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## MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

# Stability of Polymer–Monomer Particles of Synthetic Latexes

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**Abstract**—The presence of "living" macroradicals in the volume of a polymer–monomer particle may be one of the factors responsible for the loss of the aggregative stability of latexes. If the adsorption protection of a polymer–monomer particle is insufficient, high content of "living" macroradicals leads to gelation in the latex in the course of storage. Correlation between the latex life time, hydration of nonionic surfactant molecules in the adsorption layer of a polymer–monomer particle, and extent of the action of the macroradicals was determined. Naphthalenesulfonic dispersing agents enhance the stability of latex systems in the step of polymerization and distillation of the monomers owing to a decrease in the critical micelle concentration of the emulsifier, to extension of the micellar period of the polymerization, to an increase in the degree of saturation of polymer–monomer particles, and to an increase in the probability of macroradical recombination in the volume of a polymer–monomer particle. With an increase in the degree of polycondensation of naphthalene-containing dispersing agents, their surface activity increases, whereas the ability to support the aggregative stability of latexes decreases.

**Keywords:** nonionic surfactants, free macroradicals, gel effect, aggregative stability of latexes

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In many existing procedures for preparing emulsion rubbers, a dispersing agent, Leucanol, in introduced in an amount of 5–15 wt % relative to the emulsifier to enhance the protection of the adsorption layer of polymer–monomer particles (PMPs) and stability of latexes in the steps of the synthesis and heat treatment to distill off the monomers. The production of butadiene–acrylonitrile and chloroprene rubbers is characterized by the highest demand for this dispersing agent. It is also used in synthesis of thermoplastic acrylate rubbers produced at the Pilot Plant of the Research Institute of Synthetic Rubber (SKBNK5, SKBNVP, SKBEVP) [1].

Leucanol [produced according to GOST (State Standard) 6848–79, grades A и B] and its imported analog Daxad 11 are products of polycondensation of naphthalene-2-sulfonic acid with formaldehyde, followed by neutralization with sodium hydroxide.

Leucanol is a mixture of oligomers with the degree of polycondensation from 1 to 9. The degree of polycondensation of its American analog, Daxad 11, varies from 1 to 12. Higher-molecular-mass analogs are also produced; in particular, SP-1 dispersing agent with high content of oligomers with the degree of polycondensation of 12 and 13 is used in building industry as an additive to concrete.

Leucanol is incorporated in the adsorption layer of PMPs, but it itself exhibits very low surface activity and does not form micelles.

This dispersing agent is not biodegradable, and its use requires expensive systems for wastewater treatment when using the method of "salt" coagulation of latexes. Attempts were made for many years to replace Leucanol, in particular, by polymeric biodegradable compounds combining the properties of surfactants and polyelectrolytes, but no success was reached in the past 50 years [2–4].

Variation of the Leucanol composition (increase in the content of the fraction with a high degree of polycondensation) in production of SKBNK5 and SKBNVP thermoplastic rubbers causes a decrease in the aggregative stability in the course of both polymerization and distillation of the monomers.

The problems with replacement of Leucanol by an equivalent component are largely caused by poor understanding of the role of Leucanol in stabilization of latex systems (apart from incorporation in the adsorption layer of PMPs).

We have shown previously that, when using nonionic emulsifiers, the latexes obtained are unstable both during the synthesis, which leads to the formation of the coagulum on the stirrer and on the reactor walls, and in storage, which leads to the gelation in the latex volume. The gelation led to an increase in the molecular mass and degree of polydispersity of the polymer [5]. The recent studies demonstrated the possibility of prolonged existence of radicals in the PMP volume and of their effect on the adsorption layer [6, 7].

This fact allowed a conclusion that macroradicals formed in the gel effect step, whose recombination on reaching high conversion of the monomers becomes hindered because of increased viscosity of the reaction mixture, can be accumulated inside PMP and can exist in it for a long time, reducing the stabilizing ability of the PMP adsorption layer and promoting the coagulum formation in the course of polymerization and the latex gelation in storage. Recombination of macroradicals leads to changes in the molecular parameters of the polymer, in particular, to an increase in the molecular mass of the polymer in the gel.

Introduction of the Leucanol dispersing agent into the polymerization formulation decreases the coagulum amount, stabilizes the latex, and levels off the gel effect step, but does not prevent changes in the molecular parameters of the polymer.

The goal of this study was to determine the mechanism of the effect of Leucanol on the stability of latexes in the course of synthesis and storage and on the structure of the PMP adsorption layer with the aim of subsequent replacement of Leucanol by an environmentally friendlier analog.

## EXPERIMENTAL

Emulsion polymerization of styrene (St) and its copolymers with acrylonitrile (AN) was performed. A terpolymer of St, AN, and ethoxyethyl acrylate (EEA) was also prepared. As emulsifiers we used nonionic surfactants: Sintanol ALM-10 based on oxyethylated alcohols and OP-14 based on octylphenol. The use of nonionic surfactants leveled off the effect of the adsorption layer charge on the stability of the latex systems. The emulsifier content of the system was varied from 6 to 16 wt % relative to the monomer.

We used distilled water as a dispersion medium and a redox system consisting in pinane hydroperoxide (PHP), Rongalite, and the iron EDTA complex as an initiating system. The polymerization was performed in a four-necked flask with a jacket at 5°C in a nitrogen atmosphere. The constant temperature was maintained with an LOIP-530 thermostat by feeding into the reactor jacket a cooling mixture of water and ethylene glycol (70 : 30). Styrene was vacuum-distilled immediately before the synthesis to remove the homopolymer and inhibitor. Prior to starting the polymerization, the reactor was evacuated and purged two times with nitrogen. The emulsification time was 1.5 h. The polymerization formulation is given in Table 1. The experiment conditions ensured the micellar mechanism of the polymerization.

As dispersing agents we used Leucanol NF produced by OOO Poliplast-Novomoskovsk (DNF-1), Leucanol NF produced by OOO Poliplast Severo-zapad (DNF-2), and its macromolecular analog SP-1 produced by OOO Poliplast-Novomoskovsk. The compositions of the dispersing agents were determined by OOO Poliplast-Novomoskovsk using gel permeation chromatography. To determine the effect exerted by the structure of the PMP adsorption layer on the polymerization, we introduced into the reaction mixture 2-naphthol (Biochem) as a component of the emulsifier (Naphth-Em) and as an additive to the monomer (Naphth-M) in an amount of 1–2 wt % relative to the monomer.

To determine the effect exerted by the chain transfer to the monomer on the course of the process and on the stability of the latexes, we introduced into the reaction mixture *tert*-dodecyl mercaptan (TDM) as a chain-terminating agent in an amount of 0.5–1 wt % relative to the monomer. TDM was fed in two portions in the form of a 1.5–2% solution in the monomer: The first portion (70%) was added when preparing the emulsion, and the second portion (30%), on reaching 50–60% conversion.

The pH of the emulsion before introducing pinane hydroperoxide was maintained on the level of 7.5 ± 0.1. The pH values were measured with an HI 2020 device (Hanna Instruments, the United States).

**Table 1.** Polymerization formulations

| Component destination | Component | GOST (State Standard), TU (Technical Specification) | Amount, wt parts |
|---|---|---|---|
| Monomer | Styrene<br>AN | GOST 10003–90<br>GOST 11097–86 | 100 |
| Dispersion medium | Double-distilled water | | 250 |
| Emulsifier | Sintanol ALM-10<br>OP-14 | TU 2483-064-0515207–99<br>GOST 8433–81 | 6–16 |
| Initiator | Pinane hydroperoxide, 50% | TU 38.40386–92 | 0.4 |
| Redox system | $Na_2EDTA$ | GOST 10652–73 | 0.15 |
| | Rongalite | GOST 939859 | 0.25 |
| | $FeSO_4 \cdot 7H_2O$ | GOST 4148–78 | 0.3 |
| Dispersing agent | DNF-1, DNF-2 | GOST 6848–79 | 0.5–1 |
| | SP-1 | TU 5870-004-58042865–04 | 0.5 |
| | 2-Naphthol | GOST 923–80 | 1–2 |
| Chain-terminating agent | TDM | GOST 242334 | 0.5–1 |
| Radical polymerization inhibitor | Sodium dimethyldithiocarbamate | GOST 8864–71 | 0.5 |

The monomer conversion was determined from the amount of the dry residue in samples taken in the course of the polymerization. To latex samples taken for further studies, we added a stopper, sodium dimethyldithiocarbamate, as a 1.5–2% aqueous solution.

The surface tension of the latexes was determined in the course of polymerization and after its completion by the ring detachment method with a du Noüy tensiometer (ZAO Polimermash, Russia). The degree of saturation of adsorption layers $A$ (%) of the synthesized latexes was determined by Maron adsorption titration.

The weight-average ($M_w$) and number-average ($M_n$) molecular masses of the polymer were determined by gel permeation chromatography. Samples for chromatography were prepared by coagulation of latex samples with ethanol, followed by vacuum drying at 30–40°C. Then they were dissolved in tetrahydrofuran to obtain a 2 mg $mL^{-1}$ solution. Chromatograms of the samples were obtained with a Waters gel chromatograph (the United States) equipped with refractometric and UV ($\lambda$ = 100–700 nm) detectors, using Breeze system. We used a set of four columns packed with Styragel: HR-1, HR-2, HR-4, and HT-5, intended for separations in the molecular mass ranges 0.1–5, 0.5–20, 5–600, and 50–10 000 kDa, respectively. Chemically pure grade tetrahydrofuran was used as a solvent. The concentration of the solutions was 0.2 g/100 $cm^3$. The device was calibrated using close-cut polystyrene standards (Waters).

The weight-average ($d_w$) and number-average ($d_n$) hydrodynamic sizes of latex particles were determined by dynamic light scattering with a Coulter N 4 analyzer of submicrometer particle size (Coultronics, France), operating on the principle of a correlometer.

After the polymerization completion, we introduced into latex samples a 10% aqueous emulsifier solution in an amount of 5, 10, 15, 20, and 25 wt % relative to the amount present in the system in the polymerization step and measured the stability of the samples obtained. The latex stability was evaluated by its life time $t_L$, i.e., the time up to complete formation of “hard” gel in the latex volume.

The electrokinetic potential of the latexes $\zeta$ was determined with a Zetasizer Nano ZS device (Malvern Panalytical, Netherlands). We determined the surface activity of the dispersing agents and their effect on the critical micelle concentration of ALM-10 solutions.

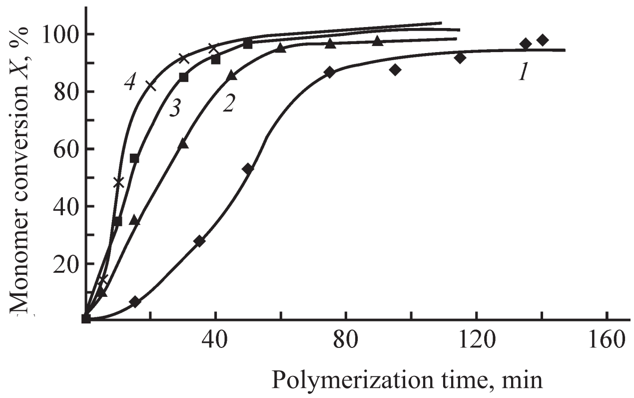

**Fig. 1.** Polymerization kinetics of styrene and mixtures of St with AN in the presence of ALM-10 nonionic surfactant. (*1*) St + 10% ALM-10, (*2*) St + 16% ALM-10, (*3*) St (75 wt %)–AN (25 wt %) mixture + 10% ALM-10, and (*4*) St (80 wt %)–AN (20 wt %) mixture + 10% ALM-10 + 1% TDM.

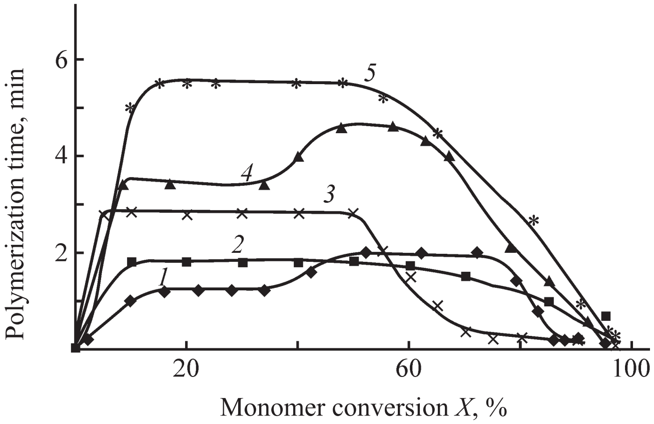

**Fig. 2.** Variation of the polymerization rate of St and St–AN mixtures in the course of the process in the presence of ALM-10 emulsifier. (*1*) 100% St + 10 wt % ALM-10, (*2*) 100% St + 16 wt % ALM-10, (*3*) 75 wt % St + 25 wt % AN + 0.5 wt % DNF-1 + 10% ALM-10, (*4*) 75 wt % St + 25 wt % AN + 10% ALM-10, and (*5*) 75 wt % St + 25 wt % AN + 1% TDM + 10% ALM-10.

## RESULTS AND DISCUSSION

The limiting monomer conversion *X* was 95–97%. Figure 1 shows the kinetic curves of styrene polymerization in the presence of 10 and 16% Sintanol ALM-10 nonionic surfactant and of styrene copolymerization with AN in the presence of TDM.

The latexes prepared in the presence of Sintanol ALM-10 nonionic surfactant appeared to be more stable than those with another nonionic surfactant, OP-14 (Table 2).

As in the case of OP-14, an increase in the content of ALM-10 emulsifier in the formulation from 10 to 16 wt % leads to an increase in the polymerization rate (Fig. 2, curves *1*, *2*), to a decrease in the mean particle size, to an increase in the degree of PMP saturation on reaching the limiting conversion, and to a decrease in the stability of the latexes in storage (Table 2). The most probable cause of the decrease in the stability is increased content of stable macroradicals in PMP on completion of the process.

The gel effect [8] manifested in polymerization of styrene with 10% ALM and described previously [5] is not observed to a noticeable extent on introducing TDM (Fig. 2, curve *5*). Introduction of TDM leads to a decrease in the molecular mass and polydispersity

**Table 2.** Influence of the emulsifier content in the formulation on the stability of the polystyrene latex

| Emulsifier | Surfactant content, wt parts per 100 wt parts of the monomer | Reaction time *t*, min | Limiting conversion of the monomer *X*, % | $d_w$, nm | Degree of saturation of adsorption layers *A*, % | Latex life time $t_L$, min |
|---|---|---|---|---|---|---|
| OP-14 | 6 | 200 | 76 | 83 | 54 | Stable |
| | 8 | 180 | 82 | 76 | 57 | 40 |
| | 10 | 160 | 90 | 73 | 58.6 | 30 |
| | 12 | 135 | 92 | 61 | 60.6 | 20 |
| | 14 | 115 | 96 | 53 | 62.2 | 16 |
| | 16 | 105 | 100 | 48 | 63.8 | 14 |
| ALM-10 | 10 | 140 | 97 | 48 | 60 | 840 |
| | 16 | 90 | 97 | 46.3 | 86 | 560 |

**Table 3.** Effect of TDM on the molecular parameters of the latex and styrene–AN copolymer (75/25)

| Parameter | TDM concentration, wt % relative to monomer | | |
|---|---|---|---|
| | 0 | 0.4 | 1 |
| Reaction time (to >97% conversion), min | 50 | 40 | 35 |
| $M_w$, kDa | 1155 | 272 | 100 |
| $M_w/M_n$ | 3.2 | 2.91 | 2.77 |
| $d_w$, nm | 62.6 | 59.1 | 51.6 |
| $d_w/d_n$ | 1.26 | 1.29 | 1.85 |
| Degree of saturation $A$, % | 65.3 | 72 | 80 |
| $t_L$, min | 15 | 30 | 40 |

coefficient of the polymer ($M_w/M_n$), to termination of the propagating macroradicals, to initiation of new propagating chains due to the chain transfer to the monomer, and to an increase in the polymerization rate after the completion of the induction period. This favors recombination of macroradicals in the PMP volume, makes their high content in PMP after the process completion less probable, and leads to an increase in the degree of saturation of the PMP adsorption layers and in the life time of the system (Table 3). Leveling-off of the gel effect in the presence of chain-terminating agents can be attributed to an increase in the solubility of the polymer in the monomer with a decrease in the molecular mass of the polymer and in the viscosity of the polymer solution.

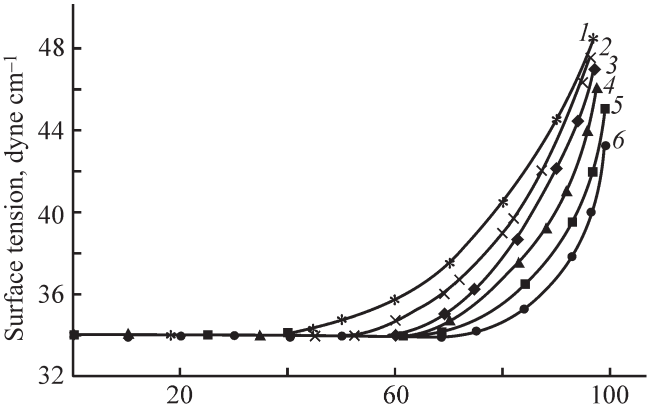

**Fig. 3.** Effect of Leucanol, ALM -10, and TDM on the duration of the micellar period of the polymerization. (*1*) 100% St + 10% ALM-10, (*2*) 75% St + 25% AN + 0.5% Leucanol + 10% ALM-10, (*3*) 75% St + 25% AN + 10% ALM-10, (*4*) 100% St + 16% ALM-10, (*5*) 75% St + 25% AN + 0.4% TDM + 10% ALM-10, and (*6*) 75% St + 25% AN + 1% TDM + 10% ALM-10.

The micellar phase of the polymerization is also made longer by increasing the emulsifier content of the formulation and by introducing the chain-terminating [9, 10] and dispersing agents. After the micellar phase of the polymerization is complete, the surface tension of the latex starts to sharply increase. Leucanol, when incorporated in the adsorption layer, increases the degree of saturation, decreases CMC of the emulsifier, increases the concentration of the micellar soap, and prolongs the micellar step of the polymerization (Fig. 3).

Under the conditions of preservation of polymerization initiators in the system and of the presence of living macroradicals in the PMP volume, the degree of saturation of the PMP adsorption layers is the major factor determining the stability of the latex system. A nonlinear increase in the saturation of PMP adsorption layers with increasing emulsifier concentration ensures attainment of the equal stability of the latexes obtained at different surfactant content of the formulation in preparation of both polystyrene latexes in the presence of OP-14 and of styrene–AN copolymers in the presence of ALM-10 (Fig. 4).

When preparing polymer samples, we took advantage of the coagulating effect of ethanol, accounted for by its dehydrating action on the PMP adsorption layers. AN exerts a similar effect. The true solubility of AN in water is 7.3% and can be attributed to the hydration of the nitrile group. The dehydrating effect of the AN nitrile group on the PMP adsorption layers may be a cause of decreased aggregative stability of AN-containing latexes compared to styrene homopolymers (Fig. 4b).

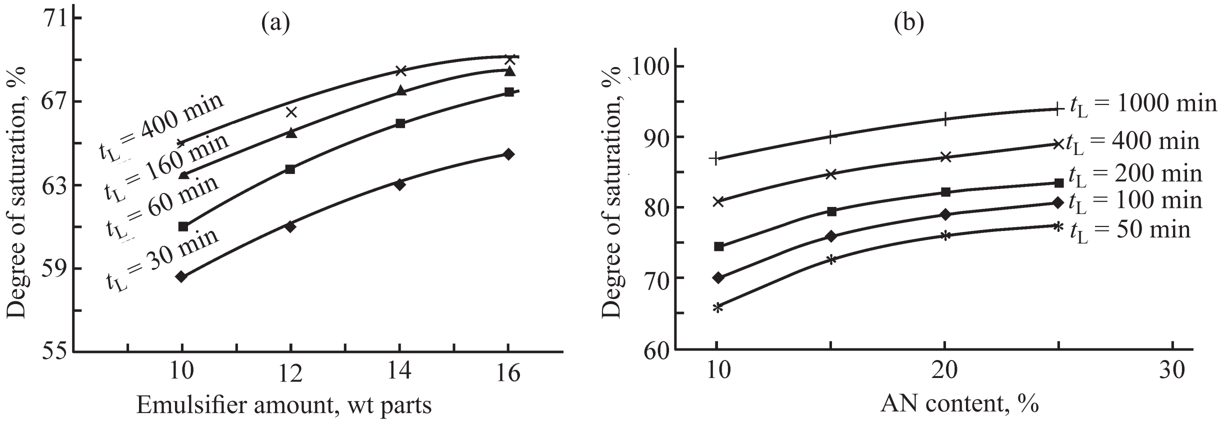

**Fig. 4.** Influence of the degree of the PMP saturation with the emulsifier on the stability of (a) polystyrene latexes at different content of OP-14 nonionic surfactant in polymerization formulation and (b) latexes of St + AN copolymers prepared in the presence of 10% ALM-10 nonionic surfactant at different content of AN in the polymerization formulation.

Introduction of dispersing agents, Leucanol and SP-1, into the polymerization formulation stabilizes the latex, prevents the gelation and coagulum deposition on the reactor walls and stirrer, decreases the mean particle size, and increases the degree of polydispersity (Table 4).

The NMR spectra of surfactant solutions show that introduction of Leucanol into a surfactant solution leads to incorporation of naphthalene units into the hydrocarbon part of surfactant micelles, which influences the structure of the PMP adsorption layer [11]. Incorporation of naphthalene units into the micellar structures of nonionic surfactants (2-naphthol in ALM-10 solution and in a solution of the monomers before the emulsification step) enhances the stability of PMPs in St/AN (75/25) + 10% ALM-10 copolymer latexes. The life time of the latex on introducing naphthol as an emulsifier component (2 wt %) into the polymerization formulation increases from 15 to 240 min.

Introduction of 2-naphthol as an emulsifier component leads to the formation of coarser particles containing the polymer of lower molecular mass but increased degree of polydispersity, as in the case of DNF and SP-1. It cannot be ruled out that incorporation of 2-naphthol into the hydrocarbon part of the PMP adsorption layer increases the role of chain termination and chain transfer to the monomer and enhances the aggregative stability of the latexes.

On the other hand, introduction of 2-naphthol into the monomer does not allow the limiting conversion higher than 75–80%, at which the latex is highly stable, to be reached under equal conditions of the experiment. In the course of polymerization, the concentration (relative to the monomer) of 2-naphthol that is not incorporated in the PMP adsorption layer increases and leads to inhibition of the radical polymerization of the monomers. This leads to an increase in the molecular mass of the polymer, in the degree of saturation of the PMP adsorption layers with the emulsifier, and in the mean PMP size.

This may be associated with the effect of 2-naphthol and its ionized derivatives (DNF-1, DNF-2, SP-1) on the structure of ALM-10 micelles and with the effect of naphthalene moieties on the termination of free macroradicals in the PMP volume.

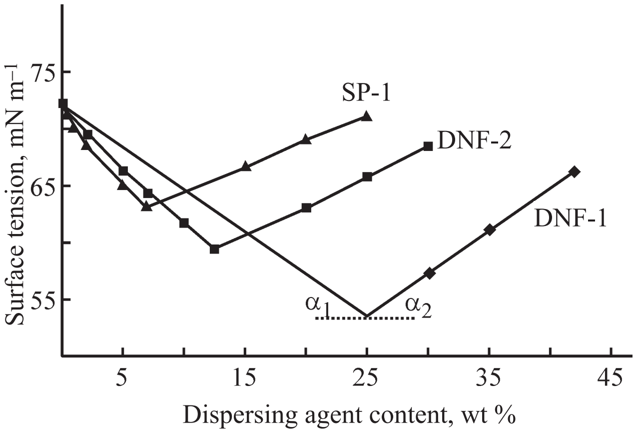

**Fig. 5.** Surface properties of aqueous solutions of dispersing agents.

**Table 4.** Effect of dispersing agents on the latex dispersity and molecular parameters of styrene–AN (75/25) copolymers prepared in the presence of ALM-10 nonionic surfactant (10 wt %)

| Dispersing agent | $c_{disp}$, wt parts | $M_w$, kDa | $M_w/M_n$ | $d_w$, nm | $d_w/d_n$ | Degree of saturation $A$, % | $t_L$, min | $X$, % | ζ, mV |
|---|---|---|---|---|---|---|---|---|---|
| – | 0 | 1155 | 3.85 | 62.6 | 1.26 | 65.3 | 15 | 97 | –1.45 |
| DNF-1 | 0.5 | 1250 | 4.37 | 50.4 | 1.53 | 80 | >3 years | 95 | –3.19 |
|  | 1 | 1413 | 5.72 | 51.6 | 1.56 | 80.6 | >3 years | 97 | –4.02 |
| DNF-2 | 0.5 | 1270 | 4.37 | 50 | 1.52 | 80.9 | 700 | 96 | –3.72 |
| SP-1 | 0.5 | 1300 | 4.45 | 49.4 | 1.49 | 81 | 500 | 98 | –4.31 |
| Naphth-Em | 1 | 500 | 4.85 | 75 | 1.5 | 68 | 240 | 97 | –5.03 |
|  | 2 | 496 | 4.64 | 80 | 1.54 | 71 | 240 | 97 | –7.62 |
| Naphth-M | 1 | 490 | 4.5 | 79 | 1.44 | 72 | >1 year | 80 | –4.32 |
|  | 2 | 489 | 4.73 | 75 | 1.5 | 71 | >1 year | 75 | –5.76 |

Introduction of ionized derivatives of sulfonaphthol into the structure of the PMP adsorption layer ensures the PMP stability at conversions $X \geq 95\%$. The presence of charged sulfo groups in the dispersing agent ensures increased hydration of the PMP adsorption layers but weakly influences the electrokinetic potential of the adsorption layer (Table 4).

The composition of DNF-1 and DNF-2 dispersing agents and of their higher-molecular-mass analog, SP-1, was analyzed by OOO Poliplast-Novomoskovsk (Table 5).

Studies of the surface properties of the dispersing agents confirmed their very low surface activity increasing with an increase in the degree of polycondensation (Fig. 5).

It follows from the results of studying the surface tension of the solution that standard micelle formation is not observed in solutions of the dispersing agents. The surface tension decreases virtually linearly with an increase in the dispersing agent concentration owing to dissolution of dispersing agent molecules in water and formation of primary associates. Accumulation of similar spherical associates usually observed in surfactant solutions in the region of critical micelle concentration (CMC1, formation of micelles with loose hydrate structure; CMC2, formation of micelles with dense packing of hydrate layers; CMC3, transition from spherical to ellipsoidal micelles and then to lamellar structures), apparently, does not occur in solutions of the dispersing agents. The concentration of the dispersing agent at which the surface tension is minimal (Fig. 5) can be considered as an analog of CMC3. As it is exceeded, associates with high degree of hydration of the surface layers are formed. Incorporation of free water into the hydrate structure of such associates is hindered, which leads to an increase in the surface tension at the solution–air interface. This is seen from comparison of the rate at which the surface tension decreases with an increase in the dispersing agent concentration to CMC3 (conventionally) with the rate at which the surface tension increases when this concentration is exceeded. Among all the agents being compared, more hydrated low-molecular-mass DNF-1 exhibits the lowest surface activity (Table 6).

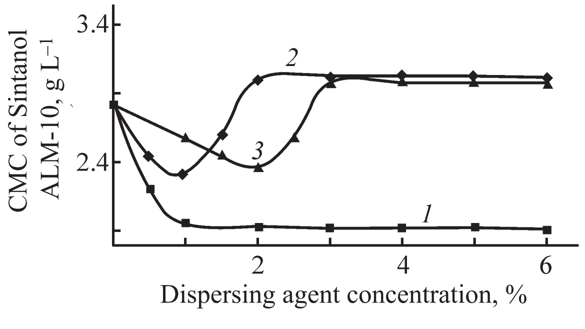

**Fig. 6.** Effect of dispersing agent additions on CMC of ALM-10. (*1*) 2-Naphthol, (*2*) DNF-1, and (*3*) SP-1.

The studies performed have shown that introduction of both the dispersing agents and 2-naphthol leads to a decrease in CMC of the emulsifier. Enhancement of the

**Table 5.** Fractional composition and molecular masses of samples of dispersing agents with different degrees of polycondensation

| Fractional composition | Content, % | | |
|---|---|---|---|
| | -1 | DNF-2 | SP-1 |
| α,β-Salts | 8.9 | 4.7 | 2.8 |
| Salts of disulfonic acids: | 1.9 | 3.4 | 5.2 |
| $n = 2–4$ | 20.8 | 10.7 | 7 |
| $n = 5–8$ | 23.6 | 15.4 | 11.7 |
| $n > 9$ | 45.7 | 65.8 | 73.7 |
| $M_w$, Da | 2942 | 3224 | 3306 |
| $M_n$, Da | 2150 | 2650 | 2340 |
| $M_w/M_n$ | 1.37 | 1.22 | 1.41 |

**Table 6.** Surface properties of naphthalene-containing dispersing agents

| Dispersing agent | Surface activity (tan $\alpha_1$) $G_1$, Gb × $10^{-8}$ | Minimum association concentration, % | Surface activity (tan $\alpha_2$) $G_2$, Gb × $10^{-8}$ |
|---|---|---|---|
| DNF-1 | 2.24 | 25 | –2.24 |
| DNF-2 | 2.68 | 12.5 | –1.65 |
| SP-1 | 2.97 | 10 | –1.45 |

**Table 7.** Surface area occupied by ALM-10 emulsifier in the adsorption laayer of latexes of styrene–AN (75/25) copolymers in the presence of various dispersing agents

| Emulsifier concentration, wt % | Dispersing agent | Dispersing agent concentration, wt % | $c_{coag}$, wt % | $S$, nm$^2$ |
|---|---|---|---|---|
| 10 | – | – | 2 | 62.7 |
| | DNF-1 | 0.5 | 0.3 | 91.6 |
| | | 1 | 0.3 | 91 |
| | DNF-2 | 0.5 | 0.6 | 85.8 |
| | SP-1 | 0.5 | 0.6 | 95.2 |
| | Naphth-Em | 1 | 0.3 | 52 |
| | | 2 | 0.3 | 51.5 |
| | Naphth-M | 1 | 0.3 | 51 |
| | | 2 | 0.3 | 52 |
| 16 | – | – | 1.5 | 67.2 |

stability in all the cases is due to hydrophobization of surfactant micelles upon incorporation of naphthalene units into the structure of the adsorption layer of emulsion droplets and PMPs.

As seen from Fig. 6, the hydrophobic part of the micelle saturated with 2-naphthol is formed at the 2-naphthol content of 10 wt % relative to the micelle-forming surfactant whose concentration is 1 wt % relative to the monomer. In this case, CMC of the emulsifier decreases to a constant level that does not change with a further increase in the 2-naphthol content. When using naphthalene derivatives containing a charged sulfo groups as dispersing agents, the hydrate layer is loosened by more mobile ionized water molecules. This leads to saturation of the structure of the mixed micelles with the dispersing agent, which, in turn, is responsible for the observed increase in CMC of ALM-10 up to a certain dispersing agent concentration corresponding to

**Table 8.** Influence of the copolymer composition on the molecular parameters and stability of latex systems

| Parameter | Styrene/AN copolymer, wt % | | | | | St/AN/EEA 60/20/20 copolymer, wt % |
|---|---|---|---|---|---|---|
| | 100 | 90/10 | 85/15 | 80/20 | 75/25 | |
| $M_{\text{w latex}}$, kDa | 468 | 585 | 605 | 863 | 1155 | 991 |
| $M_{\text{w gel}}$, kDa | 550 | 705 | 740 | 1075 | 1250 | — |
| $M_w/M_n$: | | | | | | |
| latex | 2.77 | 2.73 | 2.75 | 2.79 | 3.2 | 3.39 |
| gel | 2.82 | 2.66 | 2.85 | 3.3 | 3.47 | — |
| $M_{\text{w gel}}/M_{\text{w latex}}$ | 1.175 | 1.205 | 1.223 | 1.245 | 1.255 | — |
| $d_w$, nm | 48.2 | 52.8 | 53.8 | 62.6 | 63.6 | 58 |
| $d_w/d_n$ | 1.81 | 1.5 | 1.35 | 1.25 | 1.26 | 1.08 |
| $A$, % | 60 | 64.9 | 65.7 | 66.4 | 65.3 | 77.6 |
| ζ, mV | –0.5 | –0.8 | –1 | –1.2 | –1.45 | — |
| $V_{II}$, %· min$^{-1}$ | 1.2 | 1.7 | 1.83 | 2.2 | 3.4 | 1.14 |
| $V_{GE}$, %· min$^{-1}$ | 2 | 2.15 | 2.3 | 2.75 | 4.6 | 1.85 |
| $t_L$, min | 840 | 42 | 30 | 25 | 15 | 60 |
| $t_{\text{ж}}/V_{GE}$ | 420 | 19.53 | 13.04 | 9.1 | 3.26 | 32.43 |
| $t_L V_{GE}$ | 1680 | 90.3 | 69 | 68.75 | 69 | 111 |
| $S_e$, Å$^2$ | 72.2 | 71.3 | 70.1 | 65.4 | 62.7 | 97.2 |

the formation of the saturated hydrocarbon structure of the micelles. These changes in the hydrocarbon structure of the PMP adsorption layer are responsible for changes in the stability of the latex systems (Fig. 6).

We calculated the surface area $S$ (nm$^2$) occupied by the ALM-10 molecule in the PMP adsorption layer. Introduction of ionized naphthalene derivatives DNF-1, DNF-2, and SP-1 sharply enhances the PMP stability, decreases the amount of the coagulum formed in the course of the polymerization ($c_{\text{coag}}$), and increases the total surface area of the PMP adsorption layer per surfactant molecule ($S_e$), thus increasing the degree of its hydration (Table 7).

As follows from Table 7, the surface area occupied by a surfactant molecule (ALM-10) in the PMP adsorption layer decreases from 0.627 to 0.52 nm$^2$ in the presence of 1 wt % 2-naphthol relative to the monomer and to 0.515 nm$^2$ in the presence of 2 wt % 2-naphthol relative to the monomer.

The formation of the hydrocarbon structure of the micelles, reached at the minimal CMC of the nonionic surfactant solution, enhances the PMP stability. Dispersing agents with lower degree of polycondensation ensure the formation of more stable latex systems at equal content in the emulsion. The presence of ionized sulfo groups in the dispersing agent favors enhancement of PMP stability compared to naphthol with an insignificant change in the degree of PMP saturation and a considerable increase in the surface area occupied by the nonionic surfactant molecule due to hydration of the sulfo groups of the dispersing agent (to 0.85–0.95 nm$^2$, Table 7).

An increase in the dispersing agent concentration in the solution over the level corresponding to saturation of the hydrocarbon structure favors an increase in the hydration of the nonionic surfactant molecule and in CMC of the nonionic surfactant. As the hydrated part of the PMP adsorption layer becomes saturated with sulfo groups, CMC of the nonionic surfactant does not longer change. For the dispersing agents with the lower degree of polycondensation and higher mobility of hydrated water molecules, this saturation occurs at a lower concentration of the dispersing agent in the surfactant solution.

Comparison of the systems obtained using different naphthalene derivatives shows that the dispersing agent composition influences the latex stability in the case of preparation of both thermoplastic acrylate rubbers and styrene–AN copolymers. As can be seen, it is appropriate to use dispersing agents with lower degree of polycondensation for stabilizing PMP both in the polymerization step and in the step of distillation of the monomers.

Introduction of a polar comonomer, AN, decreases the stability of the latex system, despite certain increase in the degree of saturation of PMP adsorption layers, and leads to an increase in the molecular mass, degree of polydispersity, and mean particle diameter.

An increase in the AN content of the copolymer leads to an increase in the reaction rate, i.e., in the rate of formation of polymer chains in unit time, in the period of constant rate $V_{\mathrm{II}}$ and in the rate of accumulation of free macroradicals in the step of the gel effect ($V_{\mathrm{GE}}$), which is particularly pronounced at AN concentrations $c_{\mathrm{AN}} \geq 15$ wt %. At monomer conversions higher than 80–85%, the process decelerates, with this trend being weakly dependent on the AN content. On the other hand, an increase in the AN content leads to an increase in $M_{\mathrm{w}}$ at virtually constant degree of polydispersity at the AN content in the range 0–25%. An increase in the AN content in the range 15–25% leads to a linear increase in the molecular mass of the polymer and to a linear decrease in the area occupied by an ALM-10 molecule in the PMP adsorption layer.

An increase in the molecular mass of the polymer due to recombination of stable free radicals is observed in the gelation step when PMPs undergo coalescence and, to a minor extent, in the course of further storage of the gel, which suggests the presence of free living macroradicals in the PMP volume after the polymerization completion. The recombination of the macroradicals can be judged from an increase in the molecular mass upon gelation ($M_{\mathrm{w\ gel}}/M_{\mathrm{w\ latex}}$ ratio). This ratio does not noticeably change at the AN content of the copolymer $c_{\mathrm{AN}} \geq 10\%$ (Table 8).

Introduction of EEA into the copolymer enhances the hydration of the adsorption layer owing to the presence of the ethoxy group (similar to groups in nonionic surfactant molecules) in the comonomer, which, in turn, enhances the latex stability and leads to a considerable increase in the surface area occupied by the surfactant molecule in the adsorption layer.

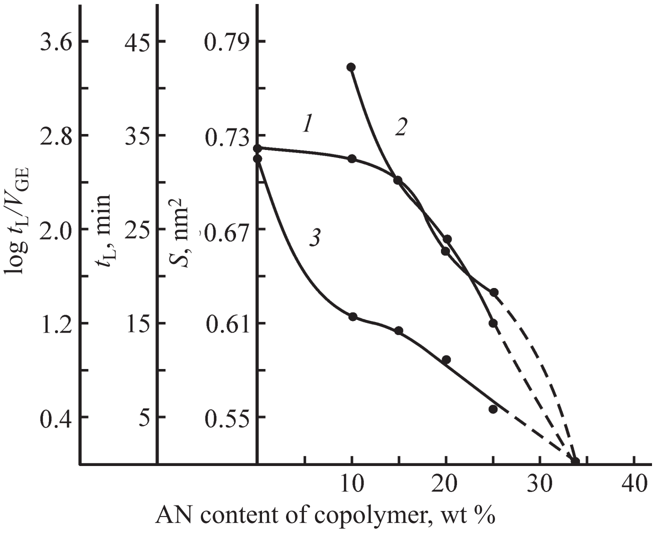

**Fig. 7.** Influence of the AN content of the copolymer on factors determining the aggregative stability of latexes. (*1*) Area of the ALM-10 molecule in the PMP adsorption layer, (*2*) life time, and (*3*) resistance to the action of macroradicals (log $t_{\mathrm{L}}/V_{\mathrm{GE}}$).

The dehydrating effect of the AN nitrile group in the copolymer on the PMP adsorption layers is due to its electrostatic effect on hydrogen bonds formed by ethoxy groups of ALM-10 emulsifier and water molecules in the adsorption layer of PMPs of this copolymer [12]. This effect is manifested at the AN content of 15–25%. The area occupied by the ALM-10 molecule in the adsorption layer decreases from 0.701 nm$^2$ for the St/AN 85/15 copolymer to 0.627 nm$^2$ for the St/AN 75/25 copolymer. However, the degree of hydration of the nonionic surfactant molecule in the PMP adsorption layer is not the main parameter determining the stability of the latex system. The latexes obtained with introduction of 2-naphthol into the emulsifier formulation exhibit high stability and are characterized by decreased area occupied by the emulsifier molecule in the adsorption layer: 0.51–0.52 nm$^2$.

We believe that the major energy factor responsible for the loss of the aggregative stability of latex systems is the activity of free macroradicals, manifested in an increase in the van der Waals–London intermolecular attraction forces. This is confirmed by the prevention of the gelation and preservation of the latex stability on introducing agents stopping radical processes. We did not have technical opportunities to determine the amount and structure of the macroradicals remaining in the PMP volume. Taking into account the fact that macroradicals are accumulated in the gel effect step, we can assume that their concentration is proportional to the rate of formation of polymer chains in the gel effect step.

If we assume that the gel effect rate determines the concentration of free macroradicals accumulating in the system and that the life time is the time of the destabilizing action of macroradicals on the adsorption layer, determining the work required to overcome the energy protection of the adsorption layer, then $t_L V_{GE}$ determines the extent of PMP stabilization by the adsorption surfactant layer (Table 8) and changes in the dispersion attraction forces that cause the particle coalescence in the course of the latex storage and sharply increase when the PMPs contain stable macroradicals in their volume. In going from the polystyrene latex to polystyrene–AN copolymers, $t_L V_{GE}$ sharply decreases already at 10 wt % content of AN in the copolymer and remains approximately constant with a further increase in the AN content from 15 to 25%. Introduction of EEA, a polar monomer containing ethoxy groups enhancing the hydration of the adsorption layer ($S_e$), into the copolymer leads to an increase in $t_L V_{GE}$ and enhances the stability of the system ($t_L$). The parameter $t_L/V_{GE}$ reflects the resistance of the system to the action of macroradicals, because $V_{GE}$ reflects the degree of recombination of macroradicals in the PMP volume in the period of viscosity growth when the monomer concentration decreases, the polymer concentration increases, the rates of diffusion processes decrease, and the rate of accumulation of macroradicals in the PMP volume increases. The quantity $t_L/V_{GE}$ sharply decreases in going from polystyrene latexes to styrene–AN copolymers (Table 8), which is due not only to the dehydrating action of the AN nitrile group on the PMP adsorption layers, but also to a sharp increase in the van der Waals intermolecular attraction forces [12] between PMPs with an increase in the AN content of the copolymer. On the other hand, introduction of EEA, which enhances the hydration of the adsorption layer, into the copolymer leads to stabilization of the system and to a sharp increase in $t_L/V_{GE}$. For polystyrene and styrene–AN copolymers, correlation is observed between the latex life time, resistance of the system to the action of stable macroradicals, and area occupied by the emulsifier molecule in the PMP adsorption layer (Fig. 7).

As follows from Fig. 7, complete destabilization of the system ($t_L = 0$) should be expected at the AN content of the copolymer higher than 34 wt %. At the AN content higher than 40%, the loss of the aggregative stability followed by gelation was observed at the monomer conversion exceeding 90%.

## CONCLUSIONS

The role of naphthalenesulfonic dispersants (Leucanol, SP-1) consists in enhancement of the stability of latex systems in the steps of polymerization and distillation of the monomers due to an increase in the degree of saturation of polymer–monomer particles, a decrease in CMC of the emulsifier, extension of the micellar period of the polymerization (from 35–40 to 60–80% monomer conversion), and shortening of the period in which stable macroradicals are accumulated in the volume of polymer–monomer particles. Introduction of 2-naphthol also decreases CMC of the emulsifier and enhances the aggregative stability of polymer–monomer particles, but to a considerably lesser extent compared to the introduction of naphthalenesulfonic compounds dramatically enhancing the stability of polymer–monomer particles owing to an increase in the hydration of nonionic surfactant molecules.

Introduction of naphthalene derivatives into the monomer emulsion alters the structure of the hydrocarbon part of the micelles and of the adsorption layer of the emulsion droplets and polymer–monomer particles formed. In the process, the recombination of macroradicals formed in the course of polymerization and localized in the volume of polymer–monomer particles is accelerated, which increases the molecular mass of the polymer. This leads to a decrease in the content of stable macroradicals in the volume of polymer–monomer particles, to a decrease in the forces of electrokinetic (dispersion) interaction between polymer–monomer particles, and to enhancement of the aggregative stability of latex systems.

An increase in the mean molecular mass of the polymer on introducing the dispersing agent under industrial conditions should be compensated by introducing chain-terminating agents like tert-dodecyl mercaptan, which prevent the formation of branched structures in copolymerization of dienes, decrease the molecular mass of the polymer with only a slight effect on the polydispersity coefficient, and control the recombination of macroradicals.

With an increase in the degree of polycondensation of naphthalene-containing dispersing agents, the surface activity of dispersing agents increases and their ability to support the aggregative stability of latexes decreases. Thus, to enhance the stability of latexes, it is more appropriate to use compounds with high content of low-molecular-mass fractions.

An increase in the acrylonitrile content in the polymerization formulation leads to a decrease in the degree of hydration of nonionic surfactant molecules in the adsorption layer of polymer–monomer particles and to an increase in the stability of the system; however, this is not the main cause of the loss of the aggregative stability of polymer–monomer particles in gelation.

Introduction of monomers that increase the degree of hydration of the surface layer of polymer–monomer particles (ethoxyethyl acrylate) into copolymers enhances the stability of the latexes.

The main cause of gelation in latexes is, apparently, the presence of stable macroradicals in the volume of polymer–monomer particles, because introduction of radical reaction stoppers prevents the gelation and stabilizes the latex systems. The ratio of the system life time to the polymerization rate in the gel effect step can be considered as a measure of the resistance of the system to the action of macroradicals.

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## REFERENCES

1. Gusev, Yu.K. and Papkov, V.N., *Kauchuk Rezina*, 2009, no. 2, pp. 2–9.
2. Poluektov, P.T. and Vlasova, L.A., *Prom. Proizv. Ispol'z. Elastom*., 2011, no. 4, pp. 31–36.
3. Poluektov, P.T., Vlasova, L.A., and Shutilin, Yu.F., *Ekol. Prom–st. Ross*., 2006, no. 12, pp. 19–24.
4. Poluektov, P.T., Vlasova, L.A., and Yurkina, L.L., *Ekol. Prom–st. Ross*., 2008, no. 1, pp. 24–28.
5. Beresnev, V.N., Kraynik, I.I., Baranets, I.V., and Agibalova, L.V., *Russ. J. Appl. Chem*., 2018, vol. 91, no. 7, pp. 1137–1145.
6. Gao, J. and Penlidis, A., *Prog. Polym. Sci*., 2002, vol. 27, no. 3, pp. 403–535.
7. Thickett, S. and Gilbert, R., *Macromolecules*, 2006, vol. 39, no. 6, pp. 2081–2091.
8. Chekal, B.P., *Understanding the Roles of Chemically-controlled and Diffusion-limited Processes in Determining the Severity of Autoacceleration Behavior in Free Radical Polymerization*, Northwestern Univ., 2002.
9. Yanlin, S. and Yanping, H., *Iran. Polym. J*., 2015, vol. 24, no. 11, pp. 935–944.
10. Tauer, K. and Hernandez, H., *Colloid Polym. Sci*., 2008, vol. 286, no. 5, pp. 499–515.
11. Shapiro, Yu.E., *Russ. Chem. Rev*., 1988, vol. 57, no. 8, pp. 717–719.
12. Ingold, C.K., *Structure and Mechanism in Organic Chemistry*, London: Cornell Univ. Press, 1969.