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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Free Macroradicals in Synthesis, Storage, and Processing of Synthetic Latexes and Polymers

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Abstract—The effect of radical polymerization inhibitors on the aggregative stability of latexes of styrene copolymers with acrylonitrile and ethoxyethyl acrylate, prepared with Sintanol ALM-10 nonionic emulsifier, was studied. Stable free macroradicals can be one of the factors responsible for the loss of the aggregative stability of the latexes. The mechanism of the action of macroradicals on the adsorption layer of polymer–monomer particles was suggested, and the stabilizing power of naphthalene-containing dispersants was accounted for on the basis of this mechanism.

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

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As shown previously [1, 2], the role of dispersants, sulfonated products of naphthalene polycondensation with formaldehyde (Daxad 11, Leukanol), consists not only in stabilization of latexes in the course of synthesis, monomer distillation, and storage, especially without radical polymerization inhibitors, but also in localization of the recombination reactions of stable free macroradicals in the volume of the polymer–monomer particle in the course of the synthesis. This was demonstrated by the example of latexes of polystyrene and its comonomers with polar monomers: acrylonitrile and ethoxyethyl acrylate. It was shown that the latex stability is determined by saturation of the adsorption layers of polymer–monomer particles, and one of the causes of the disturbance of the polymer–monomer particle stability is the activity of macroradicals in the volume of polymer–monomer particles in the gel effect step and in the final polymerization step. The stability of latex systems is enhanced by adding inhibitors of radical processes. Published data demonstrate the possibility of the desorption of radicals [3–7] from polymer–monomer particles and their destabilizing effect on the adsorption layer of latex particles [8–12]. The mechanism of the destabilizing effect of the radicals on the stability of the latexes is not fully understood, and further study of this problem can be extremely useful for understanding the relationships of radical polymerization of vinyl monomers.

This study was aimed at determining the cause of the enhancement of the latex stability on introducing inhibitors and at evaluating the effect of macroradicals on the stability of polymer–monomer particles and on the molecular parameters of the polymer in the course of the synthesis, heat treatment, and subsequent storage of the polymer.

EXPERIMENTAL

The conditions of performing the emulsion copolymerization of styrene with acrylonitrile and ethoxyethyl acrylate using nonionic surfactants were described previously [1, 2]. Latexes of acrylate rubbers (copolymers based on butyl and ethoxyethyl acrylates) with acrylonitrile and methacrylic acid were prepared in the presence of a chain-terminating agent, tert-dodecyl

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[†] Deceased.

mercaptan, similarly to the commercial formulation, in the presence of sodium alkanesulfonate, a dispersant (Leukanol), and initiators (potassium persulfate and pinane hydroperoxide). Rongalite was as a reductant.

The pH of the emulsion before introducing the initiator was 7.5 ± 0.1 in synthesis of styrene copolymers with the nonionic emulsifier and 3.5–3.7 in synthesis of carboxyl-containing acrylate rubbers.

The pH measurements were performed with an HI 2020 device (Hanna Instruments, the United States).

The monomer conversion was determined from the amount of the dry residue in the samples taken in the course of the polymerization. The limiting conversion of the monomers was ≥96%. A radical polymerization inhibitor, sodium dimethyldithiocarbamate as a 1.5–2% aqueous solution, was added to the latex samples intended for storage in an amount of up to 0.5 wt % relative to the polymer.

The polymerization temperature in synthesis of acrylate rubbers to 85–87% conversion was 35–40°C; the ≥96% conversion was reached at 55–60°C. Inhibition of latexes of carboxylate rubbers prior to distillation of the residual monomers (pH < 4.0) was performed with an $NaNO_2$ solution and with a dispersion of 2,2,6,6-tetramethylpiperidine-1-oxyl (0.35–0.5 wt % relative to the polymer).

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 the adsorption layers (A, %) of the synthesized latexes was determined by the Maron adsorption titration method.

The weight-average (M_w) and number-average (M_n) molecular mass of the polymer was determined by gel permeation chromatography. Samples for the 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. The chromatograms of the samples were obtained on a Breeze gel chromatograph (Waters, the United States) equipped with two detectors: refractometric and UV ($\lambda = 100–700$ nm). We used a set consisting of four Styragel columns: HR-1, HR-2, HR-4, HT-5, ensuring separation 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 solution concentration was 0.2 g/100 cm^3. The device was calibrated against close-cut polystyrene standards (Waters, the United States).

The weight-average (d_w) and number-average (d_n) hydrodynamic sizes of latex particles were determined by dynamic light scattering with a Coulter no. 4 submicrometer particle size analyzer (Coultronics, France) operating as a correlometer.

The influence of the kind of inhibitors on the stability of styrene copolymer latexes was studied in experiments in which these inhibitors were introduced into latexes containing nonionic emulsifiers after the polymerization completion (≥97% conversion of the monomers).

The following substances were introduced into the latexes: a solution of 2,2-diphenyl-1-picrylhydrazyl in methanol, a dispersion of a 50% solution of tetramethylpiperidine-N-oxyl in toluene (Yarsintez Research and Production Association, Russia) in a Sintanol ALM-10 solution, and an aqueous solution of sodium dimethyldithiocarbamate (OAO Vekton, Russia). The inhibitor types are presented in Table 1.

The following radical process inhibitors were used in synthesis of carboxylate acrylate rubbers at pH ≤ 4.0: a 1–1.5% $NaNO_2$ solution and an RNO dispersion. The stability of acrylate latexes was estimated from the amount of the coagulum (wt % based on the monomer) upon distillation of the monomer from the latex (65–66°C) and from the change in the latex dispersity in the course of distillation. The polymer stability in the latex was evaluated by changes in the molecular parameters of the polymers (M_w, M_w/M_n) in the course of the monomer distillation.

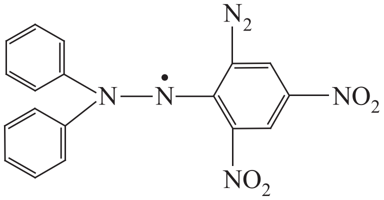
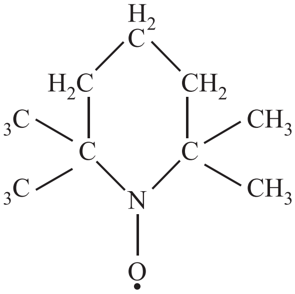
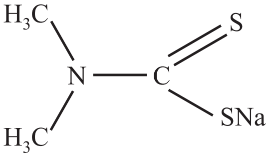
The polymerization activation energy was calculated from the data on the reaction rates.

The kinetics of a decrease in the concentration of macroradicals in the system was determined by EPR with an EPR-10 Mini device (OOO Rezonans-M, Russia) using Ippon inhibitor (tetramethylpiperidine-N-oxyl) as a marker.

RESULTS AND DISCUSSION

Previous studies on the effect of Leukanol dispersant on the latex stability both in the course of styrene homopolymerization and copolymerization with polar monomers, acrylonitrile and ethoxyethyl acrylate, and of latex storage have shown that the major cause of

Table 1. Inhibitors introduced into styrene–acrylonitrile copolymer latexes containing Sintanol LM-10 nonionic emulsifier

Designation	Name	Chemical formula	Introduction mode
DPPH	2,2-Diphenyl-1-picrylhydrazyl		0.1 wt % solution in methanol
RNO	2,2,6,6-Tetramethylpiperidine-1-oxyl, TU (Technical Specification) 2415-025-05842324–2003		0.4 wt % dispersion in 1.5% aqueous solutions of Sintanol ALM-10
DDTC	Sodium dimethyldithiocarbamate, GOST (State Standard)		1 wt % aqueous solution

the loss of the polymer–monomer particle stability is the presence of free unrecombined macroradicals in polymer–monomer particles. Such macroradicals exert a destabilizing effect on hydrate adsorption layers. With respect to the water content, the coagulum is close to the state of the gel formed in the course of the latex storage [1].

The resistance of the adsorption layer of polymer–monomer particles to the action of macroradicals can be evaluated by the radio of the latex lifetime to the polymerization rate in the gel effect step, in which the overall polymerization rate increases because of a decrease in the termination of propagating macroradicals and in the rate of diffusion processes with an increase in the viscosity in the reaction volume of polymer–monomer particles [2]. The Harkins–Yurzhenko general theory of emulsion polymerization suggests that the rates of the initiation and termination of the propagating polymer chains in the volume of polymer–monomer particles remain constant up to the onset of the gel effect. The copolymerization constants are determined at a low monomer conversion (5–7%), and the kinetic relationships, including those forming the basis for the theory of emulsion polymerization, are based on determination of the polymerization rate in the period of constant rate before the onset of the gel effect. This parameter was taken as the main parameter in optimization of the formulation for the emulsion polymerization of styrene in the presence of nonionic emulsifiers under the influence of a reversible redox system similar to that used for similar purposes in our previous studies [13]. The molecular-mass characteristics of the polymers obtained are the major factor in production of commercial emulsion rubbers (butadiene–styrene, butadiene–acrylonitrile, acrylate, etc.).

In synthesis of butadiene–acrylonitrile rubbers without chain-terminating agents in the reaction system, high-molecular-mass copolymers constituting the poorly soluble gel fraction are formed already at 5–7% conversion of the monomers [14]. Microgel-free soluble diene polymers (whose formation is determined by the presence of a double bond in the polymer structure) with the required molecular mass level are prepared by introducing chain-terminating agents leading to the chain termination and transfer to the monomer with restriction of the limiting conversion of the monomers (usually no more than 70%).

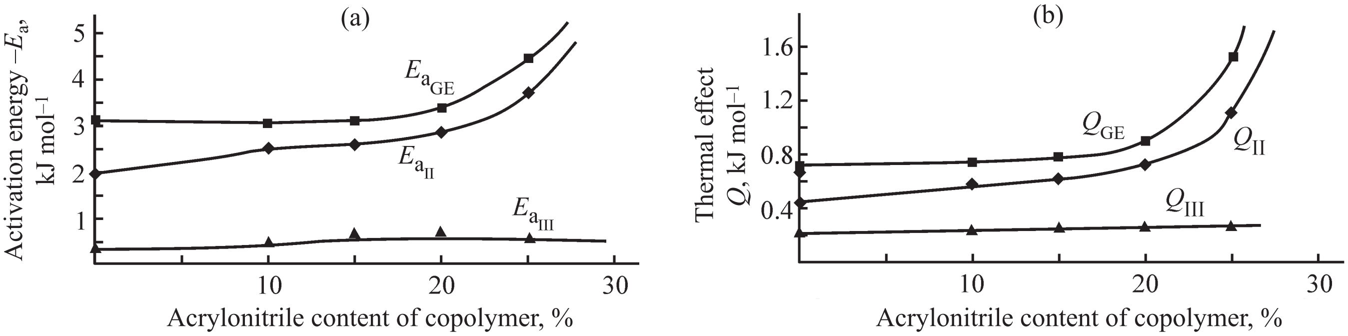


Fig. 1. (a) Activation energy of chain propagation in different steps of styrene copolymerization with acrylonitrile and (b) thermal effect of styrene copolymerization with acrylonitrile.

In polymerization of vinyl compounds (styrene, acrylonitrile, acrylates, etc.), recombination of macroradicals occurs with the backbone propagation (increase in M_w) and with an increase in the polymer polydispersity; the formation of branched and cross-linked structures and of insoluble gel is, as a rule, excluded. The emulsion polymerization theory suggests an increase in the content of unrecombined macroradicals with the consumption of the free monomer, a decrease in the contribution of the polymer chain propagation reactions, and an increase in the viscosity and in the concentration of propagating macroradicals in the reaction volume of polymer–monomer particles. Just these factors account for an increase in the polymerization rate in the gel effect step (monomer conversion 40–45%).

Analysis of variations in the polymerization rate, monitored up to high conversion of the monomers, in the molecular characteristics of the copolymer, in the size of latex particles in the course of polymerization, and in the saturation of the adsorption layers of the latex particles (Table 2) reveals the following trends.

The initial induction period is followed by a constant-rate period (up to 40 ± 5% conversion of the monomers) whose relationships form the basis of the existing emulsion polymerization theories (Smith–Ewart, Yurzhenko, Medvedev).

After the completion of the first constant-rate period (second polymerization step starting immediately after the induction period), coinciding with the disappearance of the monomer microemulsion ensuring constant composition of the saturated solution of the monomer in the polymer in the volume of polymer–monomer particles, the polymer concentration and the amount of propagating macroradicals increase, which leads to an increase in the polymerization rate (gel effect step), remaining constant up to 60–65% conversion when there are no dispersants in the system.

On reaching ≥65% conversion, which coincides with the step of exhaustion of the micellar emulsifier and with the onset of the increase in the surface tension of the latex system, the polymerization rate sharply increases (third polymerization step). This period is characterized by the particle agglomeration and by an increase in the particle diameter (d_w), in the ratio of the weight-average to number-average particle diameter (d_w/d_n), in the molecular mass of the polymer (M_w), and in the polydispersity coefficient (M_w/M_n), which is characteristic of macroradical recombination.

No gel effect is observed if the polymerization formulation contains a dispersant. When a chain-terminating agent is introduced into the reaction mixture, the molecular mass does not increase in the end of polymerization either. Naphthalene-containing dispersants, when incorporated into the structure of the adsorption layer of polymer–monomer particles, reduce the interaction of macroradicals, whereas the chain-terminating agent reduces the size of macroradicals and facilitates their recombination.

In our case, synthesis of latexes in the presence of cross-linking agents of triallyl isocyanurate type, ensuring formation of branched and cross-linked macrostructures, does not lead to a large decrease in M_w at 25% content of acrylonitrile in the copolymer and favors an increase in the copolymer polydispersity and, probably, the recombination of macroradicals remaining in the volume of the polymer–monomer particles.

We calculated the activation energies of the three distinguished polymerization steps and the heat release rates in these steps, taking into account the heat of the

Table 2. Molecular parameters of styrene–acrylonitrile copolymers in various polymerization steps

Latex type	Degree of polymerization	X, %	M_w, kDa	M_w/M_n	d_w, nm	d_w/d_n	Polymerization rate, % min^{-1}	Completeness of micellar period, %
Styrene/acrylonitrile 85/15	Beginning of second	5.2	550	2.1	50.1	1.53	1.83	52
	End of second	32	570	2.6	52.3	1.58	1.83	
	Beginning of gel effect	36	560	2.75	49.1	1.49	2.3	
	End of gel effect	64	580	2.6	50.8	1.68	2.3	
	Beginning of third	67	590	3	52.8	1.72	2.3	
	End of third	97	605	3.13	53.8	1.71	0.1	
Styrene/acrylonitrile 75/25	Beginning of second	8.5	950	3.68	63.2	1.3	3.4	55
	End of second	35	980	3.49	64.2	1.35	3.4	
	Beginning of gel effect	40	1029	3.47	65.2	1.4	4.5	
	End of gel effect	60	1078	3.52	68.9	1.73	4.6	
	Beginning of third	63	1151	3.6	73.1	2.18	4.6	
	End of third	97	1155	3.65	75.1	2.65	0.1	
Styrene/acrylonitrile 75/25 + 0.5 wt % Leukanol	Beginning of second	6	507	2.43	50.3	1.28	2	60
	Beginning of third	63	1027	3.15	47.1	1.46	2.5	
	End of third	97	1250	3.37	48.1	1.52	0.1	
Styrene/acrylonitrile 75/25 + 1 wt % Leukanol	Beginning of second	5	708	2.57	50.3	1.46	2.8	65
	Beginning of third	55	1200	3.48	50.8	2.1	1.2	
	End of third	97	1240	3.56	51.6	2	0.1	
Styrene/acrylonitrile 75/25 + 0.4 wt % *tert*-dodecyl mercaptan	Beginning of second	7	233	4.07	92.2	1.93	5.1	69
	End of second	40	326	3	65	1.28	5.1	
	Beginning of gel effect	43	312	3.93	62.1	1.31	5.3	
	End of gel effect	64	264	3.28	59.1	1.22	5.4	
	Beginning of third	68.4	242	3.1	59	1.23	5.2	
	End of third	97	229	2.97	58.9	1.24	0.1	
Styrene/acrylonitrile 75/25 + 1 wt % *tert*-dodecyl mercaptan	Beginning of second	7.5	40	2.6	94.3	2.7	5.5	70
	End of second	41	220	2.56	75.3	2.1	5.5	
	Beginning of gel effect	45.3	390	2.44	62.6	1.5	5.7	
	End of gel effect	63	150	2.49	60.6	1.7	5.8	
	Beginning of third	68.3	105	2.5	58.9	1.8	2.7	
	End of third	98	100	2.77	73.5	1.85	0.1	
Styrene/acrylonitrile 85/15 + 0.5 wt % triallyl isocyanurate	Beginning of second	5	–	–	–	–	2.35	–
	End of second	40	–	–	–	–	2.4	
	Beginning of gel effect	42	–	–	–	–	3	
	End of gel effect	60	–	–	–	–	2.9	
	Beginning of third	62	–	–	–	–	0.1	
	End of third	97	607	3.7	88.6	1.93	1.27	

Table 2. (Contd.).

Latex type	Degree of polymerization	X, %	M_w, kDa	M_w/M_n	d_w, nm	d_w/d_n	Polymerization rate, % min^{-1}	Completeness of micellar period, %
Styrene/acrylonitrile 85/25 + 0.5 wt % triallyl isocyanurate	Beginning of second	5	–	–	–	–	2.8	–
	End of second	39.1	–	–	–	–	2.8	–
	Beginning of gel effect	44	–	–	–	–	3.1	–
	End of gel effect	60	–	–	–	–	3	–
	Beginning of third	63	–	–	–	–	2.9	–
	End of third	97	995	4.52	92.3	2.1	0.1	–

polymerization of the monomers (Fig. 1), for styrene–acrylonitrile copolymers of different compositions. The results obtained demonstrate the polymerization acceleration with an increase in the copolymer polarity (acrylonitrile content), which, however, does not noticeably influence the rate in the final, third step of the polymerization. The result obtained suggests that, in our case, the adsorption layer of polymer–monomer particles, saturated in the constant-rate steps (second step and gel effect step) with he solubilized monomer before the disappearance of the micellar emulsifier from the aqueous phase, should be considered as the reaction zone (microvolume).

In the period of the initial constant rate and saturation of the volume of polymer–monomer particles with the monomer, the polymerization rate is determined by the concentration of the initiator and emulsifier, which determine the number of the polymer–monomer particles formed and the total surface area of the adsorption layer.

Based on the Medvedev's concept [15] that the polymerization is localized in the adsorption layer zone, we can account for the fact that the molecular parameters of the formed copolymer in the second polymerization step and in the gel effect step remain constant. The concentration of the monomer supplied from the volume of polymer–monomer particles before the onset of the increase in the surface tension of the latex system, caused by exhaustion of the micellar emulsifier, in the reaction volume in the gel effect step is maintained constant.

By this moment, the content of the free monomer in the volume of polymer–monomer particles becomes extremely low, and supply of the monomer to the reaction microvolume from the volume of polymer–monomer particles stops. The polymerization starts to decelerate to reach a certain constant value until the limiting conversion (≥97%) is attained. Until this moment, the monomer solubilized in the hydrocarbon moiety of the emulsifier is supplied to the reaction microvolume. The reaction rate and polymerization activation energy in the third step are considerably lower than in the initial step and in the gel effect step. In the process, the aggregative stability of the polymer–monomer particles decreases. In this step, M_w and M_w/M_n increase owing to recombination of macroradicals accumulated in the volume of the polymer–monomer particles.

Introduction of chain-terminating agents into the polymerization formulation favors a decrease not only in the molecular mass, but also in the macromolecule polydispersity.

Introduction of cross-linking agents of the triallyl isocyanurate type into the formulation leads to a slight decrease in M_w at 25% content of acrylonitrile in the copolymer and favors an increase in the copolymer polydispersity and, apparently, the recombination of macroradicals remaining in the volume of polymer–monomer particles; it also enhances the aggregative stability of the latex (Table 3). Cross-linked structures and insoluble polymer are not formed in the process.

As already noted [2], Leukanol dispersant mainly influences the stability of the adsorption layer of latex particles. It ensures high stability of the latex and prevents gelation in the latexes at concentrations higher than the concentration of saturation of the hydrocarbon part of the adsorption layer with naphthalene units. In this case, M_w and M_w/M_n increase, probably owing to recombination of the propagating macroradicals in the volume of polymer–monomer particles and reduction of their effect on the hydrate structure of the adsorption layer.

Table 3. Changes in molecular parameters of the polymers recovered from the gel after 3-month storage

Acrylonitrile content of copolymer, wt %	Latex lifetime, min	M_w, kDa		M_n, kDa		M_w/M_n		d_w, nm	
		latex	gel	latex	gel	latex	gel	latex	gel
0	840	468	550	195	197	2.77	2.82	48.2	150
10	40	585	705	214	220	2.73	2.66	52.8	145
15	35	605	740	193	200	3.13	3.7	53.8	160
20	25	863	1075	310	325	2.79	3.3	63.6	170
25	15	1155	1250	317	360	3.65	3.47	62.6	173
25 + 0.5 wt % Leukanol	>3 years	1240	–	348	–	3.56	–	50.4	–
25 + 0.4 wt % *tert*-dodecyl mercaptan	30	272	–	93.5	–	2.91	–	59.1	–
15 + 0.5 wt % triallyl isocyanurate	50	607	720	164.1	190	3.7	3.72	88.6	130
25 + 0.5 wt % triallyl isocyanurate	30	995	1100	239.1	250	4.52	4.6	92.3	150

As noted in [16] and confirmed in this study, latex systems with nonionic emulsifiers are stabilized by introducing rongalite reductant both separately and as a part of an additional portion of the whole redox system after the process completion. This fact suggests the presence of a functional group with oxidant properties in the living macroradical.

Accumulation of free macroradicals in the volume of polymer–monomer particles is possible in the gel effect step, and their recombination is possible in the third step of the polymerization when the free monomer disappears from the volume of polymer–monomer particles upon particle coalescence.

We studied the effect of radical polymerization inhibitors on the aggregative stability of latexes of styrene copolymers with acrylonitrile and ethoxyethyl acrylate with Sintanol ALM-10 nonionic emulsifier.

Two kinetic portions of latex stabilization with the inhibitors can be distinguished in the dependence of the latex lifetime on the inhibitor content of the stabilized sample (Fig. 2).

The step of the active stabilization (macroradical quenching) is the portion of a linear increase in the stability with an increase in the inhibitor content of the latex, reflecting the result of the molecular action of the inhibitor on living macroradicals affecting the stability of the adsorption layer of the polymer–monomer particles. In this step of stabilization of polymer–monomer particles, the latex lifetime is directly proportional to the inhibitor concentration. The inhibitor concentration at the end of this portion is denoted as $c_{\mathrm{lim,lin}}$.

The step of the decelerated stabilization (macroradical quenching) is the portion of an exponential increase in the stability of polymer–monomer particles with an increase in the content of the inhibitors in the latex, reflecting the kinetics of the decay of the macroradicals affecting the stability of the adsorption layers of polymer–monomer particles. Apparently, when the quenching of the stable macroradicals becomes complete, the latex system becomes stable in time. The inhibitor concentration after the completion of this portion is denoted as $c_{\mathrm{lim}\,\infty}$.

As demonstrated by the examples of 75/25 and 85/15 styrene–acrylonitrile copolymers, the inhibitors obtained strongly differ in the latex stabilization performance.

Latexes with Sintanol ALM-10 nonionic emulsifier have a low electrokinetic potential of the surface [2]. The adsorption layer is stabilized by hydration of the oxyethylene groups of the emulsifier. It was shown that anions exert a destabilizing effect on latexes and aqueous solutions of nonionic emulsifiers. The intensity of the action of anions is mainly proportional to $1/z^2$, where z is the valence of the astabilizing ion [17].

The destabilizing action of macroradicals accumulated in the volume of polymer–monomer particles can be considered to a first approximation as anionic interactions leading to the loss of stability

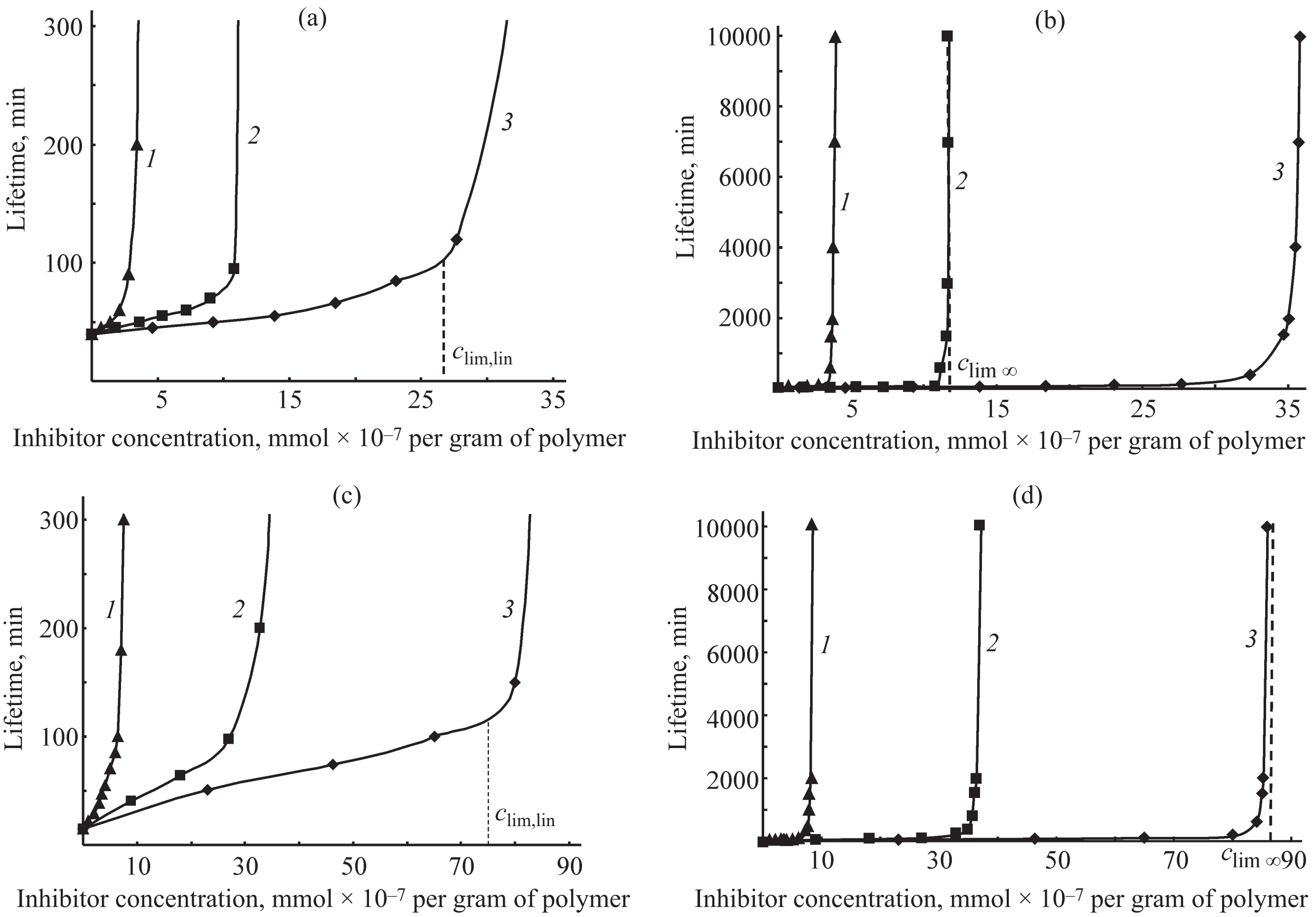
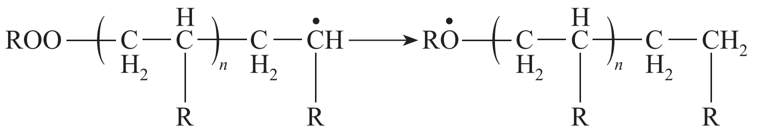


Fig. 2. Effect of radical polymerization inhibitors (*1*) diphenylpicrylhydrazyl, (*2*) 2,2,6,6-tetramethylpiperidine-1-oxyl, and (*3*) sodium dimethyldithiocarbamate on the lifetime of styrene–acrylonitrile copolymers. Acrylonitrile content of the polymer, wt %: (a, b) 15 and (c, d) 25.

(gelation) of the latex system. In radical polymerization of vinyl monomers under the action of hydroperoxides, the macroradicals can contain fragments with peroxy groups, especially when there are traces of oxygen in the system. Such fragments are capable of further decomposition in the presence of variable-valence metals introduced into the reversible redox system in the form of iron EDTA complex:



$$\mathrm{ROO}{-}\left(\underset{\mathrm{H_2}}{\mathrm{C}}{-}\overset{\mathrm{H}}{\underset{\mathrm{R}}{\mathrm{C}}}\right)_n{-}\underset{\mathrm{H_2}}{\mathrm{C}}{-}\overset{\bullet}{\underset{\mathrm{R}}{\mathrm{CH}}}\longrightarrow \mathrm{R}\overset{\bullet}{\mathrm{O}}{-}\left(\underset{\mathrm{H_2}}{\mathrm{C}}{-}\overset{\mathrm{H}}{\underset{\mathrm{R}}{\mathrm{C}}}\right)_n{-}\underset{\mathrm{H_2}}{\mathrm{C}}{-}\underset{\mathrm{R}}{\mathrm{CH_2}}$$

The electrophilicity of the radicals formed is determined by their increased electron density. Thus, analogy can be drawn between the quenching of macroradicals in their reaction with inhibitors and the action of cations in formation of uni-, di-, and trivalent salts. Then the action of sodium dimethyldithiocarbamate can be considered as the action of a univalent cation, and the performance of other inhibitors can be considered relative to sodium dimethyldithiocarbamate.

The intensity of the action of the inhibitors studied can be evaluated from the ratio of their concentrations to that of the most active diphenylpicrylhydrazyl both in the step of active stabilization of polymer–monomer particles and in the step of decelerated stabilization on reaching complete stabilization of the latex system, and also from the amount of inhibitor molecules per

Table 4. Stabilization of styrene copolymers with inhibitors

Inhibitor	Completion of step		Number of radicals per particle	Area occupied by the radical on the particle surface, 10^{-11} cm^2	Inhibitor/ diphenylpicrylyhydrazyl activity ratio	
	active stabilization, $c_{\mathrm{lim,lin}}$, $\times 10^{-7}$ mol g^{-1}	decelerated stabilization, $c_{\mathrm{lim},\infty}$, $\times 10^{-7}$ mol g^{-1}			in active stabilization step	in decelerated stabilization step
Styrene/acrylonitrile 85/15						
Diphenylpicrylhydrazyl	2.3	4.1	45.13	7.06	1	1
2,2,6,6-Tetramethylpiperidine-1-oxyl	10	12.1	100.13	3.18	4.35	2.95
Dimethyldithiocarbamate	26	37	303.98	1.05	11.30	9.02
Styrene/acrylonitrile 75/25						
Diphenylpicrylhydrazyl	6.4	8.7	115.52	3.83	1	1
2,2,6,6-Tetramethylpiperidine-1-oxyl	28	37.9	146.43	3.02	4.375	4.35632
Dimethyldithiocarbamate	76	88	449.06	0.99	11.875	10.1149
Styrene/acrylonitrile/ethoxyethyl acrylate						
Dimethyldithiocarbamate	18.9	19.5	97.8	2.4	–	–

polymer–monomer particle and from the area occupied by one inhibitor molecule on the particle surface (Table 4). Stabilization of latexes of styrene copolymers with 25% acrylonitrile, which are less stable, requires larger amount of the inhibitor compared to the latexes of the copolymers with 15% acrylonitrile.

Nevertheless, the ratio of the concentrations $c_{\mathrm{lim,lin}}$ and $c_{\mathrm{lim},\infty}$ approximately corresponds to the series $1 : 1/4 : 1/9 = 1 : 1/(2)^2 : 1/(3)^2$.

The completeness of the macroradical termination ensures not only the aggregative stability of the latexes but also the constancy of the molecular parameters of the polymers obtained. The macroradical recombination occurs in the gel formed. Its formation results from the loss of the stability of the latex particles and their coalescence. According to Smoluchowski, in this step of coagulation the coagulation rate (time) is inversely proportional to the particle concentration in the system. The number of active particles participating in the coalescence should be proportional to the concentration of macroradicals in the volume of latex particles. Let us assume conventionally that the quenching of the macroradicals becomes complete at the system lifetime tending to infinity, which is reached at the inhibitor concentration $c_{\mathrm{lim},\infty}$, and that the degree of quenching, as well as the concentration of macroradicals remaining in the latex particles, is proportional to the concentration of the introduced inhibitor.

The dependences of the latex lifetime on the concentration of the introduced inhibitor reflect the kinetics of the decrease in the amount of active macroradicals, which affect the aggregative stability of the adsorption layer of polymer–monomer particles, in the volume of the latex particles. The macroradical concentration (c_{R}) varies from 100% in the beginning of storage before introducing the inhibitor to 0 at complete quenching of the macroradicals (Fig. 3). Long-term storage of the latex is thus ensured ($t_{\mathrm{L}} \to \infty$ at $c_{\mathrm{R}} \to 0$ and the inhibitor concentration $c_{\mathrm{lim},\infty}$). By transforming the dependences $t_{\mathrm{L}} = f(c_{\mathrm{inh}})$ into $t_{\mathrm{L}} = f(c_{\mathrm{R}})$ and then into $t_{\mathrm{L}} = f(\log 1/c_{\mathrm{R}}^2)$ (Fig. 3), we obtain the linear dependences both in the initial step of active quenching of the macroradicals (up to $c_{\mathrm{lim,lin}}$) and in the step of decelerated quenching when the latex system gradually reaches the stable state (at $c_{\mathrm{lim},\infty}$), which proves the hypothesis on the effect of macroradicals on the colloidal stability of the latex systems.

The extent of changes in the molecular mass and polydispersity decreases depending on the degree of quenching of the macroradicals with the inhibitors and on the content of free macroradicals in the volume of polymer–monomer particles.

As follows from the data obtained, long-term storage of the latex stabilized with excess emulsifier is accompanied by gelation and further changes in the molecular parameters of the polymer (Table 5).

As shown previously [2], an increase in the degree of saturation of adsorption layers of polymer–monomer particles with the emulsifier leads to stabilization of latex systems. The kinetics of this stabilization resembles the kinetics of the stabilization of latex systems upon quenching of macroradicals with the inhibitors. Namely, there are steps of active and decelerated stabilization. Their duration is influenced by the polarity of the polymer obtained (acetonitrile content) (Fig. 4).

On the other hand, even introduction of excess nonionic emulsifier into the system ($A \geq 100\%$) does not prevent further gelation and changes in the molecular parameters of the polymers, caused by recombination of free macroradicals in the volume of polymer–monomer particles (Table 4). Complete stabilization of the latexes is reached on introducing Leukanol dispersant into the polymerization formulation in a concentration at which the hydrocarbon part of the adsorption layer of polymer–monomer particles is saturated with condensed aromatic naphthalene units even at incomplete saturation of the surface of polymer–monomer particles with the emulsifier. In so doing, the molecular-mass parameters of the polymer change essentially. If the concentration of naphthalene units is insufficient for complete stabilization of the latex, the system is unstable, and after the lapse of a certain time (3–5 months) the gelation occurs; the molecular parameters of the polymer increase in the course of storage as a result of interaction with living macroradicals.

The need for complete quenching of macroradicals to ensure the latex stability in the course of distillation of the residual monomers and to prevent the formation of insoluble high-molecular-mass fractions was confirmed in commercial production of acrylate rubbers using anionic emulsifiers. The presence of the high-molecular-mass fraction in some samples of the polymer obtained (6–10%) was also associated with the fact that, at higher pH values (pH 4.5–5.0) of the latex by the moment of polymerization completion and introduction of sodium nitrite stopper, the stopper decomposition and the process termination were incomplete. The propagating macroradicals that recombine in the final step of polymerization and distillation of residual monomers

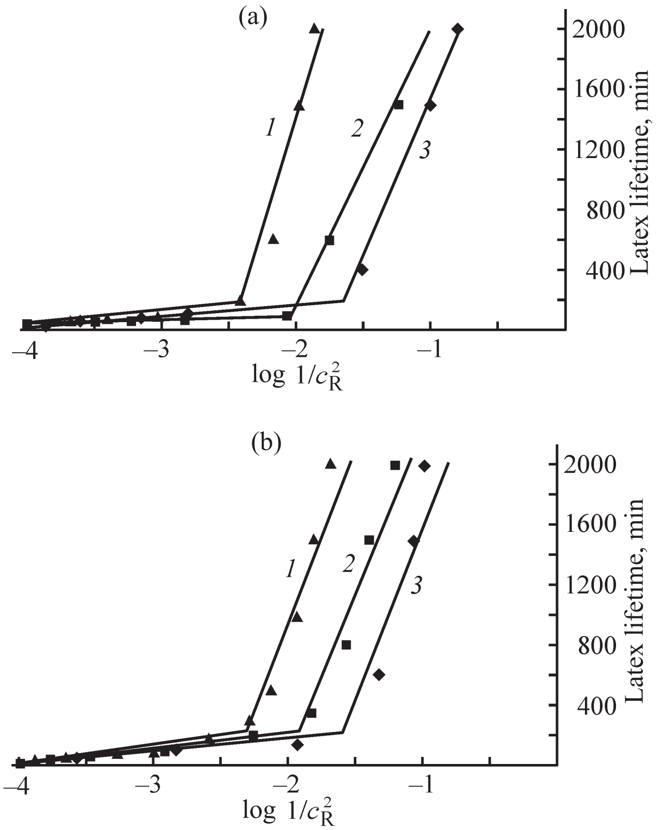


Fig. 3. Effect of the change in the concentration of macroradicals due to their quenching with (*1*) diphenylpicrylhydrazyl, (*2*) 2,2,6,6-tetramethylpiperidine-1-oxyl, and (*3*) sodium dimethyldithiocarbamate on the stability of styrene copolymers with (a) 15 and (b) 25% acrylonitrile.

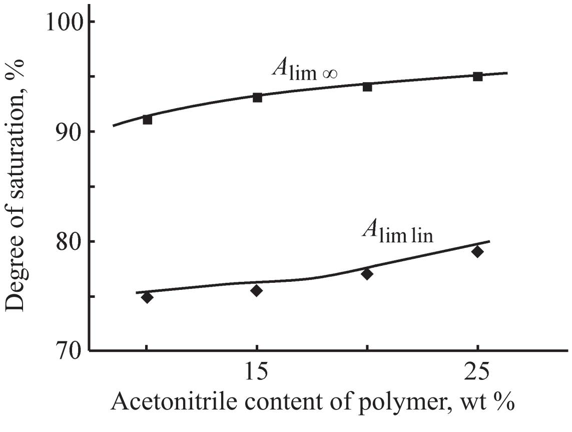


Fig. 4. Influence of the copolymer composition on the stabilizing power of Sintanol ALM-10 emulsifier.

Table 5. Lifetime of latex, molecular mass, and polydispersity coefficient of polystyrene and styrene–acrylonitrile copolymers immediately after the synthesis and after 1-month storage

Acrylonitrile content of polymer	Molecular mass of polymer, kDa	Molecular mass of polymer after 1-month storage, kDa	Polydispersity coefficient of polymer	Polydispersity coefficient after 1-month storage	Latex lifetime, min	Change in the polymer molecular mass upon storage, %	Change in the polymer polydispersity coefficient on storage, %
Polystyrene	470	505	2.77	2.82	840	6.9	1.8
15% acrylonitrile	610	673	2.73	2.76	40	9.4	1.1
25% acrylonitrile	1150	1280	2.79	3.3	15	10.2	15.5
Polystyrene with double excess of emulsifier	587	645	2.33	2.56	≈7 months	9.0	9.0
15% acrylonitrile with double excess of emulsifier	650	730	2.35	2.52	≈6 months	11.0	6.7
25% acrylonitrile with double excess of emulsifier	1240	1390	2.48	2.63	≈6 months	10.8	5.7
Polystyrene + 1 wt % dimethyldithiocarbamate	468	505	2.4	3.02	> 2 years	7.3	20.5
15% acrylonitrile + 1% wt % dimethyldithiocarbamate	605	623	3.13	3.3	> 2 years	2.9	5.2
25% acrylonitrile + 0.5 wt % dimethyldithiocarbamate	1028	1340	3.25	3.65	> 2 years	23.3	11.0
25% acrylonitrile + 0.5 wt % Leukanol	1155	1621	3.4	3.7	>2 years	28.7	8.1
25% acrylonitrile + 0.5 wt % Leukanol + 0.4 wt % *tert*-dodecyl mercaptan	100	120	2.77	2.92	> 2 years	16.7	5.1

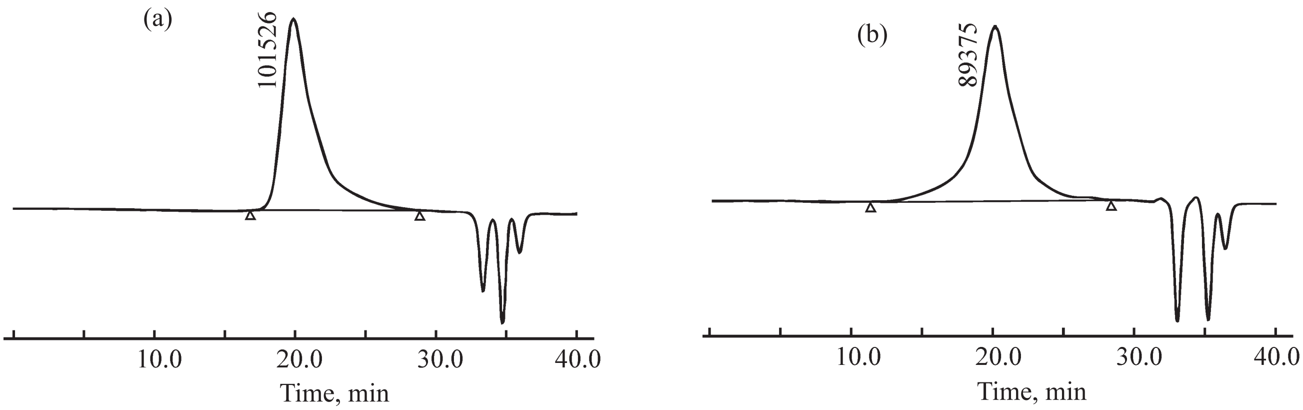


Fig. 5. Gel chromatogram of the acrylate polymer prepared (a) in the presence of Leukanol dispersant and (b) without it.

caused formation of an acetone-insoluble high-molecular-mass fraction in the ready acrylate polymer and an increase in the polydispersity coefficient.

We studied the molecular-mass characteristics of the commercially produced acrylate polymer, obtained with Leukanol dispersant added to the polymerization formulation (Fig. 5a). The narrow peak indicates that the polymer is uniform in the molecular mass, without high-molecular-mass fraction, which is the necessary condition for preparing high-strength adhesive compounds based on acrylate rubber.

A series of experiments on the synthesis of a latex of similar acrylate polymers without Leukanol dispersant in the polymerization formulation (or without polymerizable emulsifiers based on sulfonated naphthol derivatives) revealed significant difference in the molecular-mass characteristics of the isolated polymer (Fig. 5b). The figure shows the curve of the molecular-mass distribution of the acrylate rubber with high polydispersity coefficient, containing approximately 10% high-molecular-mass fraction insoluble in polar solvents in production of adhesive compounds based on this polymer. The polymer was synthesized without using sulfonated naphthol derivatives in the polymerization formulation.

The tail in the left part of the peak in the chromatogram is indicative of the presence of the high-molecular-mass fraction in the rubber, and the total peak width suggests high polydispersity coefficient.

It is known [18] that condensed aromatic structures (naphthalene, anthracene, etc.) undergo incorporation of peroxy groups into the structure of one of the aromatic rings on introducing oxygen and peroxy compounds. The formation of such compounds causes changes in the rubber color in the course of storage in the case of rubber stabilization with Neozone D (N-phenyl-β-naphthylamine), which was widely used previously. Apparently, the presence of peroxy groups in the macroradicals predetermines the formation of such structures in the hydrocarbon part of the adsorption layer

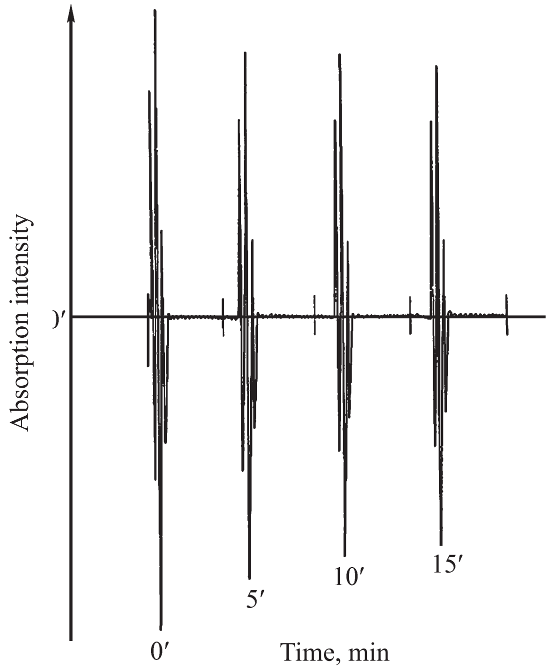


Fig. 6. EPR spectrum of 2,2,6,6-tetramethylpiperidine-1-oxyl in the latex of the styrene–15% acrylonitrile copolymer, taken immediately after the polymerization completion and after the lapse of 5, 10, and 15 min.

of polymer–monomer particles with the incorporated naphthalene units of the dispersant. These structures prevent the incorporation of the macroradicals into the polar part of the adsorption layer of polymer–monomer particles and thus eliminate the effect of macroradicals on the colloidal stability of latex particles in the course of the polymer synthesis and storage. The presence of naphthalene units in Neozone D antioxidant, which take up oxygen and peroxy compounds formed in the course of rubber vulcanization, ensures high performance of Neozone D as a rubber stabilizer.

As shown previously [2], an increase in the amount of dispersant units in the colloidal system leads to an increase in the solubility of the emulsifier in water and in the critical micelle concentration of the emulsifier. In synthesis of latexes on both nonionic and anionic emulsifiers, this leads to an increase in the degree of ionization (electrokinetic potential) and hydration of the adsorption layer of the polymer–monomer particles and to enhancement of the aggregative stability of the latexes in the synthesis step and of their thermal stability in the course of the monomer distillation.

However, in this case the amount of nonbiodegradable substances in wastewaters from emulsion rubber production increases, which is inadmissible. This problem was not solved when going from the salt method of the rubber recovery to the recovery methods using cationic polyelectrolytes. Furthermore, the use of cationic polyelectrolytes can lead to changes in the polymer properties.

As shown previously [16], the EPR spectrum of the introduced inhibitor rapidly decreases in intensity in the course of storage of the polystyrene latex, and the aggregative stability of the latex correlates with the presence of a radical polymerization inhibitor in the latex. We have measured the EPR spectrum of 2,2,6,6-tetramethylpiperidine-1-oxyl introduced into the styrene–acrylonitrile latex as an inhibitor immediately after the synthesis. The measurement confirmed a decrease in the intensity of the spectrum of the paramagnetic marker, which proves the interaction of inhibitors with macroradicals (Fig. 6).

It should be noted that introduction of the required amount of the dispersant into the polymerization formulation, favoring the termination of macroradicals in the volume of the polymer–monomer particles due to recombination (as indicated by an increase in the molecular mass and dispersity of the polymer, observed with the model systems), does not prevent the accumulation of macroradicals in the gel effect step and in the final step of the polymerization. Only joint use of dispersants and radical polymerization inhibitors allows reaching the required completeness of the macroradical termination, aggregative stability of the latexes, and stability of the molecular parameters of the polymers obtained.

CONCLUSION

Model experiments on emulsion polymerization of vinyl monomers in the presence of nonionic emulsifiers demonstrate accumulation of stable free radicals in the gel effect step and in the final polymerization step inside polymer–monomer particles. This fact suggests that the destabilizing effect of macroradicals on the structure of the adsorption layer of polymer–monomer particles is one of the factors responsible for the loss of the aggregative stability of synthetic latexes. The loss of the stability of latex particles leads to their coagulation and gel formation. Then, the recombination of free macroradicals leads to an increase in the molecular mass and polydispersity of the polymer in the gels and in the latexes stabilized with dispersants or emulsifiers in the course of storage without adding radical polymerization inhibitors to the latex. Thus, a radical polymerization inhibitor should be added to the latex after the synthesis completion to ensure constancy of the molecular parameters of the emulsion polymers.

The effect of macroradicals on the stability of latex systems is of much interest for understanding the mechanism of the radical polymerization and requires further studies.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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