyrene latexes on the nonionic emulsifier Sintanol ALM-10. (c) Concentration of the monomer. (1) AN, (2) EEA.

The magnitude of the intermolecular attraction force is directly proportional to the content of AN in the copolymer. At the same time, the AN content does not influence the force of intermolecular repulsion [11].

Samples of latex, gels, and coagulum are examined microscopically. It is established that during the gelation the phenomenon of self-organization of latex particles into ordered fibrillar and then lamellar structures takes place. After synthesis, polystyrene latex contains spherical particles up to 500 nm in diameter, as well as aggregates of spheres of arbitrary shape from 2 to 120 μm (Fig. 6a). The study of latexes in the phase contrast regime revealed a variation in the dispersion staining of aggregate sections: some of the material differs from the latex spheres only in color intensity, while some show

a different color, indicating structuring processes in the system (Figs. 6a, 6b).

The introduction of the excess of the emulsifier ALM-10 into the latex leads to a practical disappearance of aggregates of the sphere-shape, only agglomerates of 2–3 particles remain. On the contrary, the introduction of additional water into the latex leads to a substantial increase in the proportion of aggregates of sphere-shape with a changed dispersion color, up to the complete filling of the material with plate structures (Fig. 6c).

The gel obtained during the storage of polystyrene latex was studied. The study of this material under the crossed nicole demonstrates its crystalline nature (Fig. 6c). Investigation of the fine structure of water-diluted polystyrene latex showed that the interaction of latex particles is carried out through interlayers of bound water (Fig. 6d).

On the photomicrographs of a copolymer of styrene with AN (80/20), after evaporation of free water, a clear formation of a periodic colloidal structure with inclusions of immobilized water into this grid is visible (Fig. 6e).

The morphological structure of the formed gels was close to the microstructure of the flocculate formed during the first stage of electrolyte coagulation of synthetic latexes stabilized by anionic surfactants (Fig. 6f). The average particle size during gelation is significantly increased. In addition, the formation of gels substantially increases the molecular weight of the polymer (Table 4).

It is seen from the data of Table 4 that the molecular weight of the polymer increases with the increase in the AN content in the polymerization formulation (d_w is the weighted average diameter, M_w is the weight average molecular weight, M_n is the number average molecular

Table 4. Effect of AN and leucanol on the molecular weight of the polymer and gel obtained after 1 month of storage

The content of AN in the copolymer, wt %	The amount of coagulum during polymerization, %	M_w , kDa		M_n , kDa		M_w/M_n		d_w , nm	
		latex	gel	latex	gel	latex	gel	latex	gel
0	2.0	468	550	195	197	2.77	2.82	48.2	150
10	2.0	585	705	214	220	2.73	2.66	52.8	145
15	2.5	605	740	220	200	2.75	3.7	53.8	160
20	3.0	863	1075	310	325	2.79	3.3	63.6	170
25	2.5	1155	1250	300	360	3.2	3.47	62.6	173
25 + 0.5 wt % leucanol	0.3	1250	–	300	–	3.37	–	50.4	–

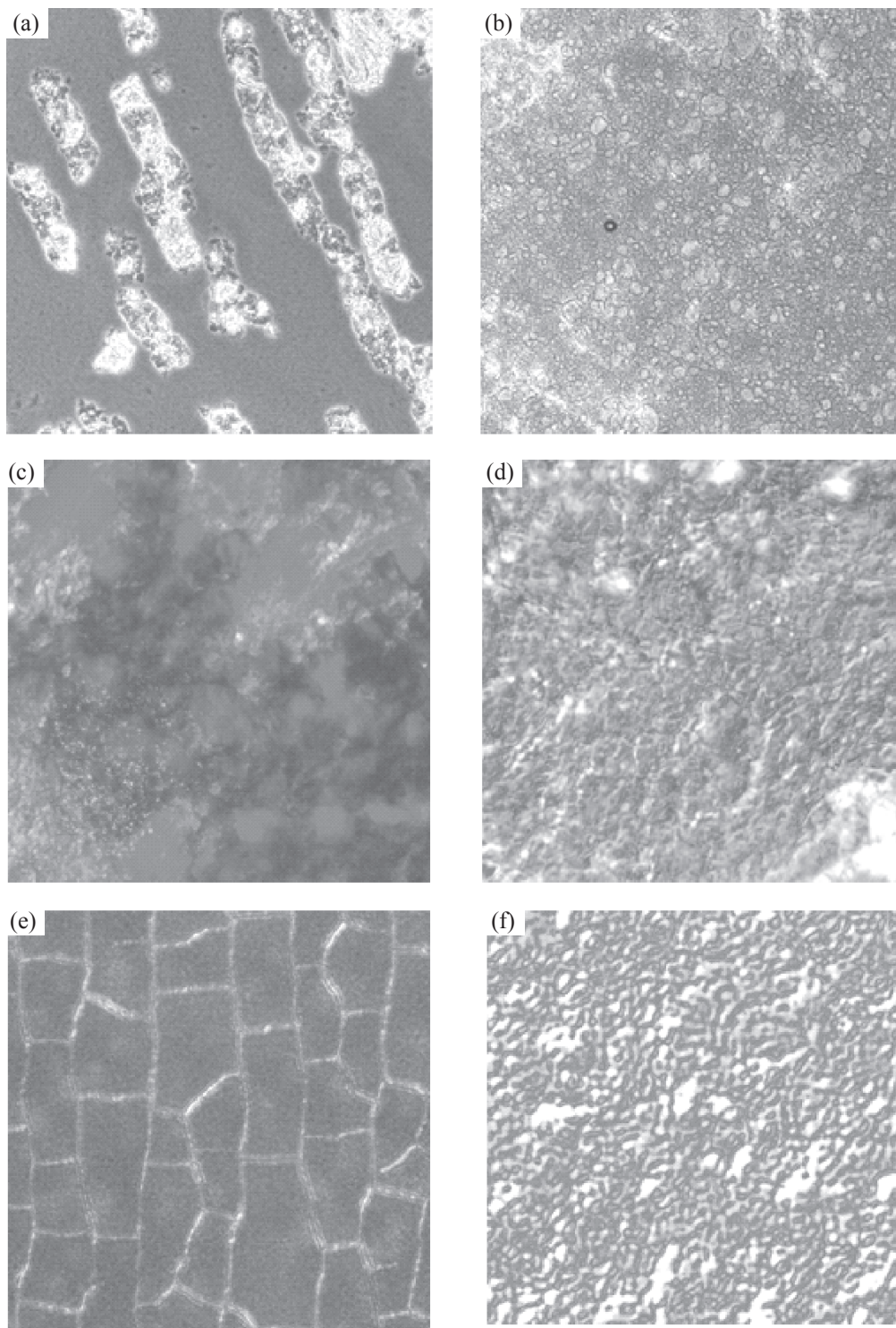


Fig. 6. Microphotographs of (a) polystyrene latex, (b) diluted polystyrene latex, (c) solid polystyrene gel, (d) diluted solid polystyrene, (e) styrene–NA copolymer (80/20) after evaporation of free water, (f) butadiene-nitrile latex at the beginning of salt coagulation. Mode: (a, b) phase contrast, the size of $670 \times 670 \mu\text{m}$; (c) crossed nicole, size $500 \times 500 \mu\text{m}$; (d) differential-interference contrast, size $100 \times 100 \mu\text{m}$; (e) crossed nicole, size $100 \times 100 \mu\text{m}$; (f) differential-interference contrast, size $50 \times 50 \mu\text{m}$.

weight, and M_w/M_n is the polydispersity coefficient). Also, the molecular weight of the gel formed during the storage of latex, measured after 1 month of storage, increases compared to the molecular weight of the polymer in the stabilized latex.

The introduction of leucanol completely stabilizes the system, prevents the formation of coagulum, reduces the average particle diameter, but contributes to an increase in the molecular weight of the resulting polymers, which may result from the recombination of macroradicals in the volume of a polymer-monomer particle.

CONCLUSIONS

When studying the process of polymerization of polystyrene latexes and styrene–ethoxyethyl acrylate and acrylonitrile on nonionic emulsifiers Sintanol ALM-10 and OP-14, it was shown that the obtained latexes are unstable, which leads to the formation of coagulum on the stirrer and reactor walls at the stage of the gel effect and solid gel when storing latex.

An increase in the content of polar monomers of acrylonitrile leads both to an acceleration of the polymerization process at all stages and to acceleration of gelation. The process of gelation obeys the Smoluchowski coagulation law.

When the gel is formed, an increase in the average particle size of the latex and the average molecular weight of the polymer is recorded, which may be a consequence of the recombination of free macroradicals accumulating from the gel effect stage and remaining within the polymer-monomer particle upon completion of the polymerization process. This leads, presumably, to a change in the mobility of water in the surface layer and its hydrophobization, to the coalescence of the particles, and to further gelation. The introduction of ethoxyethyl acrylate increases the stability of the system by forming the surface hydrogen bonds of the ethoxy groups of the polymer and water.

Light microscopy showed that the gel forms due to the binding of free water and has a crystal-like periodic

colloidal structure similar to the structure of the flocculate formed during the electrolyte coagulation of industrial latexes on anionic emulsifiers.

When the leucanol dispersing agent is added to the polymerization formulation, the stage of the gel effect on the kinetic curves is smoothed, the molecular weight of the polymer and the degree of polydispersity increase, but the molecular weight remains unchanged when the latex is stored and the latex system retains colloidal stability.

The mechanism of action of leucanol can consist in screening the effect of macroradicals on the adsorption layer of polymer-monomer particles and their faster recombination in the volume of PMP during the synthesis. This makes it possible to explain the minimization of the gel effect stage, the disappearance of the coagulum, and the increase in the molecular weight of the polymer when leucanol is used.

REFERENCES

1. Gusev, Yu.K. and Papkov, V.N., *Kauchuk i rezina* (Rubber and rubber), 2009, no. 2, pp. 2–9.
2. Poluektov, P.T. and Vlasova, L.A., *Prom. Pr-vo Ispol'z. Elastomerov*, 2011, no. 4, pp. 31–36.
3. Casey, B., Morrison, B., and Gilbert, R., *Progress Polym. Sci.*, 1993, vol. 18, no. 6, pp. 1041–1096.
4. Abad, C. and Asua, J., *Chem. Eng. Sci.*, 1994, V. 49, no. 24, pt. 2, pp. 5025–5037.
5. Gao, J. and Penlidis A., *Progress Polym. Sci.*, 2002, vol. 27, no. 3, pp. 403–535.
6. Thickett, S. and Gilbert, R., *Macromolecules*, 2006, vol. 39, no. 6, pp. 2081–2091.
7. Thickett, S., Gaborieau, M., and Gilbert, R., *Macromolecules*, 2007, vol. 40, no. 13, pp. 4710–4720.
8. Thickett, S., Morrison, B., and Gilbert, R., *Macromolecules*, 2008, vol. 41, no. 10, pp. 3521–3529.
9. Beresnev, V.N. and Fermor, N.I., *Zh. Prikl. Khim.*, 1970, vol. 43, no. 6, pp. 1325–1335.
10. Hossein, A., Jaber, N.G., and Mohammad, S., *J. Colloid Sci.*, 2015, vol. 293, no. 8, pp. 2445–2450.
11. Ono, H. and Sato, F., *J. Colloid Polym. Sci.*, 1975, vol. 253, no. 7, pp. 538–543.