UDC 541.64:547(538.141+1’128)

COLLOID-CHEMICAL PROPERTIES OF SILICONE SURFACTANT USED IN THE SYNTHESIS OF POLYSTYRENE LATEXES

I.A. Gritskova[1], A.A. Amelichev[1,@], O.A. Satskevich[2], A.V. Shkolnikov[1], A.A. Ezhova[1], G.A. Simakova[1], V.A.Vasnyov[3], N.A. Lobanova[1], B.A. Izmaylov[3]

[1] Moscow Technological University (Institute of Fine Chemical Technologies), Moscow, 119571 Russia
[2] Peoples' Friendship University of Russia, Moscow, 117198 Russia
[3] Nesmeyanov Institute of Organometallic Compounds RAS (INEOS), Moscow, 119991 Russia
[@] Corresponding author e-mail: amelichev.88@mail.ru

The synthesis of polymeric suspensions with a narrow particle size distribution is an urgent problem in modern science. The resulting polymeric microspheres are applicable in various fields of chemistry, pharmaceuticals, biology and medicine. In particular, they can be used as carriers of bioligands to create diagnostic test systems. This article presents the results of a study on the colloid-chemical characteristics of water-insoluble fluorinated silicone surfactants and their effect on the polymerization process. The results were compared with data from studies on the properties of surfactants of similar structure not containing fluorine atoms in their structure. Studying these substances’ rheology enabled to determine the most suitable surfactants for adsorption forming a strong interfacial layer during the formation of polymer-monomer particles during the polymerisation. The ability of fluorinated silicone surfactants to form a stable polymeric slurry was proved during heterophase polymerization of vinyl monomers. The resulting polymeric suspensions were characterized by a narrow particle size distribution and high aggregative stability during the synthesis and in storage.

Keywords: *silicone surfactant, synthesis of polystyrene latexes, heterophase polymerization, medium bioligands, colloidal-chemical characteristics.*

Introduction

Synthesizing polymeric suspensions with particles of a certain diameter and a narrow size distribution is a burning problem, because the area of their application is extremely wide [1–3].

Polymeric suspensions are of special interest for biology and medicine, where suspension particles can be used instead of erythrocytes as carriers of bioligands [4, 5].

These suspensions should be characterized by a narrow size distribution and have an average diameter of particles in the range 0.4–5.0 μm. They should also be stable in physiological solutions, in which immunological reactions are carried out. Their surface should contain functional groups for covalent bonding with the functional groups of the bioligand.

The polymeric microspheres obtained by heterophase polymerization of vinyl monomers in the presence of water-insoluble organosilicon surfactants capable to form strong interfacial layers

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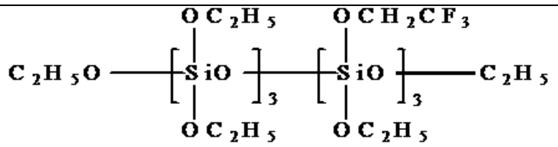
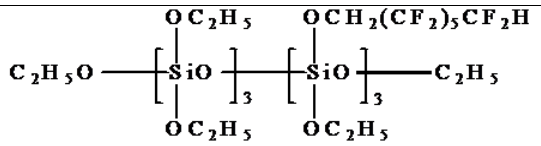
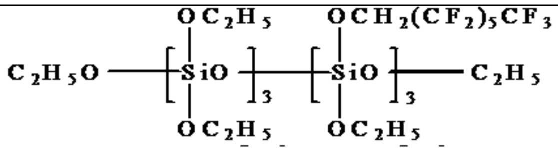
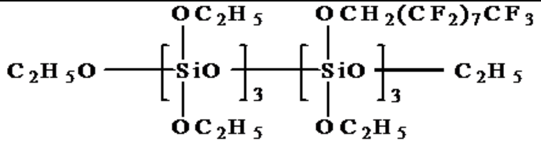
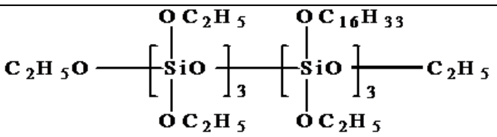
on the surface of polymer-monomer particles (PMP) starting from low conversion degrees of the monomer [5–9] conform to such requirements.

Experimental

In this work water-insoluble fluorinated organosilicon surfactants (Table 1) containing a different amount of $–CF_2$ groups (PAV-1-PAV – 4) were studied. It was expected that stable polymeric suspensions containing polymeric microspheres with a narrow size distribution in a wide range of diameter values would be obtained at their presence. The obtained results were compared to the experimental data on the properties of a surfactant of a similar structure containing no fluorine atoms in its structure (PAV-5).

Table 1. Organosilicon surfactants

Surfac-tant No	The number of F atoms	Name	Formula	Mol. weight
1	9	Undecaethoxy(tri(2,2,2-trifluoroethoxy))hexasiloxane	 $C_2H_5O-\left[\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}O\right]_3-\left[\underset{OC_2H_5}{\overset{OCH_2CF_3}{Si}}O\right]_3-C_2H_5$	927.3
2	36	Undecaethoxy(1*H*, 1*H*, 7*H*-perfluorohepta-1-oxy)hexasiloxane	 $C_2H_5O-\left[\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}O\right]_3-\left[\underset{OC_2H_5}{\overset{OCH_2(CF_2)_5CF_2H}{Si}}O\right]_3-C_2H_5$	1281.5
3	39	Undecaethoxy(1*H*, 1*H*-perfluorohepta-1-oxy)hexasiloxane	 $C_2H_5O-\left[\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}O\right]_3-\left[\underset{OC_2H_5}{\overset{OCH_2(CF_2)_5CF_3}{Si}}O\right]_3-C_2H_5$	1297.4
4	51	Undecaethoxy(1*H*, 1*H*-perfluoronona-1-oxy)hexasiloxane	 $C_2H_5O-\left[\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}O\right]_3-\left[\underset{OC_2H_5}{\overset{OCH_2(CF_2)_7CF_3}{Si}}O\right]_3-C_2H_5$	1445.5
5	0	Undecaethoxy(hexadecyloxy)hexasiloxane	 $C_2H_5O-\left[\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}O\right]_3-\left[\underset{OC_2H_5}{\overset{OC_{16}H_{33}}{Si}}O\right]_3-C_2H_5$	1468.5

Heterophase polymerization of vinyl monomers in the presence of slightly water-soluble organosilicon surfactants containing and not containing fluorine atoms was carried out under the following conditions: polymerization temperature: 80±0.5ºC (in case of vinyl-acetic ester polymerization temperature: 60±0.5ºC); monomer/water volume ratio: 1:9; concentration of the initiator (potassium persulphate): 1% mass calculated for the monomer; concentration of the surfactant: 1% mass calculated for the monomer.

Results and Discussion

Because these substances (see Table 1) are novel type surfactants, it was necessary to study first of all their colloid-chemical properties and the ability to form stable initial emulsions of monomers.

The work was started by studying the interfacial tension on the (toluene solution of the surfactant)/water boundary by the anchor-ring method [10]. Interfacial tension isotherms are presented in Figure 1.

Colloid-chemical properties of the surfactants are presented in Table 2.

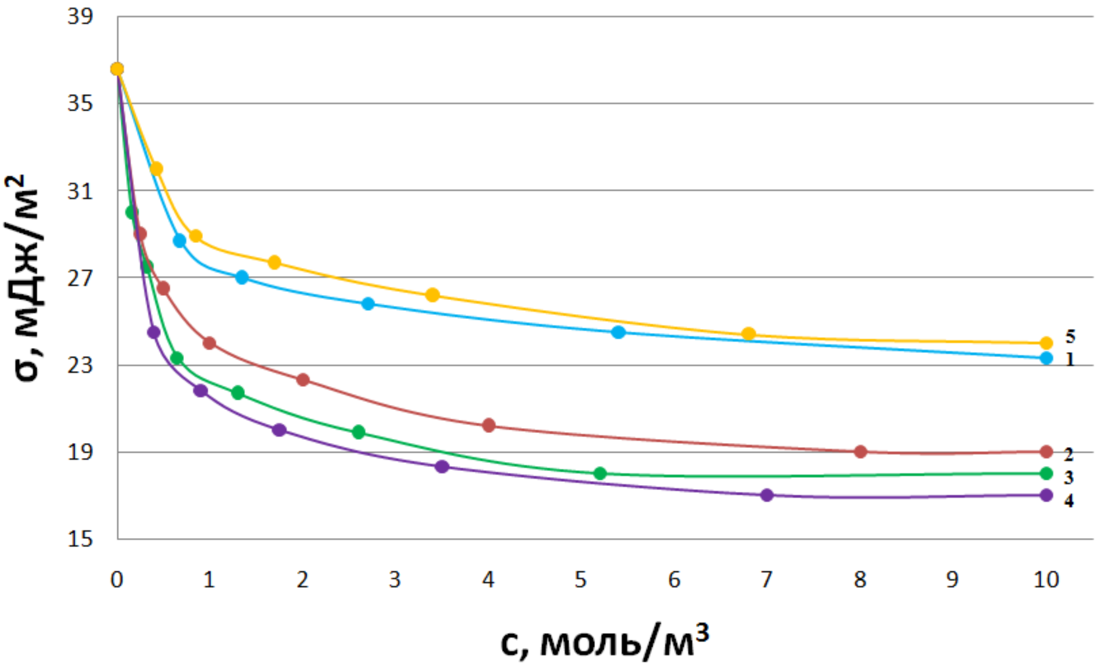


Figure 1. Interfacial tension isotherms of fluorinated organosilicon surfactants with different content of –CF_2 groups: 1 – PAV-1 (9 fluorine atoms); 2 – PAV-2 (36 fluorine atoms); 3 – PAV-3 (39 fluorine atoms); 4 – PAV-4 (51 fluorine atoms); 5 – PAV-5 (does not contain fluorine atoms). [мДж/м^2 means mJ/m^2; моль/м^3 means mol/m^3]

Table 2. Colloid-chemical properties of the adsorption layers of surfactants at the toluene/water boundary at T≈24°C

Surfactant No	$\sigma_{12\min}$, mN/m	CCA*, mol/m^3	Surface activity g×10^{-2}, mN·m^2/mol	$\Gamma_{\max}$×10^{-6}, mol/m^2	Area occupied by molecule, σ_0×10^{-18}, m^2	Layer thickness, δ×10^{-10}, m
1	23	0.8	1.8	5.4	0.31	52
2	19	0.4	3.8	6.5	0.26	87
3	18	0.4	5.8	7.5	0.22	101
4	17	0.4	6.7	7.9	0.21	109
5	24	0.8	1.6	5.1	0.33	78

* critical concentration of the association

It can be seen that all the surfactants show surface activity and decrease interfacial tension. The highest surface activity (6.7×10^2 and 5.8×10^2 mJ · m/mol, respectively) is shown by the high-fluorinated surfactants containing 39 and 51 fluorine atoms (PAV-3 and PAV-4). The surfactant containing no fluorine atoms in the structure (PAV-5) is characterized by the value of surface activity equal to 1.6×10^2 mN · m^2/mol.

The high-fluorinated PAV-3 and PAV-4 are characterized by the greatest values of adsorption: 7.5×10^{-6} and 7.9×10^{-6} mol/m^2, respectively. The thickness of the interfacial adsorption layer formed on the interface boundary is 101×10^{-10} and 109×10^{-10} m, respectively. This is much higher than the values for PAV-5 containing no fluorine atoms.

The surfactant concentration, at which the minimum value of interfacial tension is attained, corresponds to complete formation of the interfacial adsorption layer.

The analysis of results of calculation according to the Langmuir's model showed that the areas falling within a molecule of PAV-5 containing no fluorine atoms and of the fluorinated surfactant containing three –CF_2 groups (PAV-1) are close by values and much larger than those observed in case of the high-fluorinated surfactants. This means that the high-fluorinated surfactants are associated, and polylayer adsorption occurs in their presence. This assumption is confirmed by data obtained by studying Langmuir's films at Brewster's angle. In can be seen in microphotos (Figure 2) that aggregates are formed at high extents of film compression. Cluster structures and the interfacial layer are formed from these aggregates on the interphase boundary.

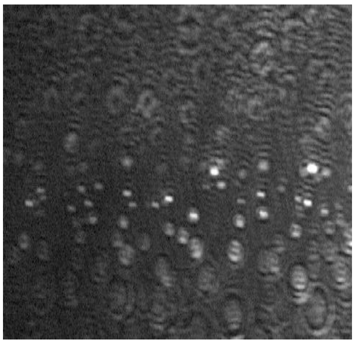


Figure 2. Optical microphotos at Brewster's angle at compression of Langmuir's films for PAV-4 containing 51 atoms of fluorine to value $\pi = 9.9$ mN m^{-1}.

The increase in the content of $-CF_2$ groups in a surfactant molecule results in its compaction, which can be the cause of interfacial tension reduction. The multilayer adsorption of a surfactant does not allow determining the true value of the layer thickness, and the values of the interfacial layer thickness given in Table 2 are theoretical values calculated with the use of Langmuir's model for surfactants of the conventional type.

The stability of the styrene emulsions containing dissolved surfactants with the greatest number of fluorine atoms at their concentration 1% and the volume ratio of the aqueous and hydrocarbonic phases equal to 1:4, respectively, turned out to be low, and they were destroyed within 5–10 min. The stability of the emulsions significantly increased when dissolving polystyrene with molecular weight M_w=355000 (1% mass) in the hydrocarbonic phase.

We estimated the durability of the interfacial adsorption layer on the water / (toluene solution of PAV-3 containing 39 fluorine atoms) boundary in the presence of polystyrene and without it, with the use of the method of torsion of a glass disk placed on the water / [toluene surfactant solution (1%)] boundary with the use of a Rehbinder-Trapesnikow elastoviscometer. The critical shear stress characterizing the layer durability in the first case was $P_{rs}=5\times10^{-3}$ mN/m, and in the second case it was minimal and equal to $P_{rs}=1\times10^{-3}$ mN/m. The time of the interphase adsorption layer formation was 20 min.

It is assumable that when carrying out heterophase polymerization, high molecular weight polystyrene which is formed at initiation of the polymerization on the interphase boundary will participate along with the surfactant in the formation of the interfacial adsorption layer and will increase the stability of the polymeric and monomeric particles.

Kinetic curves of conversion vs time are shown in Figures 3 and 4. It can be seen that the polymerization of butyl acrylate, butyl methacrylate, vinyl acetate and methyl methacrylate is characterized in both cases by almost identical high rate according to the reactivity of radicals and monomers, starting from early stages of the monomer conversion. The general time of polymerization of butyl acrylate, butyl methacrylate, vinyl acetate and methyl methacrylate up to complete conversion of the monomers does not exceed 3.5 h, and in case of styrene, 7 h.

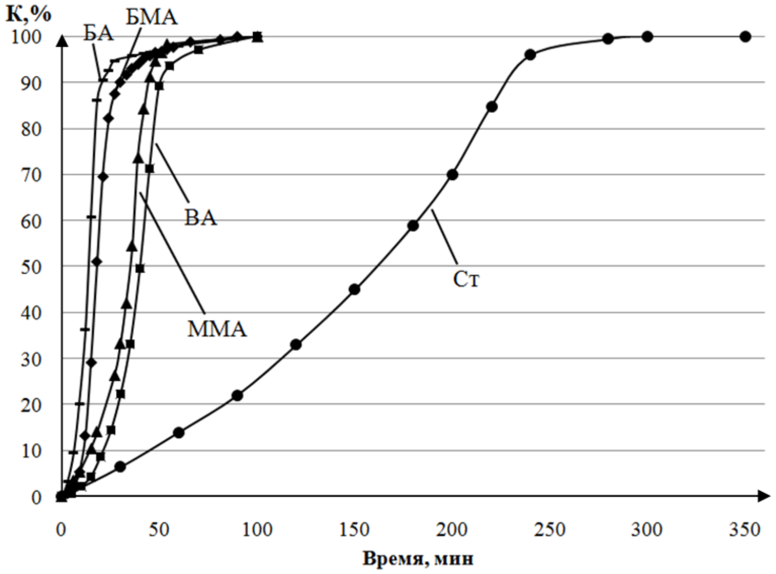


Figure 3. Curves of conversion vs time obtained upon polymerization of vinyl monomers in the presence of PAV-5 (no fluorine atoms).

[К (Конверсия мономера) means C (Conversion of monomer); Время, мин means Time, min; БМА means BMA; БА means BA; ВА means VA; ММА means MMA; Ст means St]

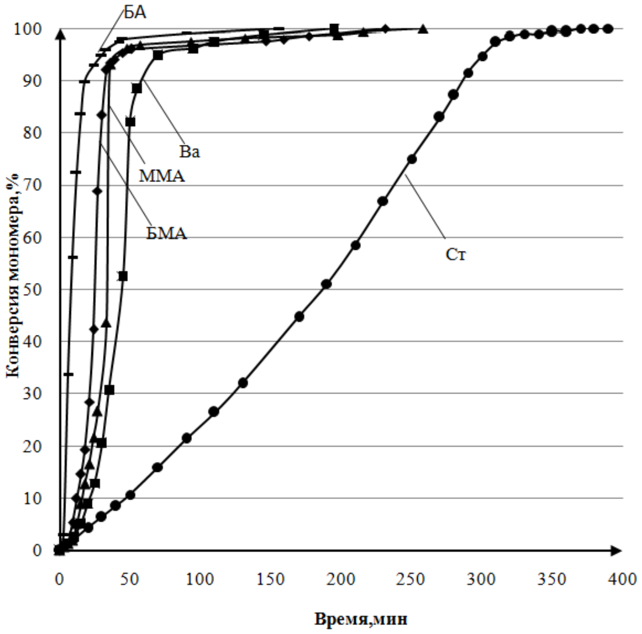


Figure 4. Curves of conversion vs time obtained upon polymerization of vinyl monomers in the presence of organosilicon PAV-4 (containing 51 fluorine atoms).

[К (Конверсия мономера) means C (Conversion of monomer); Время, мин means Time, min; БМА means BMA; БА means BA; ВА means VA; ММА means MMA; Ст means St]

Characteristics of the synthesized polymeric suspensions are presented in Tables 3 and 4.

All the obtained polymeric suspensions are characterized by high aggregate stability as evidenced by the fact that there is no coagulum in the reaction system. Diameters of the microspheres are in the range from 0.38 to 0.70 μm, the polymeric suspensions being characterized by narrow particle size distribution.

Figures 5 and 6 present histograms of particle size distribution and microphotos of polymeric suspensions obtained by polymerization of monomers of various nature in the presence of organosilicon surfactants containing and not containing fluorine atoms. It can be seen that polymeric suspensions with narrow particle size distribution and close values of diameters are formed in the presence surfactants of both types.

Table 3. Characteristics of polymeric suspensions stabilized by non-fluorinated PAV-5

Monomer	**Polymerization rate**		**d, μm**	**ζ-potential, mV**	**D_w/D_n**	**Coagulum**
	V_p, %/min	**$V_p \times 10^6$, mol/l·s**				
Styrene	0.33	0.47	0.70	–13.1	1.002	–
Vinyl acetate	1.15	2.09	0.62	–7.79	1.006	–
Methyl methacrylate	1.39	2.18	0.38	–24.8	1.094	–
Butyl methacrylate	2.63	2.76	0.40	–21.0	1.138	–
Butyl acrylate	2.97	3.45	0.46	–11.6	1.015	–

Table 4. Characteristics of polymeric suspensions stabilized by fluorinated PAV-4 containing 51 fluorine atoms in the structure

Monomer	Polymerization rate		d, µm	ζ-potential, mV	D_w/D_n	Coagulum
	V_p, %/min	$V_p \times 10^6$, mol/l·s				
Styrene	0.31	0.46	0.55	–15.9	1.013	–
Vinyl acetate	1.10	1.99	0.32	–14.9	1.052	–
Methyl methacrylate	1.37	2.14	0.39	–22.2	1.245	–
Butyl methacrylate	2.21	2.32	0.42	–23.4	1.188	–
Butyl acrylate	2.53	2.69	0.58	–21.6	1.002	–

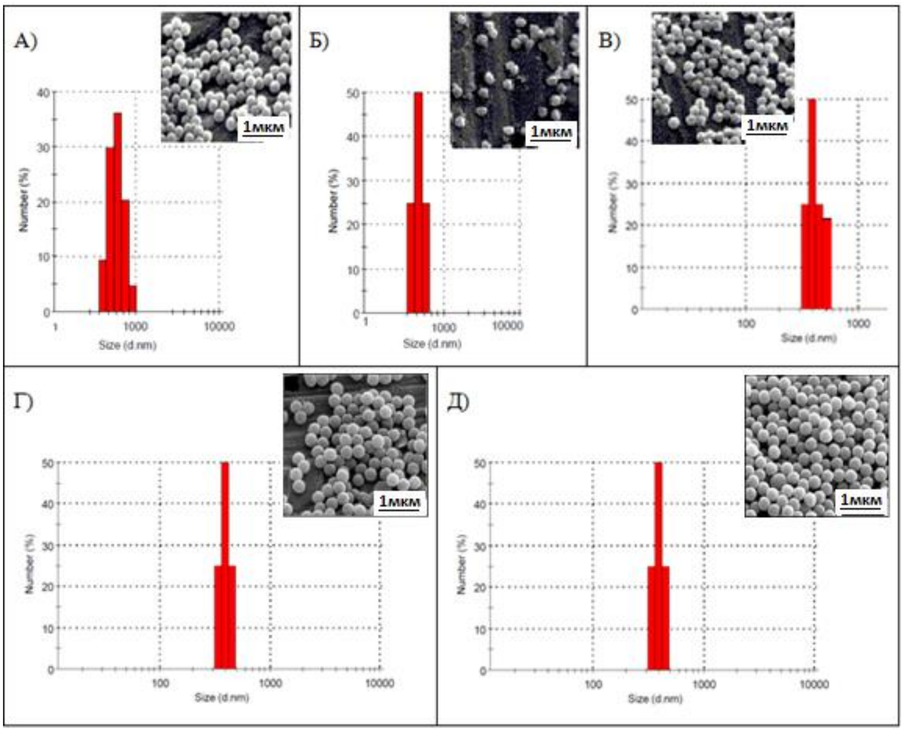


Figure 5. Histograms of size distribution and microphotos of polymeric particles of different nature obtained in the presence of non-fluorinated PAV-5:
A – styrene, B – butyl acrylate, C – butyl methacrylate,
D – methyl methacrylate, E – vinyl acetate.
[А) means A); Б) means B); В) means C); Г) means D); Д) means E); мкм means µm]

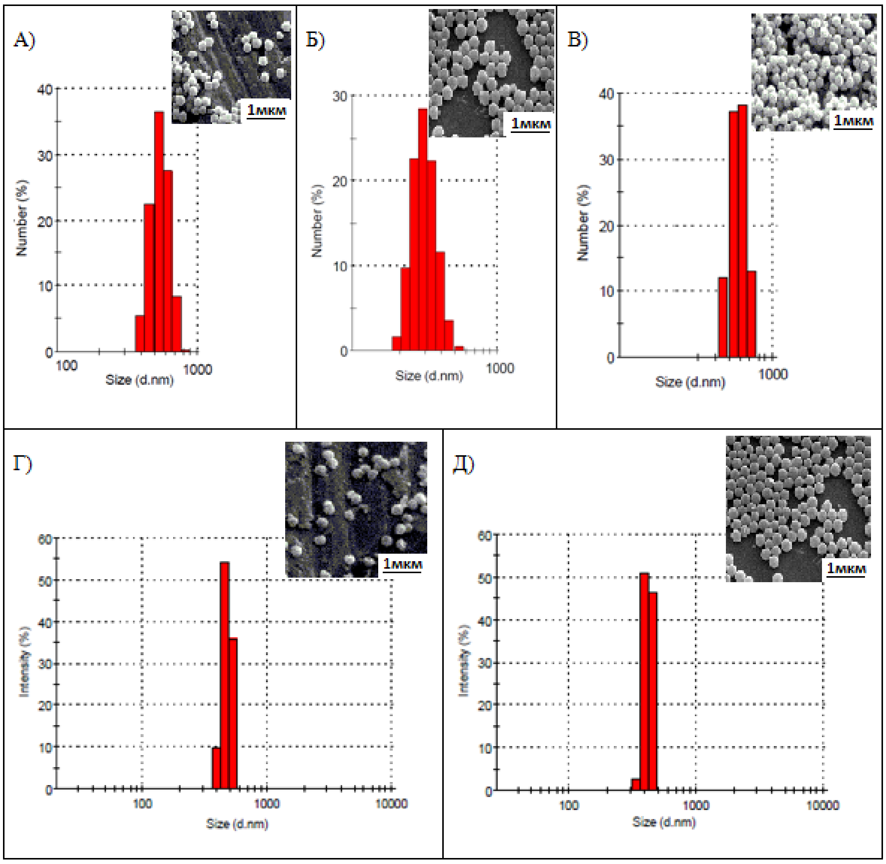


Figure 6. Histograms of size distribution and microphotos of polymeric particles of different nature obtained in the presence of PAV-4 containing 51 fluorine atoms:
A – styrene, B – vinyl acetate, C – methyl methacrylate,
D – butyl methacrylate, E – butyl acrylate.
[А) means A); Б) means B); В) means C); Г) means D); Д) means E); мкм means μm]

Conclusions

The obtained results allow recommending fluorinated organosilicon substances as surfactants for the synthesis of polymeric suspensions with narrow particle size distribution stable in the course of the synthesis and at storage, with diameters in the range 0.3–0.8 μm. The obtained polymeric suspensions can be used also for obtaining hydrophobic coatings on various materials, and the polymeric microspheres, as carriers of bioligands when creating diagnostic test systems.

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