

## Synthesis of oligosiloxanes with 3-aminopropyl groups and their testing as surfactants in the preparation of polymer microspheres

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Polydimethyl-*co*-methyl(3-aminopropyl)siloxanes differing in the content of amino groups and molecular weight were synthesized by two pathways, namely, by hydrosilylation of oligodimethyl-*co*-methylhydrosiloxane with *N*-(trimethylsilyl)allylamine (TMSAA) and by copolymerization of octamethylcyclotetrasiloxane with methyl(3-aminopropyl)cyclosiloxanes. The colloid-chemical properties of the synthesized oligomers were studied. The oligosiloxanes possess high surface activity and can reduce the interfacial tension in the interface surfactant solution in toluene–water to 6.7–4.2 mJ m<sup>2</sup>. Aggregatively stable polystyrene suspensions with particle of 0.5 and 0.8 μm in diameter were obtained in the presence of the synthesized oligomers.

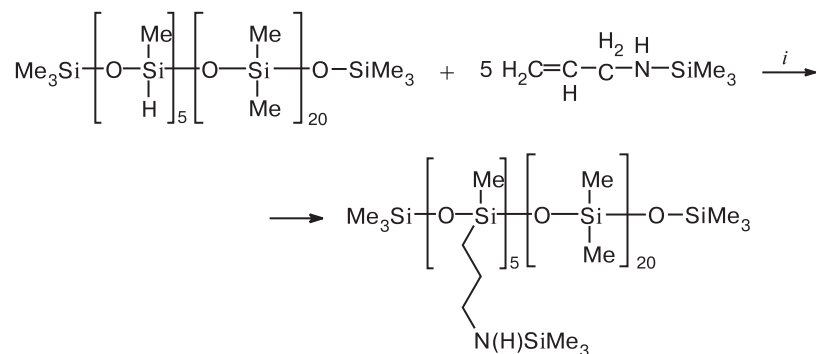
**Key words:** heterophase polymerization, polystyrene, siloxanes, surfactants, polymer suspension.

Nowadays, monodisperse polymer particles are commercially available products which found application as calibration standards for flow cytometers, particle analyzers and hematology analyzers, electrochemical potential measuring instruments, templates for the preparation of porous materials; they are also used in nephelometric and turbidimetric analysis, immunoanalysis, *etc.* There are many different approaches to the synthesis of such monodisperse particles, for example, nucleation,<sup>1,2</sup> emulsifier-free,<sup>3</sup> dispersion<sup>4</sup> polymerization, *etc.*<sup>5,6</sup> However, most of them are either technically and technologically quite complex, time-consuming and laborious, or difficult to reproduce. In this regard, it is interesting to try organosilicon oligomers as surfactants for the synthesis of monodisperse polymer particles.<sup>7,8</sup>

The works<sup>9,10</sup> reported that linear organosilicon oligomers containing at the siloxane chain ends 10-carboxydecyl, 3-aminopropyl, 3-glycidoxypropyl, or oligo(ethylene oxide) fragments can be successfully used as stabilizers in the synthesis of polymer suspensions by heterophase polymerization. In their presence, stable

polymer dispersions with particles from 0.4 to 2.0 μm in diameters were obtained with a narrow particle size distribution and a polymer content of up to 20 wt.%. In order to develop this method to obtain polymer suspensions with a larger diameter of particles and a higher polymer content in the suspension, it seems reasonable to broaden the range of organosilicon oligomers used as surfactants in the heterophase polymerization of vinyl monomers. Oligodimethylsiloxanes containing functional groups in the main siloxane chain, rather than at the ends, are of particular interest. In such copolymers, it is possible to purposefully change the content of functional groups and, as a consequence, the hydrophilic-lipophilic balance of surfactants for a given molecular weight (MW) of the polymer. It is expected that the presence of organosilicon surfactant with a high content of functional groups will not only provide increased stability of forming polymer particles, but also increase the concentration of functional groups on their surface. This is essential for the subsequent modification of the surface of polymer particles, in particular, when they are used as carriers of bioligands in diagnostic test systems.<sup>11,12</sup>

Scheme 1



**Reagents and conditions:** *i.* Karstedt catalyst, 105–120 °C.

The purpose of the present work is to synthesize polydimethyl-*co*-methyl(3-aminopropyl)siloxanes (PDMS-MAPS) and to study the heterophase polymerization of styrene in their presence as stabilizers of the polymer dispersion.

### Results and Discussion

We carried out the synthesis of a number of PDMS-MAPS, differing in both the content of amino groups and molecular weight.

The synthesis of amino-containing siloxanes was conducted according to two schemes: 1) by hydrosilylation of oligodimethyl-*co*-methylhydrosiloxane (G-5/20) with *N*-(trimethylsilyl)allylamine (TMSAA); 2) by copolymerization of octamethylcyclotetrasiloxane with methyl(3-aminopropyl)cyclosiloxanes.

Hydrosilylation of G-5/20 ( $M_n = 1950$ ) containing 20 mol.% of methylhydrosiloxane units was performed according to Scheme 1.

The process was carried out with a 10% molar excess of TMSAA with respect to the Si–H groups. A mixture of TMSAA with the catalyst (Karstedt catalyst, 2 mg of Pt per 1 kg of the reaction mixture) was added slowly dropwise to hydrosiloxane G-5/20 heated to 90 °C with stirring, which was accompanied by heating of the reaction mixture to 120 °C. The temperature of the mixture (105–110 °C)

was regulated by the speed of addition. After the addition of TMSAA, the reaction mixture was stirred for 3 h at 100 °C until complete conversion of the Si–H groups, which was determined by  $^1\text{H}$  NMR. Then, the protecting trimethylsilyl groups were removed by treatment of the reaction mixture with a three-fold molar excess of anhydrous ethanol for 3 h at 50 °C. Volatile products were removed using a water-jet pump (~20 Torr). The obtained copolymer I was characterized by  $^1\text{H}$  NMR. The content of amino groups was determined by acid-base titration using 0.1 N aqueous HCl (Table 1). The synthesis of PDMS-MAPS with a higher content of amino groups and a higher MW was carried out by copolymerization of octamethylcyclotetrasiloxane with the hydrolysis product of methyl(3-aminopropyl)dimethoxysilane. This approach was chosen because the hydrosilylation is always accompanied by side reactions of dehydrocondensation of Si–H groups, which, with a high content of such groups and high molecular weights, leads to the formation of branched polymers, including cross-linked structures.

In the first stage, methyl(3-aminopropyl)dimethoxysilane (MAPDMS) was hydrolyzed according to Scheme 2.

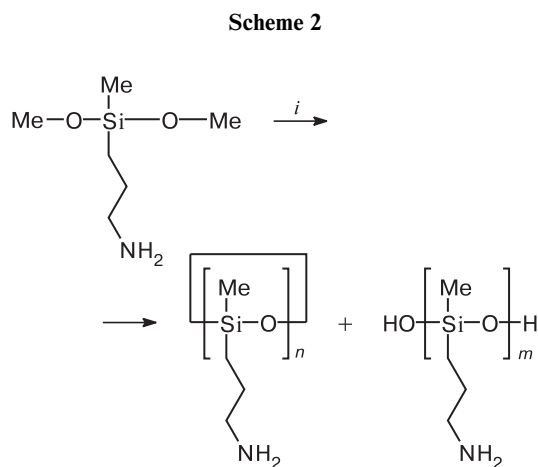
The starting MAPDMS was added slowly dropwise to vigorously stirred distilled water. Then, the reaction mixture was stirred at 80 °C for 4 h. The process was carried out until the signals for the methoxy protons disappeared from the  $^1\text{H}$  NMR spectrum.

**Table 1.** Properties of synthesized polydimethyl(methyl(3-aminopropyl))siloxanes of general formula  $\text{MD}_n \cdot \text{D}^{\text{Pr}(\text{NH}_2)}_m \text{M}$  ( $\text{M} = [(\text{CH}_3)_3\text{SiO}_{0.5}]$ ,  $\text{D} = [(\text{CH}_3)_2\text{SiO}]$ ,  $\text{D}^{\text{Pr}(\text{NH}_2)} = [(\text{CH}_3)((\text{CH}_2)_3\text{NH}_2)\text{SiO}]$ )

Copolymer	<i>n</i>	<i>m</i>	Methyl(3-aminopropyl)siloxane units (mol.%)		[NH <sub>2</sub> ] (wt.%)	
			Theory	Experiment*	Theory	Experiment**
I	20	5	20.0	16.5	6.1	5.2
II	50	50	50.0	47.6	8.2	8.1
III	300	60	16.7	16.3	3.3	3.2

\* Determined by  $^1\text{H}$  NMR.

\*\* Determined by titration.

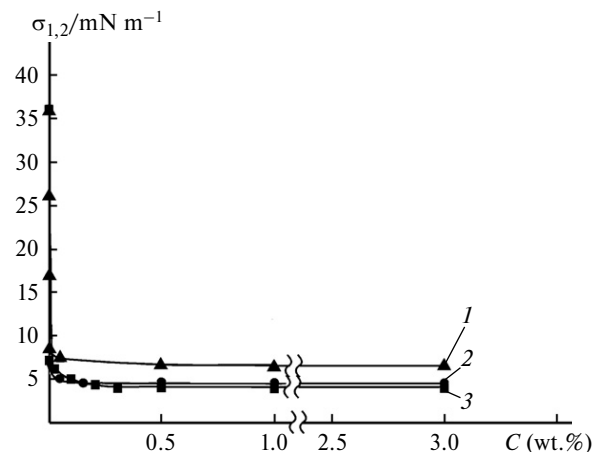


**Reagents and conditions:** *i.* H<sub>2</sub>O, 80 °C.

In the second stage, the hydrolysis products of MAPDMS were copolymerized with methylsiloxane liquid PMS-50 (in the synthesis of copolymer **II**) or with octamethylcyclotetrasiloxane (D<sub>4</sub>) and methylsiloxane liquid PMS-5 (in the synthesis of copolymer **III**) in the presence of tetramethylammonium hydroxide (TMAH) (Scheme 3).

The process was carried out at 100 °C with the molar ratios of reagents providing the number of units *n* and *m* in the copolymer equal to 50 and 50 (copolymer **II**) or 300 and 60 (copolymer **III**). The reaction progress was monitored by the content of volatile components in the reaction mixture. The resulting copolymers **II** and **III**, which are transparent viscous liquids with a yellowish tint, were characterized by the <sup>1</sup>H NMR and GPC. The content of amino groups was determined by acid-base titration using 0.1 N aqueous HCl (see Table 1).

The content of methyl(3-aminopropyl)siloxane units was from 16.3 to 47.6%, with the number of amino groups in the copolymers being close to expected.

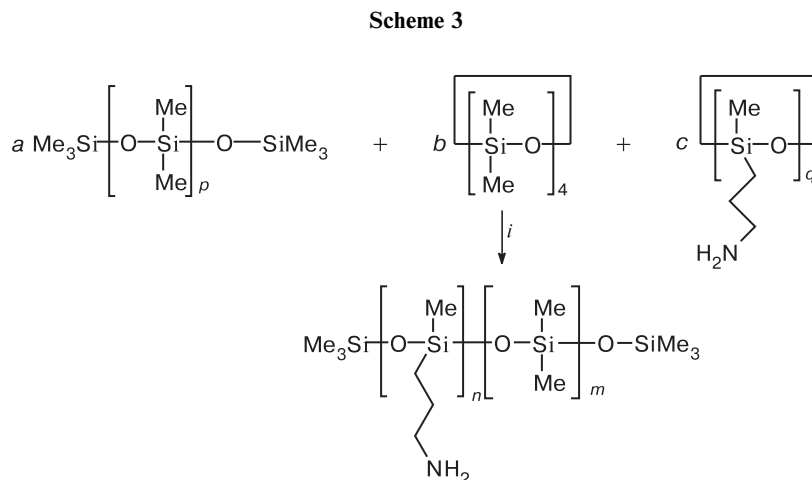


**Fig. 1.** Interfacial tension isotherms at the toluene solution of surfactant–water interface: 1, copolymer **I**, 2, copolymer **II**, 3, copolymer **III**.

For all the synthesized surfactants (**I–III**), we obtained interfacial tension isotherms at the surfactant toluene solution–water interface, from which the colloid-chemical properties of the copolymers under study were calculated (Fig. 1, Table 2).

As can be seen from Fig. 1, the obtained isotherms are characterized by an abrupt drop in the interfacial tension already at concentrations of organosilicon surfactants equal to ~0.025 wt.%, which is an order of magnitude lower than the concentrations for the previously described organosilicon surfactants with terminal aminopropyl groups. The minimum values of interfacial tension for all three copolymers are close and lie in the range from 4.2 to 6.7 mN m<sup>-1</sup>, with the minimum achievable values of this parameter decreasing with the increase in MW of the copolymer and the content of amino groups.

All the surfactants under investigation form a layer with a thickness of 2.9 to 33.5 nm at the interface. An abrupt decrease in the interfacial tension at low concentrations



**Reagents and conditions:** *i.* 100 °C, if *a* = 1, *b* = 0, *p* = 50, *c* · *q* = 50, polymer **II**; *a* = 1, *b* = 73, *p* = 8, *c* · *q* = 60, polymer **III**.

**Table 2.** Colloid-chemical properties of synthesized copolymers

Copolymer	$M_n$	$\sigma_{1,2}/\text{mJ m}^{-2}$	$G_{\text{max}} \cdot 10^6/\text{mol m}^{-2}$	$G/(\text{mN m}^2) \text{ mol}^{-1}$	$S_0/\text{\AA}^2$	$\delta/\text{nm}$
<b>I</b>	2200	6.7	1.3	3.6	124	2.9
<b>II</b>	9600	4.5	3.4	9.4	48	32.7
<b>III</b>	29400	4.2	1.1	14.2	145	33.5

indicates a high surface activity of the synthesized substances, the value of which varies in the range of 8.3–14.2 ( $\text{mN m}^2$ )  $\text{mol}^{-1}$ .

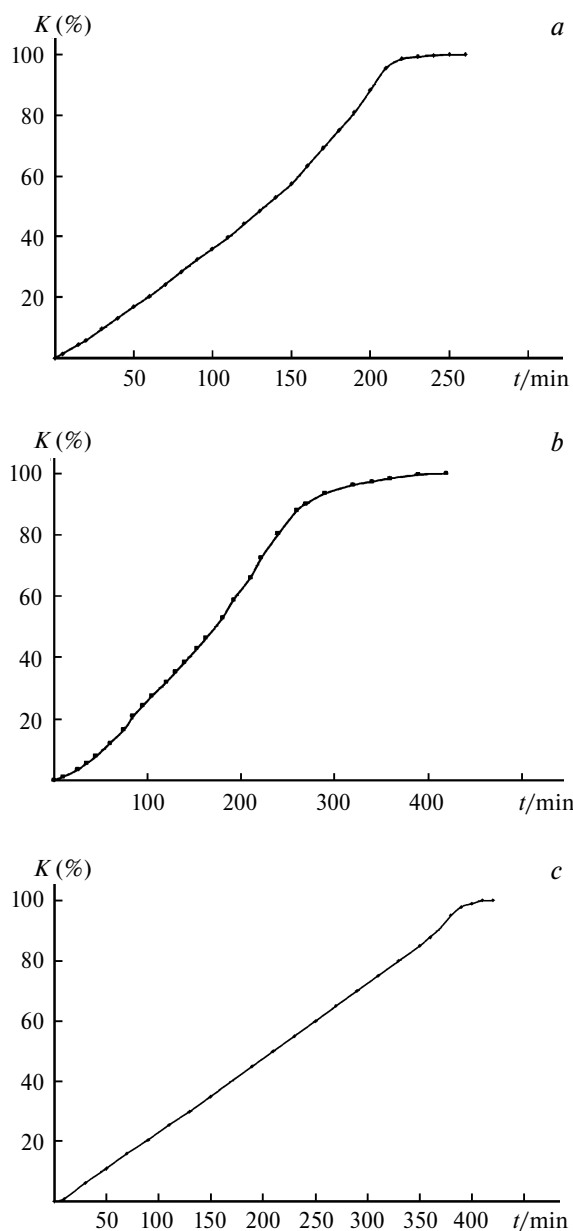
The heterophase polymerization of styrene in the presence of the synthesized PDMS-MAPS copolymers was carried out under the following conditions: the volume ratio styrene : water was 1 : 9, the initiator (potassium persulfate) concentration was 1 wt.% based on monomer, the temperature was  $80 \pm 0.5$  °C. The surfactant concentration was 0.25, 0.5, and 1 wt.% based on monomer for copolymers **III**, **II** and **I**, respectively. The kinetic curves in the "styrene conversion—time" coordinates, as well as the properties of the obtained polymer suspensions, are presented in Fig. 2 and Table 3.

From Fig. 2, it follows that in all the cases the polymerization of styrene proceeds without a pronounced induction period at a constant rate of up to 90% conversion of the monomer in the presence of copolymer **III** and 60% conversion in the presence of copolymers **I** and **II**. The absence of the induction period indicates a high rate of the formation of polymer-monomer particles (PMP). At high monomer conversions, the polymerization rate, on the one hand, should decrease due to a decrease in the monomer concentration and, on the other hand, increase due to the gel effect caused by an increase in the reaction medium viscosity. These two processes determine the change in the rate of synthesis at conversions above 60% in the presence of copolymers **I** and **II**.

The resulting polystyrene suspensions are characterized by aggregative stability, as evidenced by the absence of coagulum. The negative charge on the surface of polymer microspheres is explained by the localization of the terminal sulfo groups of the polymer chains on the surface of the PMP, the fragments of molecules of potassium persulfate used as an initiator.

The diameter of polystyrene particles depends on the dispersion degree of the monomer and on the time of formation of stability barriers in the interfacial layers of the PMP. An increase in the concentration of surfactant and its MW reduces the dispersion degree of the monomer droplets formed in the system, which leads to an increase in the diameter of polymer particles from 0.5 to 0.8  $\mu\text{m}$ .

Figure 3 shows micrographs of the obtained polystyrene particles, from which it is seen that the polymer particles have a spherical shape and are characterized by high polydispersity. It can be assumed that the high polydispersity



**Fig. 2.** The dependence of the conversion ( $C$ ) on time in the polymerization of styrene at a volume ratio of monomer—aqueous phase = 1 : 9 in the presence of organosilicon surfactant: *a*, copolymer **II** (0.5 wt.% based on monomer); *b*, copolymer **I** (1 wt.% based on monomer); *c*, copolymer **III** (0.25 wt.% based on monomer).

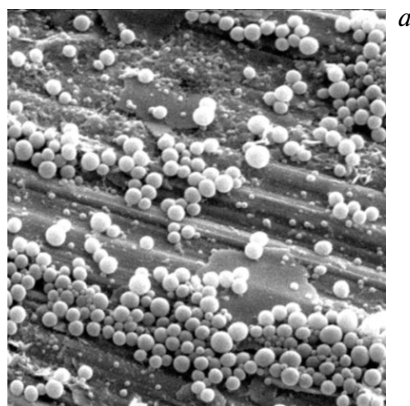
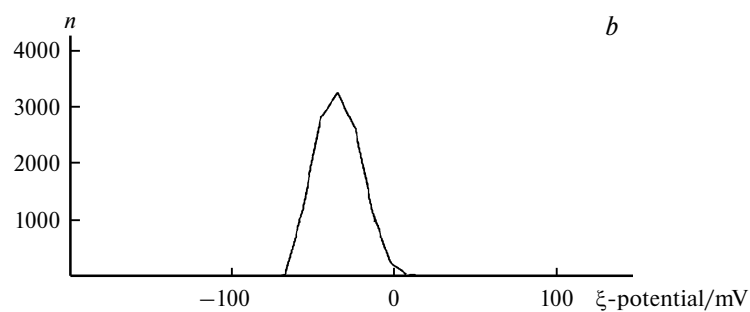
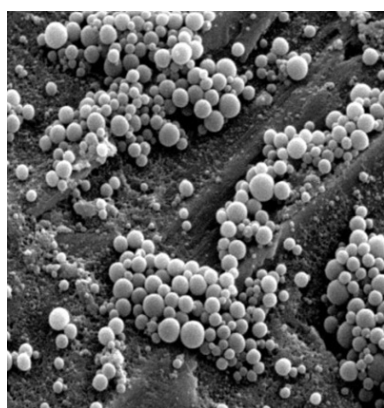
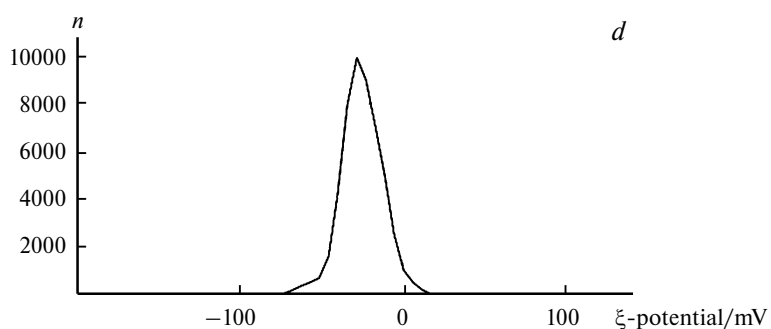
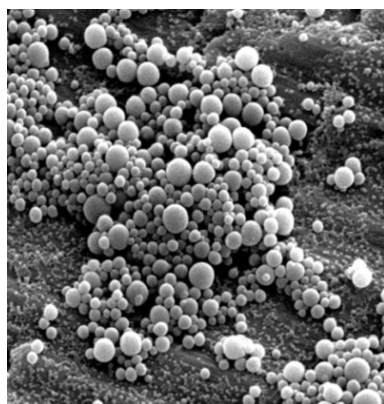
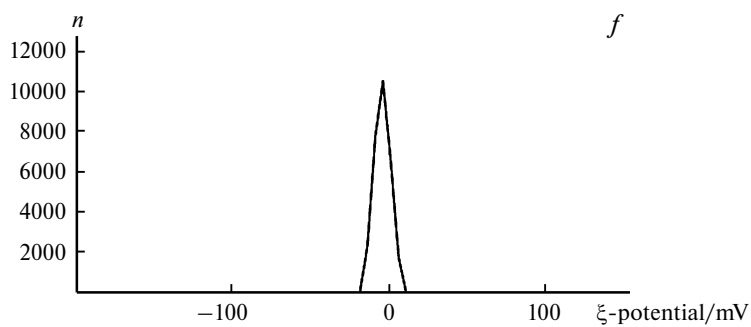
**Table 3.** Characteristics of polystyrene suspensions

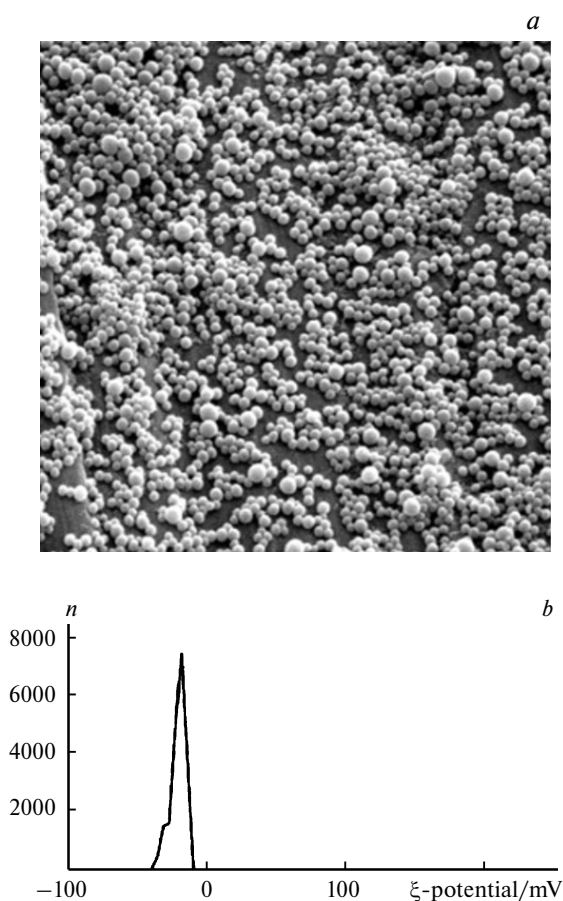
Surfactant	[Surfactant]* (wt.%)	[NH <sub>2</sub> ]** (wt.%)	$V_p \cdot 10^7$ *** /mol (L s) <sup>-1</sup>	$d$ /μm	$\xi$ /mV	Coagulum content in suspension
Copolymer I	1	4.8	2.5	0.8	-25.6	—
Copolymer II	0.5	8.1	4.8	0.5	-12.0	—
Copolymer III	0.25	3.2	1.7	0.8	-15.0	—

\* Surfactant content (% from polymer weight).

\*\* Content of NH<sub>2</sub> groups in surfactant.

\*\*\* Polymerization rate.

*a**b**c**d**e**f***Fig. 3.** Micrographs (*a, c, e*) and histograms of the particle distribution by the  $\xi$ -potential (*b, d, f*) for polystyrene particles stabilized by an organosilicon surfactant: copolymer I (*a, b*); oligomer 5/20 (*c, d*); copolymer II (*e, f*).



**Fig. 4.** Micrograph and histogram of the particle distribution by the  $\zeta$ -potential for polystyrene particles at the phase ratio monomer : water = 1 : 2 stabilized by an organosilicon surfactant, copolymer **III** at a concentration of 0.5 wt.% based on monomer.

of the polymer suspension is associated with the participation of small droplets in the formation of the PMP. Apparently, at the initial stage of the process, before the initiation of polymerization in monomer drops, the Ostwald ripening does not reach completion. The increase in the surfactant concentration to 0.5 and 1% accelerates the Ostwald ripening, and the final polymer suspension is characterized by a narrow particle size distribution.

Of particular interest is the possibility of obtaining polystyrene suspensions stabilized by organosilicon surfactants at a concentration of 0.5 wt.% based on the monomer and at a high content of polymer (the volume ratio styrene : water, 1 : 2). It was impossible to obtain such results in the presence of organosilicon surfactants with alternative structure.

Figure 4 shows the micrograph of the obtained polystyrene particles and the  $\zeta$  potential distribution histogram. It is seen that the polymer particles have a spherical shape and are characterized by high stability, as evidenced by the absence of coagulum. Especially note the high stability of the polymer suspension with a polymer content of about

33% at a surfactant concentration of 0.5 wt.%. This concentration of surfactant is 4–6 times lower than that used in the case of organosilicon surfactants with terminal aminopropyl groups<sup>9</sup> and 8–10 times lower than in the case of hydrocarbon surfactants.

From the results obtained, it can be concluded that the synthesized organosilicon oligomers can be used as stabilizers for polymer suspensions in the heterophase polymerization of styrene. The high stability of polymer suspensions is achieved at low concentrations of surfactants, which makes this polymerization process economically and environmentally more advantageous as compared to emulsion polymerization in the presence of hydrocarbon surfactants.

### Experimental

1,1,3,3,5,5,7,7-Octamethylcyclotetrasiloxane ( $D_4$ ) (97%, ABCR); methyl(3-aminopropyl)dimethoxysilane (Jingzhou-Jiangnan Fine Chemical Co.), methylsiloxane liquids PMS-5 (Penta-91 Ltd.) and PMS-50 (Penta-91 Ltd.), tetramethylammonium hydroxide (TMAH) (Aldrich), hexamethyldisilazane (Ekos-1), allylamine (Acros, 98%), hexamethyldisiloxane (Acros, 98%), BS-94 polymethylhydrosiloxane (Wacker Chemie AG), sulfocationite resin KU-23 (Akvakhim), 2% solution of Karstedt catalyst (platinum(0)–1,2-divinyl-1,1,3,3-tetramethyldisiloxane complex, ABCR) were used in the work without additional purification. Toluene (Khimmed, analytical grade) was dried and distilled over calcium hydride. The starting oligodimethylmethylhydrosiloxane (G-5/20) was synthesized from hexamethyldisiloxane,  $D_4$  and polymethylhydrosiloxane according to the known procedure<sup>13</sup> in the presence of sulfocationite KU-23. <sup>1</sup>H NMR of G-5/20 ( $CDCl_3$ ),  $\delta$ : 0.10 (m, 3 H, Me–Si); 4.70 (m, 1 H, H–Si).

<sup>1</sup>H NMR spectra were recorded on a Bruker AM-360 Fourier-spectrometer (360 MHz), using tetramethylsilane as an internal standard. Low-boiling-point products were analysed by GLC on a LKhM-72 chromatograph with a thermal conductivity detector at a temperature programmed from 50 to 280 °C at the rate of heating 12 deg min<sup>-1</sup>, a 2-m column filled with Chromaton N-AW (0.250–0.315), using 5% SE-30 as a liquid phase and helium as a carrier gas at a rate of 40 mL min<sup>-1</sup>, the temperature of the detector and the injector was 290 °C and 300–350 °C, respectively.

TMSAA was synthesized from allylamine and hexamethyldisilazane in the presence of ammonium chloride as a catalyst.

**Hydrosilylation of *N*-(trimethylsilyl)allylamine.** Oligodimethyl-*co*-methylhydrosiloxane G-5/20 ( $M_n = 1950$ , 20 mol.% of methylhydrosiloxane units) (20 g, 0.01 mol) was placed into a 50-mL four-neck flask equipped with a reflux condenser with a calcium chloride drying tube, a thermometer, a dropping funnel with a bypass, and a shaft mixer. The content of the flask was heated in an oil bath to 100 °C, followed by a dropwise addition of a mixture of TMSAA (7.3 g, 0.057 mol) and Karstedt catalyst ( $5.4 \cdot 10^{-2}$  mg) with stirring. The molar ratio of oligomer : trimethylsilylallylamine was 1 : 5.5. The process was accompanied by an increase in the temperature of the reaction mixture to 120 °C and its viscosity. No gas evolution or turbidity was observed. The reaction mixture was stirred for 3 h.

**Removal of silyl protection.** Anhydrous ethanol (1.5 g, 0.033 mol) was added into the same reaction flask after the dropping funnel

was replaced with a capillary for supplying an inert gas (argon) and. The content of the flask was heated to 50 °C. Argon was fed from a cylinder with a reducer through the capillary, volatile products were distilled off *in vacuo* of a water-jet pump (20 Torr) for 3–4 h. The target oligomer 5/20 (a viscous pale yellow liquid) was obtained in 92% yield (20.4 g).

**Hydrolysis of methyl(3-aminopropyl)dimethoxysilane.** Distilled water (9.10 g, 0.506 mol) was placed into a 100-mL three-neck flask equipped with a magnetic stirrer, a dropping funnel, and a water reflux condenser with a drying tube filled with NaOH, followed by a dropwise addition of methyl(3-aminopropyl)-dimethoxysilane (MAPDMS) (16.43 g, 0.100 mol) with vigorous stirring, an increase in the temperature of the reaction mixture to 60 °C was observed. After the addition of MAPDMS, the flask was placed in an oil bath and the stirring was continued for 2 h at 70 °C. Then, toluene (30 mL) was added to the flask and the toluene-methanol-water mixture was distilled off using a Dean–Stark trap at a temperature of up to 125 °C. The residual solvents were distilled off at 125 °C (3 mbar). The MAPDMS hydrolyzate (11.3 g, 96%) was obtained as a clear colorless viscous liquid.

**Synthesis of copolymer II.** Polysiloxane liquid PMS-50 (4.75 g, 0.064 mol of D-units), MD<sub>50</sub>M, MAPDMS hydrolyzate (7.56 g, 0.06432 mol of DPr(NH<sub>2</sub>) units), and tetramethylammonium hydroxide (CH<sub>3</sub>)<sub>4</sub>NOH · 5H<sub>2</sub>O (0.03 g) were placed into a 50-mL three-neck flask equipped with a magnetic stirrer, a dropping funnel, and a water reflux condenser with a drying tube filled with NaOH. The flask was placed in an oil bath and the reaction mixture was stirred for 18 h at 100–105 °C. Then, the catalyst was decomposed at 140–145 °C during 3 h, after which the volatile components were distilled off at 140–150 °C and a reduced pressure of 2–3 mbar to obtain copolymer II as a viscous transparent liquid with a yellowish tint (11.4 g, 93%); the content of amino groups according to the acid-base titration was 8.1 wt. %.

**Measurement of interfacial tension.** The interfacial tension was measured by the Du Nouy ring detachment method at the toluene solution of surfactant–water interface using a KRUSS K-9 tensiometer (Germany). The characteristics of the surface layer were calculated based on the interfacial tension isotherms according to the corresponding equations.<sup>14</sup>

**Polymerization process.** Polymerization of styrene was carried out until the monomer was completely converted at a temperature of 80 ± 0.5 °C. The polymerization rate was determined by the dilatometric method. The depth of polymerization was calculated by the formula (1)

$$P = (\Delta H / \Delta H_{\max}) \cdot 100\%, \quad (1)$$

where  $P$  is the degree of polymerization, %;  $\Delta H$  is the current level change in the dilatometer capillary, cm;  $\Delta H_{\max}$  is the level change in the dilatometer capillary corresponding to the 100% conversion, cm, calculated by the formula (2)

$$H_{\max} = V_m \cdot (\rho_p - \rho_m) / (S \cdot \rho_p), \quad (2)$$

where  $V_m$  is the monomer volume, cm<sup>3</sup>;  $\rho_m$  is the monomer density, g cm<sup>-3</sup>;  $\rho_p$  is the polymer density, g cm<sup>-3</sup>;  $S$  is the capillary section area, cm<sup>2</sup>.<sup>5</sup>

The particle sizes of polymer suspensions were determined by electron scanning microscopy using a HITACHI S-570 instrument (Japan) and optical microscopy using a COIC XSZ-G microscope (China) equipped with a photo and video recording system. For optical microscopy, a 0.1% aqueous suspension of polymer particles was prepared, the sample was applied to the glass and photographed. The particle diameter was determined from the obtained micrographs using the Image-ProPlus 6.0 program (Media Cybernetics Inc.).

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Received July 25, 2018;  
accepted August 26, 2018