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FUNCTIONAL ORGANOSILICON SUBSTANCES AS STABILIZERS OF POLYMERIC SUSPENSIONS*

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The review presents schemes for obtaining homologous series of the linear α,ω-carbofunctional oligodimethylsiloxanes with the silicone chain length from 6 to 60 siloxane units containing carboxydecyl, aminopropyl and glycidoxypropyl groups at the chain ends allowing to obtain organosilicon surfactants with reproducible structure and properties. Data on the surfactant colloid-chemical properties and kinetic regularities of styrene polymerization in their presence are provided. Systematic research of heterophase styrene polymerization kinetic regularities in the presence of water-insoluble α,ω-carbofunctional oligodimethylsiloxane allowed to formulate the fundamental differences of polymerization kinetic regularities from those observed in the presence of water-soluble surfactants. The mechanism of interfacial adsorption layers formation with water-insoluble α,ω-carbofunctional oligodimethylsiloxanes on the surface of monomer drops and polymer-monomeric particles was considered. This mechanism consists in the forced surfactant replacement by the formed polymer (because of their incompatibility) to the interfacial adsorption layer and in the formation of the surfactant supermolecular structures. The latter in total with the polymer provide its high durability.

Keywords: *surfactants, heterophase polymerization, polystyrene, polymer suspension, functional oligodimethyl-siloxanes.*

One of promising approaches to the synthesis of polymeric suspensions with narrow particle distribution by the sizes is the heterophase polymerization of vinyl monomers in the presence of water-insoluble surfactants forming oil-in-water emulsions, such as monoalkyl phthalates, di(*p*-tolyl)carbalcoxyphenylcarbinol, oligomeric peroxyesters and oligodimethylsiloxanes containing functional groups in the organic substituent at the silicon atom (carboxy, epoxy or amino groups) [1–6].

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The topicality of heterophase polymerization of monomers in the presence of water-insoluble surfactants is caused by the possibility of providing not only environmentally friendly methods of synthesizing polymeric suspensions allowing to exclude the stage of water purification from surfactants, generally non-biodegradable ones, but also by the possibility of providing processes of synthesizing polymeric suspensions with narrow particle distribution by the sizes. Creation of a set of particles (bank of particles) of different diameters with narrow distribution by the sizes opens new prospects of their application in biotechnology, for example: as carriers of bioligands in reactions of latex agglutination, in which they are used instead of biological analogs; as calibration standards in electron and optical microscopy and in diffusion of light; in counting aerosol and virus particles and small-angle refraction of X-rays; for the determination of the pore sizes of filters and biological membranes; for the creation of model samples of photonic crystals. The severe requirements to the polymeric microspheres applied for this purpose (narrow distribution by the sizes; diameters of polymeric microspheres in a wide range of values; the existence of functional groups on the surface of the polymeric microspheres providing the possibility of further modification of the particles when obtaining composite materials; stability in isotonic solutions and at storage; etc.) require using special surfactants when creating methods for their synthesis. These surfactants should be capable of forming strong interfacial adsorption layers on the surface of the microsphere.

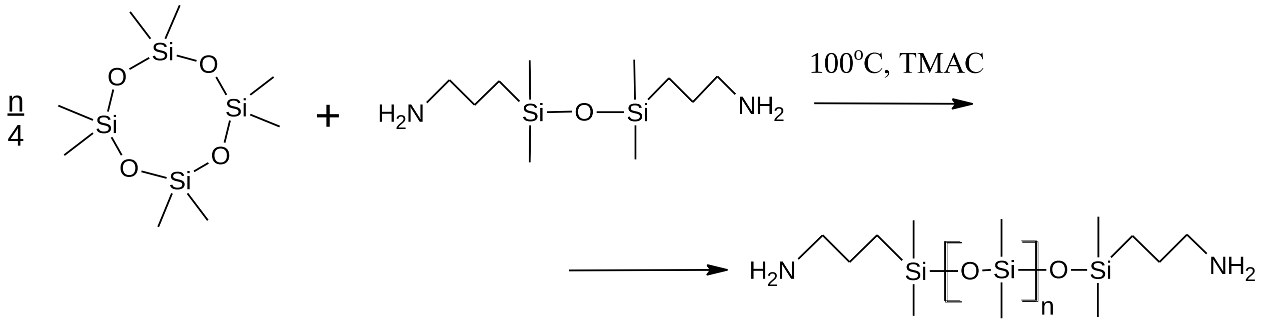
α,ω-Carbofunctional oligodimethylsiloxanes are of special interest as stabilizers of polymeric suspensions, first of all due to the well-developed methods of their synthesis, including those used commercially, and also due to their structural similarity to organic surfactants, so-called gemini surfactants showing much higher performance in comparison with traditional organic surfactants [7–10].

This review generalizes methods for the synthesis and the properties of oligodimethylsiloxanes containing functional groups at the ends of the polymeric chains. Besides, it considers the main regularities of styrene heterophase polymerization in the presence of such oligodimethylsiloxanes and properties of the resulting polymeric suspensions.

In works [3–5] and [11–14] oligodimethylsiloxanes containing 3-aminopropyl, 10-carboxydecyl or 3-(glycidoxy)propyl groups at the ends of the polymeric chains were used for the synthesis of polymeric microspheres with narrow particle distribution by the sizes. The surface of the microspheres contains functional groups necessary for their further modification.

Methods of synthesizing such functional organosilicon polymers include both polymerization (or catalytic rearrangement) of cyclosiloxanes and hydrosilylation of methylhydroxysiloxane oligomers. These methods enable obtaining oligomers with the adjustable content of functional groups, minimal content of low-molecular products and reproducible molecular mass characteristics.

Aminofunctional oligodimethylsiloxanes were synthesized the by anionic copolymerization of 1,3-bis-(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane and octamethylcyclotetrasiloxane (D_4) under the action of an initiator – α,ω-bis(tetramethylammoniumoxy)polydimethylsiloxanolate (TMAS) according to the following scheme [5]:



n=9, 30, 45, 60

The reaction was carried out at 100 °C and various ratios of the reagents for 8–10 h until equilibrium determined by the termination of change in the content of volatile substances in the reaction mass was attained. Then the initiator was decomposed at elevated temperature (140 °C), and volatile reaction products were removed by high-temperature vacuum distillation. The composition and structure of the synthesized oligomers were confirmed by ^{1}H and ^{29}Si NMR. Characteristics of the oligomers are provided in Table 1.

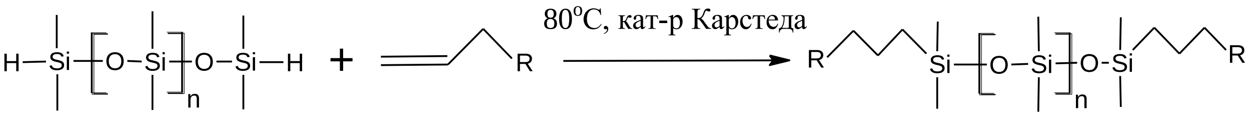
Table 1. Properties of synthesized α,ω-bis-(3-aminopropyl)-oligodimethylsiloxanes of general formula$H_2N(CH_2)_3(CH_3)_2SiO[Si(CH_3)_2O]_n\,Si(CH_3)_2(CH_2)_3NH_2$

Oligomer code	n		Content of volatile substances, %		Viscosity η^{20}, cSt	Content of amino groups, %			Oligomer yield, mass %
	theor.	exp.	before distillation	after distillation		theor.	exp.*	exp.**	
PDMS-NH_2-10	9	10	18.2	4.0	41.8	1.60	1.52	1.53	81.4
PDMS-NH_2-32	30	32	18.0	6.5	137.7	1.30	1.28	1.26	82.5
PDMS-NH_2-46	45	46	17.0	4.5	172.0	0.94	0.93	0.90	82.7
PDMS-NH_2-63	60	63	16.5	5.0	245.0	0.70	0.67	0.67	83.0

* according to acid-base titration with a 0.1 N HCl solution;
** according to ^{1}H NMR.

According to gel-permeation chromatography the synthesized oligomers are characterized by molecular mass distribution with a heterogeneity index equal to 2–2.5.

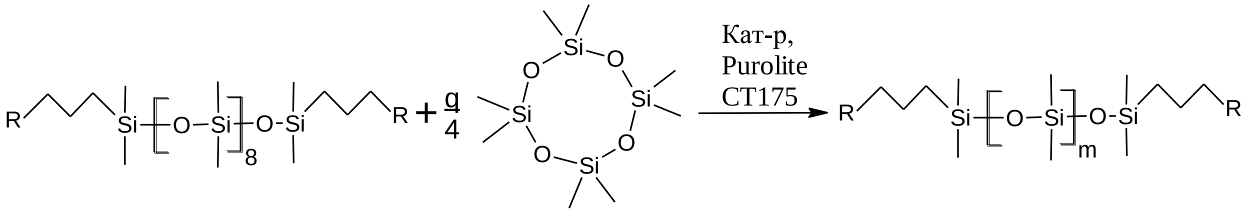
Carboxyl-containing oligodimethylsiloxanes with the adjustable content of COOH groups were synthesized according to a two-step scheme [4, 5]. First, an oligomer with the average number of siloxane units equal to 8 was obtained by hydrosilylation of a short-chain α,ω-dihydridooligodimethylsiloxane with trimethylsilyl ester of undecenoic acid:



n=8, R=$(CH_2)_7C(O)OSi(CH_3)_3$ для ПДМС-COOH-8; n=30, R=$OCH_2CH(O)CH_2$ для ПДМС-эпокси-30;

[кат-р Карстеда means Karstedt's catalyst; для ПДМС-COOH-8 means for PDMS-COOH-8; для ПДМС-эпокси-30 means for PDMS-epoxy-30]

Then a number of carboxyl-containing oligodimethylsiloxanes with chain lengths from 10 to 60 siloxane units were synthesized by the catalytic rearrangement of the obtained oligomer with the octamethylcyclotetrasiloxane:



q=2, 12, 22, 37, 52; m=10, 20, 30, 45, 60; R=$(CH_2)_7C(O)OH$.

[Кат-р means catalyst]

The choice of undecenoic acid as a carboxyl-containing reagent was due to a combination of two important factors: 1) the presence of a double bond at the end of the hydrocarbonic chain, which considerably facilitates hydrosilylation; 2) the maximum availability of this acid in comparison with other carboxylic acids containing a double bond at the end of the chain, which allows to consider these oligomers as suitable for their industrial production.

Hydrosilylation was carried out at the equimolar ratio of silicon hydride and nonsaturated groups. The process was conducted until not less than 92% conversion of SiH groups was attained. Then the protective trimethylsilyl group was removed with methanol, and low-molecular reaction products were distilled off in vacuum, after which their content did not exceed 3% mass. As a result, carboxyl-containing oligodimethylsiloxane PDMS-COOH-8 was obtained.

The catalytic rearrangement of the obtained oligomer PDMS-COOH-8 with octamethylcyclotetrasiloxane was carried out at various content of D_4. As a result, a number of α,ω-bis(10-carboxydecyl) oligodimethylsiloxanes (PDMS-COOH) were obtained. Their properties are presented in Table 2.

Table 2. Properties of the synthesized α,ω-bis(10-carboxydecyl)-oligodimethylsiloxanes of general formula $HOOC(CH_2)_{10}(CH_3)_2SiO[Si(CH_3)_2O]_nSi(CH_3)_2\,(CH_2)_{10}COOH$

Oligomer code	n		Viscosity, η^{20},·cSt	M_n	M_w/M_n	Content of carboxy groups, %		
	theor.	exp.**				theor.	exp.*	exp.**
PDMS-COOH-8	8	8	140	610	1.8	9.5	9.2	9.2
PDMS-COOH-12	10	12	143	720	1.9	7.2	6.8	6.7
PDMS-COOH-32	30	32	173	2300	2.5	3.3	2.8	2.9
PDMS-COOH-47	45	47	202	4100	2.1	2.3	2.2	2.2
PDMS-COOH-62	60	62	299	4600	2.5	1.8	1.6	1.6

* according to acid-base titration with a 0.1 N NaOH solution;
** according to ^{1}H NMR.

It can be seen from the table that the content of carboxyl groups in the synthesized PDMS-COOH is from 1.6 to 9.2% by mass. According to gel-permeation chromatography the synthesized carboxy-containing oligomers are characterized by molecular mass distribution with a heterogeneity index equal to 1.8–2.5.

The epoxy-containing oligodimethylsiloxane (α,ω-bis-(3-glycidoxypropyl)oligodimethylsiloxane (PDMS-epoxy-30) was synthesized by the hydrosilylation of α,ω-dihydridooligodimethylsiloxane containing the average number of siloxane units equal to 30 (the content of active hydrogen 0.078% by mass) with allyl glycidyl ether according to the above scheme [5].

The hydrosilylation was carried out at 3% molar surplus of allylic groups with respect to silicon hydride groups in the presence of Karstedt's catalyst. When the process was complete, the conversion of SiH groups was 94.2%. Volatile reaction components were distilled off in vacuum. As a result, α,ω-bis(3-glycidoxypropyl)oligodimethylsiloxane (PDMS-epoxy-30) with epoxy groups content 3.26% by mass was obtained in 94.4% yield. This corresponds to the calculated value. The composition of the obtained oligomer was confirmed by ^{1}H and ^{29}Si NMR.

The obtained functional organosilicon oligomers were used as surfactants for the synthesis of polymeric suspensions.

The solubility of the surfactants in water and in nonsaturated monomers – styrene and methyl methacrylate – was preliminarily determined (Table 3) [5].

Table 3. Solubility of organosilicon surfactants in styrene*

Surfactant	Solubility, mass % (t=20°C)
PDMS-COOH-8	21
PDMS-COOH-10	19
PDMS-COOH-30	34
PDMS-COOH-50	11
PDMS-COOH-60	16
PDMS-NH_2-9	9
PDMS-NH_2-30	16
PDMS-epoxy-30	24

* All the studied surfactants are miscible in all proportions with methyl methacrylate and water-insoluble.

It can be seen from Table 3 that all the functional PDMS's are water-insoluble, but soluble either partially of infinitely in nonsaturated monomers. It was shown that, when mixing a surfactant solution in styrene with water, an oil-in-water emulsion is formed [5].

Figure 1 presents interfacial tension isotherms obtained on the (organosilicon surfactant toluene solution)/water boundary, and Table 4 shows calculated colloid-chemical characteristics of the surfactant [5].

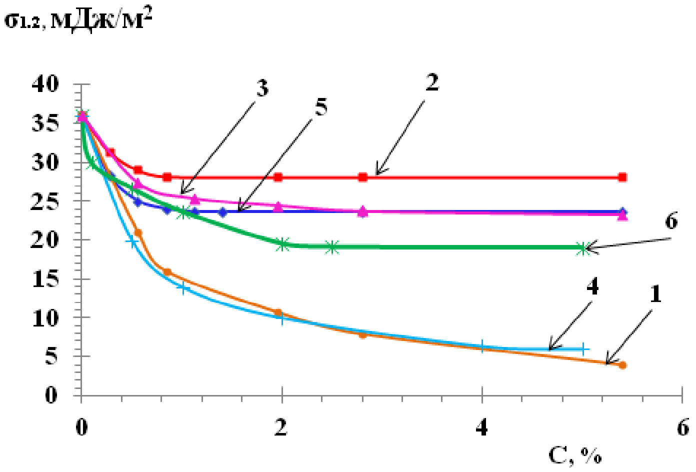


Figure 1. Interfacial tension isotherms obtained on the water/(surfactant toluene solution) boundary, where the surfactants are: 1 – PDMS-COOH-8; 2 – PDMS-COOH-30; 3 – PDMS-COOH-60; 4 –PDMS-NH_2-9; 5 – PDMS-NH_2-30; 6 – PDMS-epoxy-30. [мДж/м^2 means mJ/m^2]

Table 4. Colloid-chemical characteristics of organosilicon surfactants [5]

No	Surfactant	$\sigma_{1,2}$, mJ/m^2	$\Gamma_{max}\cdot10^6$, mol/m^2	G, mN·m^2/mol	S_0, Å^2	$\delta\cdot10^9$, m
1	PDMS-COOH-8	3.9	5.16	6.85	32.4	5.15
2	PDMS-COOH-30	28.1	2.79	4.60	59.5	7.96
3	PDMS-COOH-60	23.3	2.10	1.80	125.0	4.30
4	PDMS-NH_2-9	6.0	3.90	3.20	42.6	3.76
5	PDMS-NH_2-30	23.6	2.85	7.60	58.3	7.50
6	PDMS-epoxy-30	18.9	2.08	16.7	79.9	5.49

It can be seen from Table 4 that, as the length of the siloxane chain increases from 8 to 30 units, interfacial tension $\sigma_{1,2}$ on the (surfactant toluene solution)/water boundary increases in case of the carboxyl-containing organosilicon surfactants 7-fold, and in case of the amino-containing ones, 4-fold. The value of maximum adsorption changes only slightly, and surface activity decreases a little. The main conclusion of the performed research is that all the studied organosilicon compounds can be used as surfactants for the synthesis of polymeric suspensions by heterophase polymerization.

The initial emulsions of monomers obtained in the presence of organosilicon surfactants are unstable and break down after the stirring stops. Their stability considerably increases if the polymerization is initiated and the polymer is formed in the surface layer of the polymeric-monomeric particles (PMP) [11]. This is caused by the fact that the polymer participates in the formation of a structural and mechanical barrier in the interfacial adsorption layer of the PMP and increases its durability [15].

Kinetic regularities of styrene polymerization in the presence of the synthesized organosilicon surfactants were studied in detail, and the influence of the monomer/aqueous phase volume ratio, the process temperature, the initiator and surfactant concentrations on the characteristics of the formed polymeric suspensions was determined. On the basis of these data conditions for the synthesis of stable polymeric suspensions with narrow particle distribution by the sizes of different diameters were formulated.

First, styrene polymerization in bulk in the presence of surfactants and without them was studied in order to evaluate the influence of the organosilicon surfactants on the elementary reactions of the polymerization (initiation, chain growth and chain stopping) (Figure 2, Table 5).

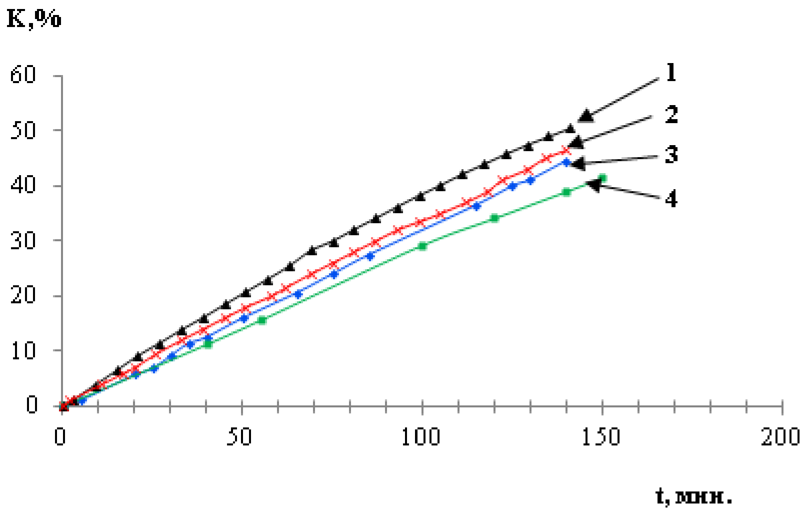


Figure 2. Conversion-time curves obtained upon styrene polymerization in bulk:
1) without surfactants; 2) 1% mass of PDMS-COOH-30; 3) 1% mass of PDMS-NH_2-30;
4) 1% mass of PDMS-epoxy-30.
[K, % means Conversion, %; мин means minutes]

Table 5. Molecular weights of polymers obtained upon styrene polymerization in bulk in the presence of organosilicon surfactants and without them

Surfactant	Surfactant concentration, % mass	AAD* concentration, % mass	Molecular weight, $M_\eta \cdot 10^{-5}$
Emulsifier-free polymerization	–	0.5	1.10
PDMS-COOH-30	1.0	0.5	1.25
PDMS-NH_2-30	1.0	0.5	1.26
PDMS-epoxy-30	1.0	0.5	1.29

*AAD – azoisobutyric acid dinitrile

It can be seen from the data provided in Figure 2 and in Table 5 that in the presence of organosilicon surfactants the polymerization rate and molecular weights of the polymer are close to those observed without surfactants.

Figure 3 shows conversion – time kinetic curves obtained upon polymerization of the monomers in the presence of organosilicon surfactants of various structure. The curves are S-shaped, which is typical of heterophase polymerization, and are characterized by three regions: a pronounced induction period [the period of the polymeric-monomeric particles (PMP) formation – from 10 to 60 min]; a region of constant rate; and a region, in which the process rate decreases. The PMP formation time upon styrene polymerization in the presence of water-insoluble surfactants fundamentally differs from that observed in the presence of water-soluble surfactants. These differences are due to different mechanisms of the interfacial adsorption layer formation.

In the presence of a water-insoluble surfactant the interfacial adsorption layer is formed from the polymer obtained upon the polymerization initiation in the surface layer of the particles and precipitated on the interphase boundary, because water is a precipitator of the polymer and of the surfactant. The latter is displaced by the formed polymer to the interfacial adsorption layer because of their incompatibility [3, 17–20]. In this case supramolecular structures are formed in the course of the interfacial adsorption layer formation. This was shown by the example of model systems using Langmuir method with a Brewster device [21].

The interfacial adsorption layer formed by surfactants of this type is characterized by high strength, and the interaction of the initiating radical with the monomer requires overcoming a certain energy barrier. This is the reason of the emergence of an induction period on the conversion-time curve and determines its duration.

In the presence of a water-soluble surfactant the interfacial adsorption layer is also formed from the polymer obtained upon the polymerization initiation in the surface layer of the particles. However, the surfactants are adsorbed on the surface of the particles from the aqueous phase and form a monolayer. In this case there is no significant energy barrier for the transfer of the initiating radical from the aqueous phase into the monomeric one.

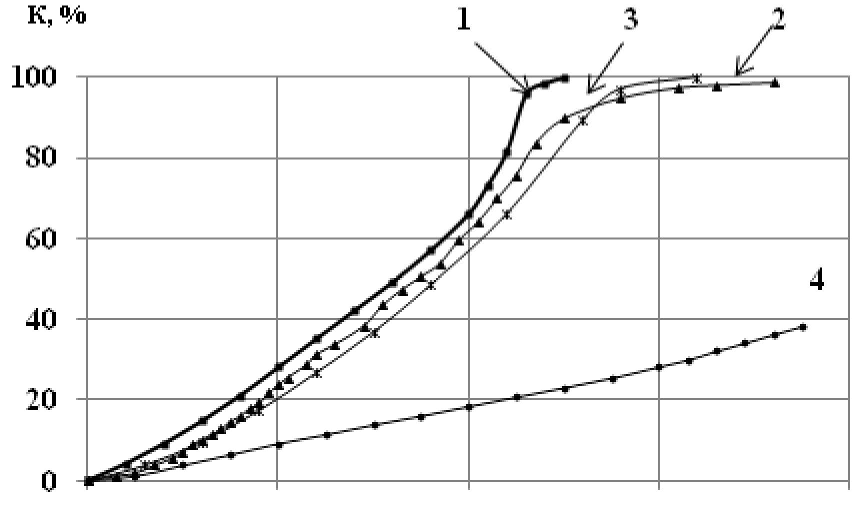


Figure 3. Conversion-time curves obtained upon styrene polymerization in the presence of 1 mass % of surfactants: 1 – PDMS-epoxy-30; 2 – PDMS-NH_2-30; 3 – PDMS-COOH-30; 4 – polymerization in bulk.
[K, % means Conversion, %; мин means minutes]

It can be seen from Figure 3 that the rates of styrene polymerization in the presence of functional organosilicon surfactants (curves 1–3) essentially do not differ and are much higher than the rate of polymerization in bulk (curve 4). Complete conversion of the monomer is attained within 5 h.

Figure 4 presents microphotos of polystyrene microspheres and histograms of their distribution by the sizes and by ξ-potentials. All the synthesized polymeric suspensions were stable in the course of the synthesis, but significantly differed in the diameters and molecular weights. It can be seen from Table 6 that in the presence of carboxy- and epoxy-containing surfactants polystyrene microspheres with diameters of 0.55 and 0.70 μm, respectively, and with narrow particle distribution by the sizes are formed. The polystyrene suspensions obtained in the presence of the amino-containing surfactant contained two sets of particles with diameters differing in size by an order of magnitude. Each of the particle sets was characterized by narrow distribution by the sizes. These results will be considered in detail below when analyzing data on the influence the medium pH.

Table 6. Characteristics of polystyrene suspensions synthesized in the presence of functional organosilicon surfactants [11]

Surfactant	d, μm	ζ, mV	D_w / D_n	$M_\eta \cdot 10^{-5}$	Stability in KCl, M
PDMS-epoxy-30	0.70	–34.7	1.018	1.62	0.25
PDMS-NH_2-30	0.4 and 1.8	–22.6	Bimodal distribution	6.42	0.25
PDMS-COOH-30	0.55	–36.7	1.014	0.31	0.20

The change in the diameters of the particles of the polymeric suspension in the process of styrene polymerization in the presence of the epoxy- and carboxy-containing surfactants is presented in Tables 7 and 8.

Microphotos of the particles and histograms of their distribution by the sizes at different stages of styrene polymerization with the particles obtained in the presence of the carboxy-containing surfactant as an example are shown in Figure 5. It can be seen that even at early stages of the monomer conversion polymeric suspensions with narrow particle distribution by the sizes are formed, and the particle diameters essentially do not change as the monomer conversion increases.

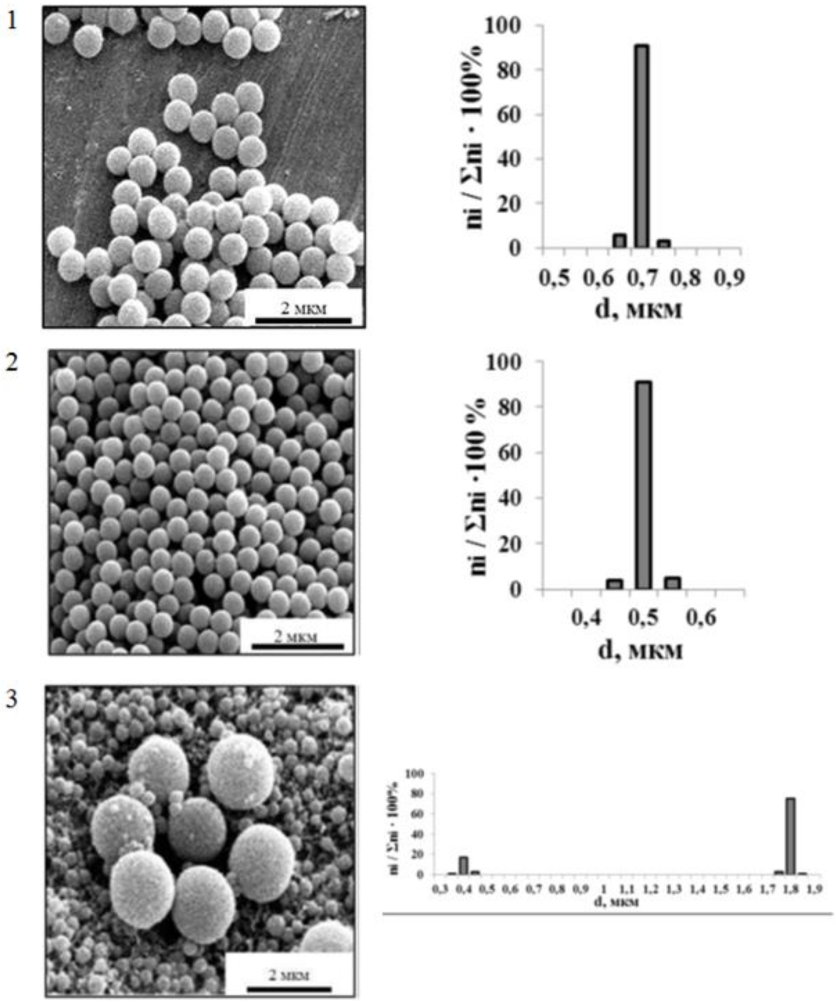


Figure 4. Microphotos and histograms of distribution by the sizes and by ξ-potentials for the particles of polystyrene suspensions obtained in the presence of 1% mass of: 1 – PDMS-epoxy-30; 2 – PDMS-COOH-30; 3 – PDMS-NH_2-30. [мкм means μm]

Table 7. Characteristics of polystyrene suspensions stabilized with PDMS-epoxy-30 at different steps of the monomer conversion [5]

Styrene conversion, %	d, μm	D_w / D_n	ξ, mV	Stability in KCl, M
10	0.53	1.035	–42.2	0.15
20	0.57	1.029	–39.4	0.20
30	0.59	1.025	–37.3	0.20
50	0.65	1.020	–35.9	0.25
100	0.70	1.018	–35.2	0.25

Table 8. Characteristics of polystyrene suspensions stabilized with PDMS-COOH-30 at different steps of the monomer conversion [5]

Styrene conversion, %	d, μm	D_w / D_n	ξ, mV	Stability in KCl, M
10	0.34	1.032	–41.8	0.15
20	0.35	1.039	–39.0	0.15
30	0.40	1.027	–37.1	0.20
50	0.45	1.015	–36.5	0.20
100	0.50	1.014	–36.1	0.25

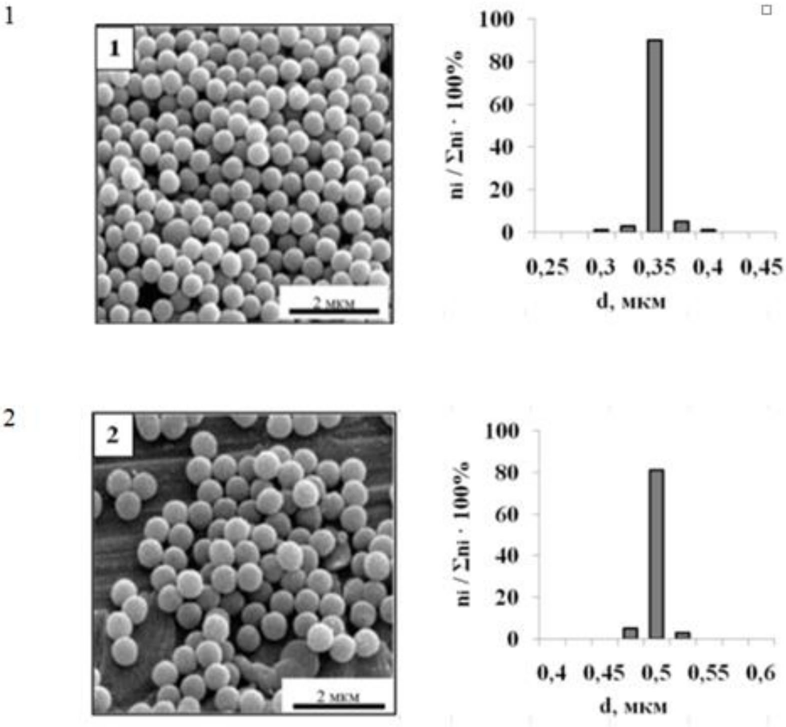
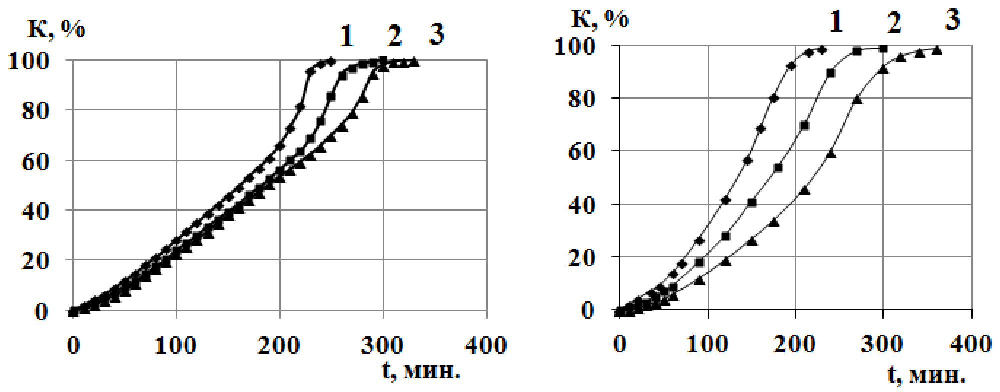


Figure 5. Microphotos and histograms of distribution by the sizes for the polystyrene particles obtained in the presence of 1% mass of PDMS-COOH-30 at different stages of polystyrene conversion: 1 – 20%; 2 – 100%. [мкм means μm]

One of the key parameters affecting the size of the polymeric suspension particles is the monomer / aqueous phase volume ratio [22, 23]. Conversion – time kinetic curves are given in Figure 6 by the example of the epoxy- and the carboxy-containing surfactant obtained at various volume phase ratios.



а

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Figure 6. Conversion – time kinetic curves obtained upon styrene polymerization in the presence of PDMS-epoxy-30 (a) and PDMS-COOH-30 (b) at monomer / aqueous phase volume ratios: 1 – 1:9; 2 – 1:6; 3 – 1:4.
[K, % means Conversion, %; мин means minutes; a, б means a, b]

It can be seen that, as styrene concentration increases, the polymerization rate decreases. Complete conversion of the monomer is attained within 4–5 h. As the monomer concentration increases, the diameter of the particles increases to 1.1 µm, the narrow particle distribution by the sizes remaining (Table 9). Further increase in the monomer concentration reduces the reaction system stability.

Table 9. Characteristics of polystyrene suspensions stabilized with PDMS-epoxy-30 and with PDMS-COOH-30 at various volume ratios of the phases [11]

Surfactant	Volume ratio of the phases	d, µm	D_w / D_n	ξ, mV	$M_\eta \cdot 10^{-5}$	Stability in KCl, M
PDMS-epoxy-30	1:9	0.70	1.018	–35.2	3.10	0.25
	1:6	0.86	1.023	–34.7	2.39	0.25
	1:4	1.10	1.035	–30.2	1.75	0.15
PDMS-COOH-30	1:9	0.55	1.015	–36.7	4.20	0.20
	1:6	0.73	1.086	–33.5	3.26	0.20
	1:4	0.80	1.021	–31.9	2.49	0.15

An increase in the concentration of potassium persulphate (PPS) usually used as the initiator leads to rate increase to the power of 0.5, and the molecular weights of the polymers decrease in inverse proportion to the power of 0.5 (Figures 7 and 8). These studies were conducted with the polymerization in the presence of PDMS-epoxy-30 and PDMS-COOH-30 as an example at various PPS concentrations (Table 10).

Figure 9 shows microphotos and histograms of distribution by the sizes of the polystyrene particles obtained in the presence of PDMS-epoxy-30 at various PPS concentrations.

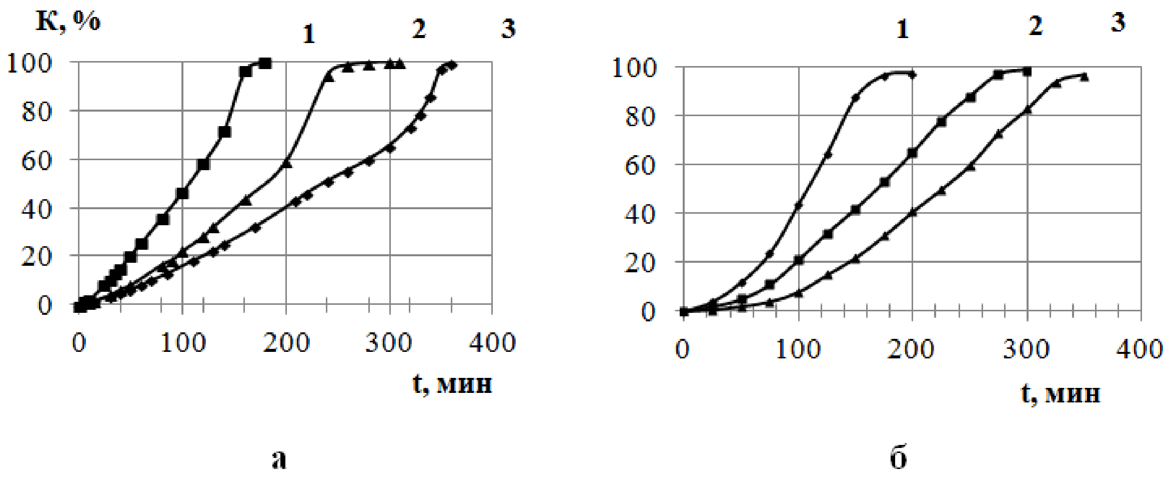

Figure 7. Conversion – time kinetic curves obtained upon styrene polymerization in the presence of 1 % mass of PDMS-epoxy-30 (a) and PDMS-COOH-30 (a) at various PPS concentrations (% mass calculated for the monomer): 1 – 2%; 2 – 1%; 3 – 0.5%.
[K, % means Conversion, %; мин means minutes; a, б means a, b]

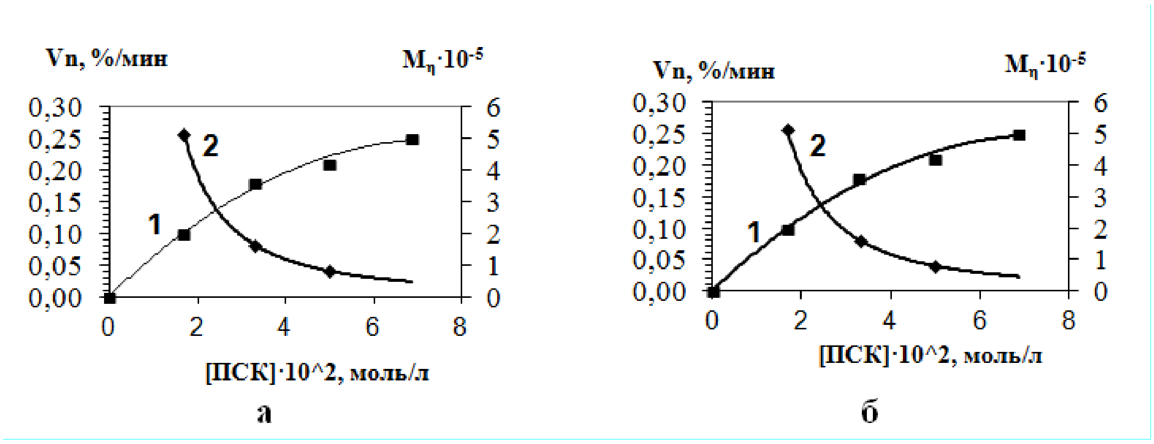

Figure 8. Dependences of polymerization rate (1) and of the polymers molecular weight (2) on PPS concentration obtained in the presence of PDMS-epoxy-30 (a) and PDMS-COOH-30 (b).
[%/мин means %/min; [ПСК] means [PPS]; моль/л means mol/l; a, б means a, b]

Table 10. Characteristics of polystyrene suspensions stabilized with PDMS-epoxy-30 and PDMS-COOH-30 at various PPS concentrations (% mass calculated for the monomer) [13]

Surfactant	PPS concentration, %	d, μm	ξ, mV	D_w / D_n	$M_\eta \cdot 10^{-5}$	Stability in KCl, M
PDMS-epoxy-30	0.5	0.67	–7.6	1.010	5.13	0.25
	1	0.59	–35.2	1.018	1.62	0.25
	2	0.78	–41.0	1.011	0.80	0.25
PDMS-COOH-30	0.5	0.43	–30.1	1.036	4.10	0.20
	1	0.50	–36.7	1.014	1.70	0.20
	2	0.53	–39.5	1.019	0.87	0.20

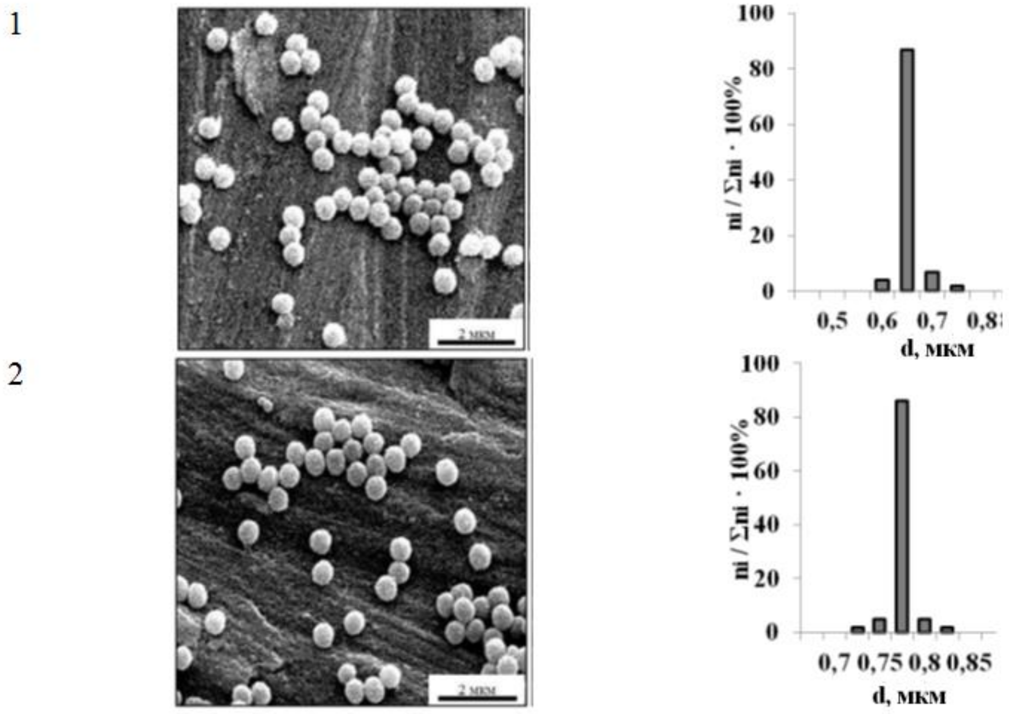

Figure 9. Microphotos of particles of polystyrene suspensions and histograms of their distribution by the sizes and by ξ-potentials obtained at various PPS concentrations in the presence of PDMS-epoxy-30: 1) 0.5%; 2) 2.0%.
[мкм means μm]

The influence of the initiator nature on the polymerization rate, average particle sizes and their distribution by diameters was predictable. In the presence of potassium persulphate (PPS) initiation efficiency and polymerization rate are higher than in the presence of azoisobutyric acid dinitrile (AAD) and benzoyl peroxide (BP). Characteristics of the polystyrene suspensions synthesized in the presence of initiators of various nature with styrene polymerization as an example in the presence of carboxy-containing surfactants are shown in Table 11.

Table 11. Characteristics of polystyrene suspensions obtained in the presence of 1% mass of PDMS-COOH-30 and 1% mass of initiators of various nature, T = 70°C [4]

Initiator	d, μm	ζ, mV	D_w / D_n	Stability in КCl, M
AAD	0.67	–21.3	1.028	0.20
BP	0.70	–20.4	1.037	0.20
PPS	0.65	–21.7	1.045	0.20

The particles of the polystyrene suspensions are characterized by narrow distribution by the sizes: their diameters are 0.65, 0.67 and 0.70 μm, respectively. The dependences of the polymerization rate and molecular weight of the polymers on the concentration of the oil-soluble initiators are close to those usually observed for radical polymerization.

The surfactant concentration influence on the kinetic regularities of the polymerization is shown in Figure 10.

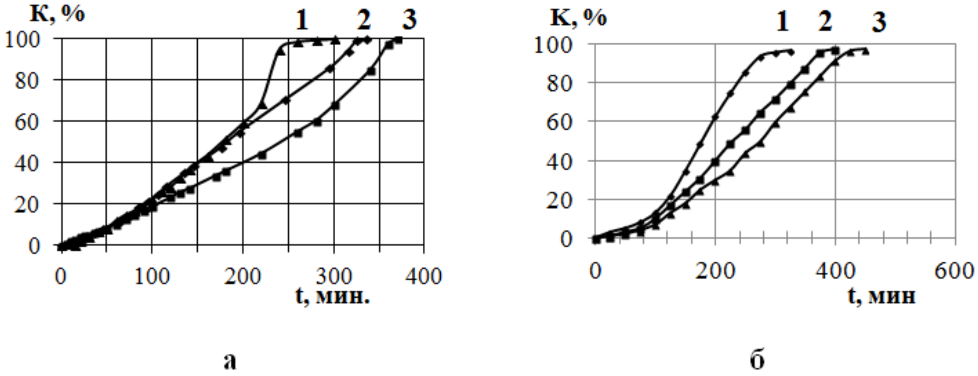

Figure 10. Conversion – time curves obtained upon styrene polymerization at various concentrations of PDMS-epoxy-30 (a) and PDMS-COOH-30 (b) (% mass calculated for the monomer): 1 – 1%; 2 – 2%; 3 – 5%.
[K, % means Conversion, %; мин means minutes; а, б means a, b]

As the surfactant concentration calculated for the monomer increases to 5% mass, the polymerization rate decreases, the particle size slightly increases, the ζ-potential significantly decreases, and the molecular weight of the polymers increases (Table 12). The polymeric system is stable at all surfactant concentrations in the course of the synthesis, and the particle distribution by the sizes (Figure 11) remains narrow. Such influence of the surfactant on the kinetic regularities of styrene polymerization can be explained by the reduction of the monomer dispersion degree and, consequently, of the number of PMP. As for the reduction of ζ-potential, it can be accounted for by shielding of the functional groups of the polymeric chains due to the reduction of their mobility caused by the increase of the environment viscosity.

Table 12. Influence of PDMS-epoxy-30 and PDMS-COOH-30 concentration on the characteristics of the polystyrene suspensions [22]

Surfactant	Surfactant concentration, %	d, μm	ξ, mV	D_w / D_n	V_n ×10^7, mol/l·s	M_η ×10^{-5}	Stability in KCl, M
PDMS-epoxy-30	0.1	0.61	–35.6	1.041	–	–	0.10
	0.5	0.60	–35.9	1.027	–	–	0.20
	1	0.59	–37.1	1.018	1.59	1.61	0.25
	2	0.52	–11.5	1.012	1.02	2.01	0.25
	5	0.57	–9.0	1.011	0.58	2.96	0.25
PDMS-COOH-30	0.1	0.65	–26.6	1.040	–	–	0.10
	0.5	0.63	–32.3	1.038	–	–	0.15
	1	0.50	–36.1	1.026	5.23	0.31	0.20
	2	0.50	–23.7	1.014	3.92	0.41	0.20
	5	0.55	–15.6	1.114	3.34	0.56	0.20

The obtained results differ from those observed in the presence of all types of water-soluble surfactants, where the increase in the surfactant concentration leads to the increase in the polymerization rate and in the reduction of the particles diameter. These results are similar to the dependences observed for the water-insoluble surfactants of different structure [24].

Of special note is that the polymeric suspensions are characterized by stability in the course of the synthesis, even at low concentrations of the organosilicon surfactant (0.1% mass), while the polymerization in the presence of ionogenic surfactants requires surfactant concentration not less than 5–6% mass to ensure stability of the reaction system in the polymerization process.

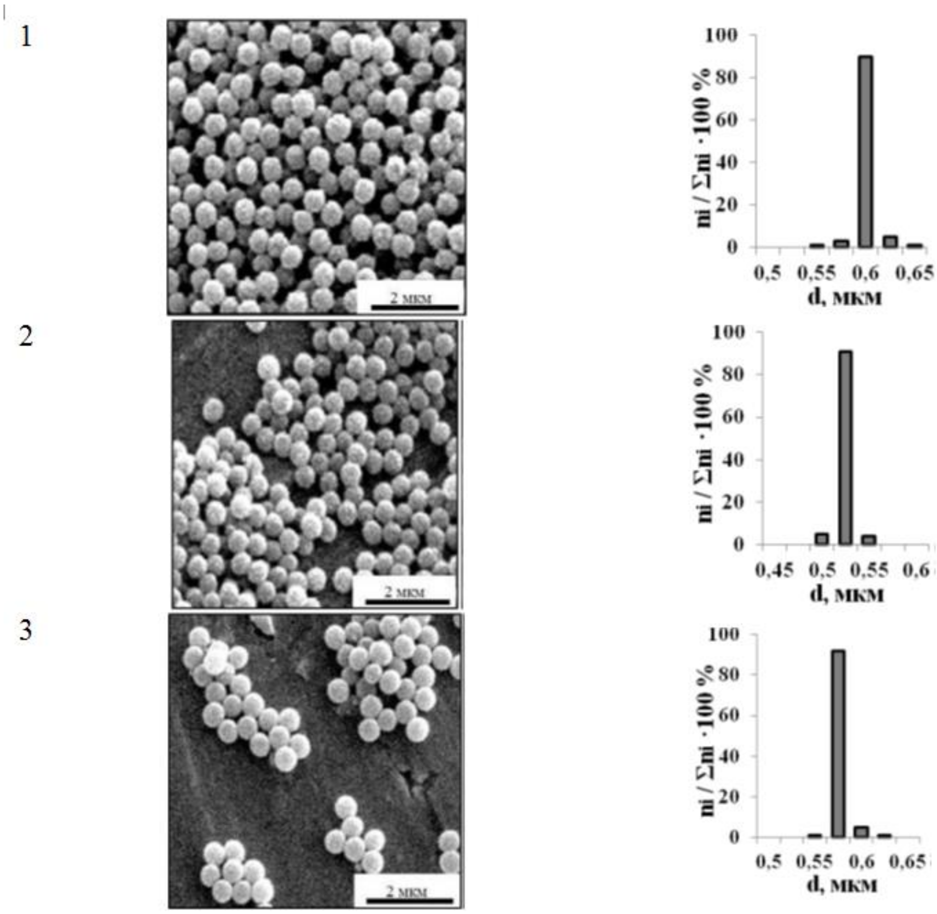

Figure 11. Microphotos and histograms of distribution on the polystyrene suspension particles by sizes obtained at various concentrations of PDMS-epoxy-30:
1 – 0.1% mass; 2 – 2.0% mass; 3 – 5.0% mass.
[мкм means μm]

The influence of the synthesis temperature on the particle size is shown in Table 13 with styrene polymerization in the presence of the carboxy-containing surfactant as an example.

Table 13. Characteristics of polystyrene suspensions obtained in the presence of PDMS-COOH-30 at various synthesis temperatures [11]

Temperature, °C	d, μm	D_w/D_n	Stability in KCl, M
60	0.65	1.045	0.20
70	0.58	1.032	0.20
80	0.55	1.014	0.20

The decrease in the polymerization temperature increases the diameters of the polystyrene microspheres from 0.5 μm (at 80 °C) to 0.65 μm (at 60 °C). Activation energy of the polymerization is 107.1 kJ/mol.

As mentioned above, initiating styrene polymerization with potassium persulphate in the presence of the amino-containing surfactant (PDMS-NH_2-30) gave polymeric suspensions containing two sets of particles with diameters differing in size more than by an order of magnitude (Figure 12). Each of the particle sets was characterized by narrow distribution by the sizes. Particles of the polymeric suspension had a negative charge (ξ = –40 mV).

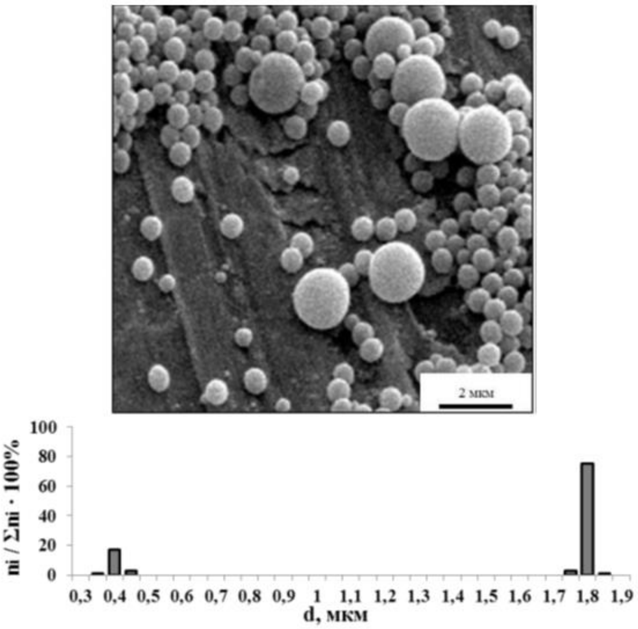

Figure 12. Microphoto and histogram of the distribution by the sizes for polystyrene particles obtained in the presence of 1% mass of PDMS-NH_2-30,
T = 80°C, pH 7 before the polymerization.
[мкм means µm]

Bimodal distribution of the particles of the polystyrene suspensions synthesized in the presence of PDMS-NH_2-30 is observed even at 10% conversion of styrene. When the monomer conversion is 100%, the sizes of the polystyrene particles are 0.4 and 1.8 µm (Table 14).

Table 14. Characteristics of polystyrene suspensions stabilized with PDMS-NH_2-30 at different stages of the monomer conversion

Styrene conversion, %	d, µm	ξ, mV	D_w / D_n
5	0.26	–45.8	1.251
10	0.13 and 0.42	–43.5	bimodal distribution
20	0.19 and 0.55	–42.5	bimodal distribution
30	0.21 and 0.92	–38.0	bimodal distribution
100	0.4 and 1.8	–22.6	bimodal distribution

Since potassium persulphate was used as an initiator, and it produces sulfate ions upon its decomposition, the interaction with the amino group of PDMS-NH_2-30 surfactant gives a salt, α,ω-bis[3-aminopropyl]polydimethylsiloxane sulfate. This salt is a surfactant characterized by higher hydrophilicity than initial PDMS-NH_2-30. So, it is reasonable to assume that its formation at the initial stage of the polymerization leads to more effective dispersion of the monomer, which is the reason of the formation of the finely dispersed fraction of particles in the polymeric suspension. The formation of α,ω-bis[3-aminopropyl]polydimethylsiloxane sulfate is confirmed by its participation in the formation of interfacial adsorption layers with the formation of a negative charge on the PMP surface (ζ-potential is equal to –20÷–30 mV).

It was assumed that the formation of PMP of large diameters is due to the fact that, after PDMS-NH_2-30 is consumed in the interaction with the sulfate ions of the initiator, the remaining quantity of the surfactant reduces the monomer dispersion in bulk of the particles [16].

When the polymerization is initiated with potassium persulphate, pH changes from 7 to 2, and the reaction proceeds in an acidic medium. Because epoxy and amino groups are sensitive to pH changes, we studied the influence of the aqueous phase pH on the stability of the polymeric suspension particles in the course of the synthesis and at storage upon the heterophase polymerization of styrene in the presence of PDMS-NH_2-30. For this purpose the medium pH was changed before the polymerization from 7 to 11, and the pH of the polymeric suspension was fixed. Characteristics of the particles of the polystyrene suspensions obtained in the presence of the amino-containing surfactant are presented in Table 15.

Table 15. Characteristics of polymeric suspensions obtained in the presence of PDMS-NH_2-30 at various pH

pH before polymerization	pH after polymerization	d, μm	ξ, mV	D_w / D_n	$M_\eta \times 10^{-5}$	Stability in KCl, M
7	2	0.4 and 1.8	–22.6	bimodal distribution	2.01	0.20
8	3	0.2 and 1.2	–35.8	bimodal distribution	2.21	0.20
9	7	0.43	–33.8	1.028	1.66	0.20
10	8	0.53	–31.9	1.013	1.77	0.25
11	8.5	0.44	–38.7	1.019	1.80	0.25

It can be seen from the table that the reaction proceeds in neutral or weakly basic media (pH 7, 8, 8.5) only if pH of the aqueous phase is changed to 9, 10 and 11 (before the polymerization). This results in the formation of polystyrene microspheres with narrow distribution by the sizes with diameters 0.43, 0.53 and 0.44 μm, respectively. In the process, an increase in ζ-potential from –33.8 to –38.7 mV is observed. All the polymeric suspensions synthesized in the presence of the amino-containing surfactant at various pH are stable in the course of the synthesis and in solutions of weak electrolytes. Microphotos of the particles and histograms of their distribution by the sizes are shown in Figure 13.

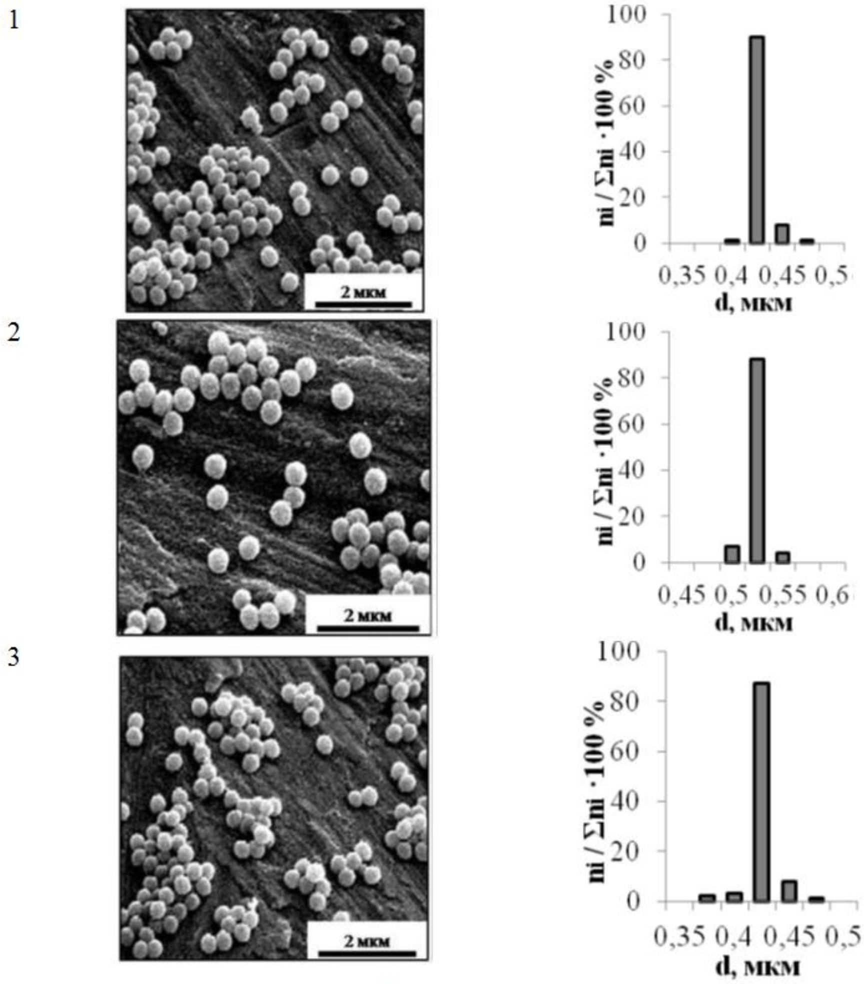

Figure 13. Microphotos and histograms of the distribution by the sizes and by ζ-potentials for polystyrene particles obtained in the presence of PDMS-NH_2-30 at various pH of the aqueous phase:
1 – pH 9; 2 – pH 10; 3 – pH 11.
[мкм means μm]

Thus, the polymerization of styrene in the presence of water-insoluble organosilicon surfactants is a promising method of synthesizing functional polymeric suspensions with narrow distribution by the sizes. These suspensions are stable with respect to aggregation.

The obtained results allowed stating specific features of the heterophase polymerization of lowly water-soluble monomers in the presence of water-insoluble organosilicon surfactants.

These features are follows.

– The formation of polymeric-monomeric particles has long "induction periods" on conversion – time curves (~ 15 min.).

–The particle diameters are constant starting from the low conversion of the monomers to the full transformation of the monomer into the polymer, the narrow distribution by the sizes being preserved.

–The diameter of the polymeric-monomeric particles increases as the concentration of the organosilicon surfactant increases.

–It is possible to synthesize polymeric suspensions stable in the course of the synthesis with narrow particle distribution by the sizes at low surfactant concentration (0.5–1.0% mass calculated for the monomer).

–It is possible to carry out emulsion or microsuspension polymerizations using organosilicon surfactants with various lengths of the siloxane chain.

–The mechanism of the interfacial adsorption layer formation on the surface of the polymeric-monomeric particles is specific: the surfactant is replaced from the bulk of the polymeric-monomeric particles into the surface layer due to their incompatibility and their surface-active properties. The strength of the interphase adsorption layers increases due to the formation of a polymer with a high molecular weight on the interphase boundary upon initiation of the polymerization from the surfactant supramolecular structures.

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