

Article

Effect of Molecular Architecture of Surface-Active Organosilicon Macromers on Their Colloidal Properties in Relation to Heterophasic Radical Polymerization of Styrene and Methyl Methacrylate

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Abstract: The effects of the molecular architecture of water-insoluble organosilicon polymerizable surfactant macromers (SAMs) on their colloidal-chemical characteristics and on their efficiency in heterophase radical polymerization of styrene and methyl methacrylate were studied. It was shown that despite considerable differences in the structure of three synthesized oligomers (linear α,ω -dipropylmethacrylatepolydimethylsiloxane with a number of repeated siloxane units $n = 20$ —l-SAM; branched γ -methacryloxypropyl containing dimethylsiloxane oligomer—b-SAM; and “spherical” oligo-(γ -methacryloxypropyl)silsesquioxane—s-SAM), the colloidal-chemical characteristics (interfacial tension, layer thickness, adsorption, etc.) were rather similar. In particular, they all form “thick” multimolecular adsorption layers on the toluene–water interphase. All three SAMs were shown to act as effective colloidal stabilizers in heterophase radical polymerization of styrene and methyl methacrylate, which resulted in one-step preparation of large (0.5–1.5 μm) polymer particles with narrow particle size distribution. The obtained results are consistent with the published data on the use of water-insoluble polymerizable oligomers of various chemical structures on the heterophase radical polymerization. The use of these colloidal stabilizers may be considered as an effective way to obtain stable suspensions with large particles and narrow particle size distribution.

Keywords: polymerizable macromers; organosilicon surfactants; heterophase copolymerization; narrow particle size distribution; conversion; polymeric microspheres



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1. Introduction

Polymer suspensions are valuable materials in many areas such as applied physics, building technology, non-woven materials, calibrating particles, adhesives, material for bio-medical applications, etc. [1–6]. For example, the polymer suspensions with an average diameter of the particles of 30 nm are used in electron microscopic observation of fine materials both as a marker and as a standard to indicate the absolute size [7]. The potential of the use of the dispersion in any of the areas is determined not only by the chemical nature of the particles but by their dimensions, the particle size distribution and their colloidal stability. For the particles formed via heterophase radical polymerization, those parameters are created in the course of their synthesis and controlled by the nature of the monomer, initiator and surfactant and by the mechanism of the particle formation.

For a number of application areas, the particles are required to be rather large (~1 μm) with narrow particle size distribution and definite surface chemistry (functionality). The majority of the described techniques for synthesis of large polymer particles are based on

the application of water-soluble surfactants and seed polymerization. They are lengthy, multistage and poorly reproducible [8–14]. Moreover, they are not ecologically friendly because the waste water contains the remains of the used surfactants.

One of the examples is the use of large polymer particles whose surface is modified with bioligands, such as proteins and specific antibodies, which are used for passive agglutination immunodiagnostic assays [15,16]. The function of these assays is based on the immunochemical reaction between an antigen and antibodies yielding an ‘antigen-antibody’ complex [17]. The reaction in which this complex is formed is highly immunospecific and results on the formation of network agglomerates, which can be detected by various methods, for example, by spectrophotometry, turbidimetry, nephelometry, laser self-correlation spectroscopy, etc. These methods may require use of special expensive equipment for the detection of ‘antigen-antibody’ complexes. However, when antigens (or antibodies) are bound to a polymeric carrier, the complexes can be detected even by the naked eye as crowding of agglomerates of the carrier particles.

The first communication on successful use of polyvinyltoluene and polystyrene microspheres with a narrow particle size distribution in the diagnosis of rheumatoid arthritis was published in 1956 [18]. It was reported that the interaction of antigens present in the blood serum of a patient with gamma-globulin adsorbed on the microsphere surface of a suspension resulted in the agglutination of the polymeric particles affording large agglomerates, easily discernible by the naked eye. Later, publications appeared [19,20] dealing with the use of polystyrene and poly(methyl methacrylate) suspension particles as protein carriers for preparing diagnostic test-systems for other types of diseases.

However, the use of particles of polymeric suspensions in the development of immunodiagnostic tests has been limited by irreproducibility of the results of analysis, which is caused, as has been suggested by Yen et al. [20], by the fact that on slight variations in the conditions (pH, ionic strength of the medium, temperature, etc.), the protein adsorbed on the surface of particles is desorbed to the aqueous phase; this lowers the sensitivity of the tests and leads to nonspecific reactions with other biological objects.

Polymeric suspensions containing particles with surface functional groups capable of forming covalent bonds with bioligands have proved to be free of these drawbacks. Polymeric suspensions based on copolymers of methyl methacrylate (MMA), 2-hydroxyethyl methacrylate, acrylic and methacrylic (MAA) acids, acrylamide, vinylpyridine, etc., have been synthesized and used successfully for developing immunodiagnostic tests [12].

Considerable progress in control of the synthesis of polymer suspensions by means of heterophase radical polymerization was attained by using polymerizing surface-active macromers (SAMs) [21–36]. The preparation and properties of SAMs were first described in the works of Bistline et al. [37]. The authors synthesized sodium salts of allyl esters of α -sulfopolymethic and α -sulfostearic acids. It was shown that the obtained compounds had surface-active properties—they significantly reduced the surface tension at the interface between an aqueous SAM solution/air and an aqueous SAM solution/hydrocarbon.

The work [38] describes the synthesis of SAMs classified by the authors according to the nature of the vinyl group. Monomers based on styrene, vinyl phenyl ketone and acrylamide were obtained. These compounds were used as copolymerizable emulsifiers in the emulsion copolymerization of butadiene with styrene. Coatings made from the resulting latexes improved cohesion and water resistance compared to coatings made from latex polymers made using conventional emulsifiers.

Another example is heterophase radical polymerization of styrene and butyl acrylate in the presence of anionic SAM (dodecyl ester of potassium salt of methylcinnamic.) [39]. The rate of polymerization and the colloidal stabilities of the reaction system and of the resulting polystyrene latex were noticeably better than in the presence of traditional non-polymerizable anionic surfactants even at the lower surfactant concentrations. The surface tension of the reaction system reached the value of the pure water at 70% styrene conversion, which indicates the practical absence of the surfactant in the aqueous phase. It was explained with the fact that the surfactant copolymerizes with the forming polystyrene presumable at the early stages

of formation of the polymer–monomer particles. Similar behavior was shown when using cationic SAM (N-dodecyl-2-methyl-5-vinylpyridinium bromide).

However, despite a number of obvious positive effects, the use of water-soluble surfactants as a way to manufacture polymeric suspensions with required particle size and particle size distribution displayed some limitations. The technique did not provide manufacturing of the particles larger than 1.5 μm , and the particle size distribution was rather wide (in one lot, the diameter of particles varied nearly twice) and further improvement of the particle parameters required complex multistep procedures.

In refs [40,41], it was shown that the use of water-insoluble oligomeric surfactants of various chemical structures (hydrocarbon and organosilicon) enables to synthesize such dispersions via one-step heterophase radical polymerization. The mechanism of the effect was based on the assumption that the surface-active oligomers being incompatible with the forming polymer are pushed onto the interface of the monomer droplet with water and build their “thick” and strong adsorption layer, which provides stability of the system in the whole course of polymerization. Polymerization of monomers in the presence of water-insoluble surfactants is a specific type of heterophase polymerization process because the formation of a surfactant adsorption layer on the surface of monomer droplets occurs via its migration from the monomer phase. As a result, in contrast to the polymerization of monomers in the presence of water-soluble surfactants, polymer–monomer particles retain a narrow particle size distribution from the beginning of polymerization to complete conversion of the monomer, and the diameters of polymer particles increase with increasing surfactant and monomer concentration.

Of particular interest are water-insoluble silicone surfactants consisting of a polydimethylsiloxane skeleton linked to one or more polar groups [42–45]. Silicone surfactants are characterized by the following properties:

- The ability to reduce surface tension to a value of 20 mN/m compared to 30 mN/m for typical hydrocarbon surfactants, which is associated with structural features of the siloxane chain;
- Exhibit surface-active properties, both in aqueous and non-aqueous media;
- The ability to form helical structures with outwardly oriented alkyl groups due to the high flexibility of the siloxane chain and the tendency of weak Si-O dipoles to intramolecular compensation [46].

The stability of the suspensions is additionally supported if the surface-active oligomer contains reactive double bonds (SAM), which could be copolymerized with the main monomer [47–51].

This approach also solves the ecological safety problem, i.e., no surfactant remains in the waste water after the completion of the reaction.

However, the structural parameters of the above-mentioned adsorption layers related to the polymerization kinetics and the parameters of the resulting polymer suspensions in their connection to the molecular structure of the used SAMs are not fully understood.

In this work, in order to investigate this problem, we synthesize three organosilicon oligomers containing the same polymerizable (methacrylic) groups but with different molecular architectures: linear α,ω -dipropylmethacrylatepolydimethylsiloxane (l-SAM), branched γ -methacryloxypropyl containing dimethylsiloxane oligomer (b-SAM) and poly-cyclic “spherical” oligo-(γ -methacryloxypropyl)silsesquioxane (s-SAM) (Figure 1).

The paper describes the properties of the synthesized SAMs, their efficiency in the heterophase radical polymerization of styrene and methyl methacrylate and the characteristics of the polymer dispersions obtained by the reactions.

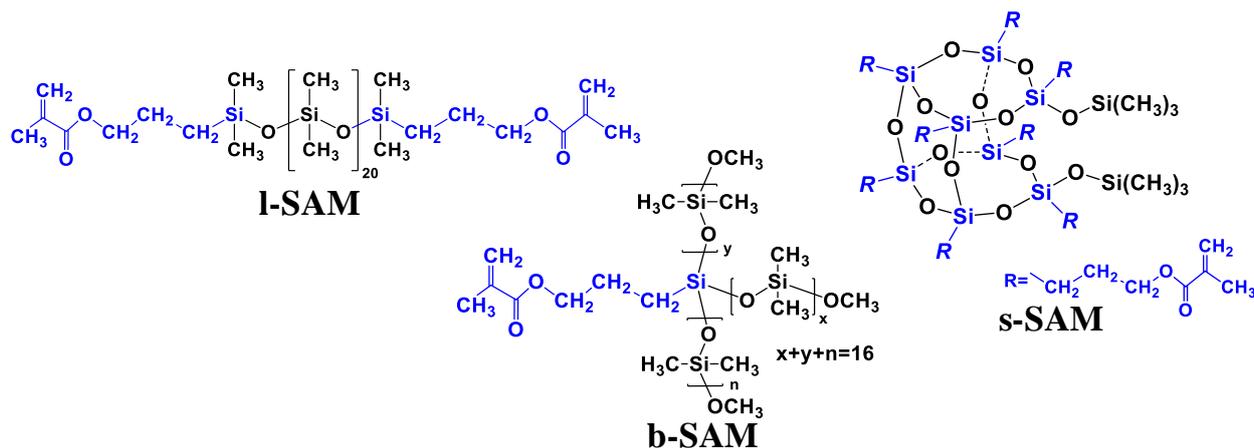


Figure 1. Structure of the studied compounds.

2. Experimental Section

2.1. Materials

Allyl methacrylate and methyl methacrylate were purchased from Acros Organics. Pyridine and polydimethylsiloxane hydride were purchased from Penta-91, Moscow, Russia. CT-175 sulfonic acid resin was purchased from Purolite, Llantrisant, Great Britain. Octamethylcyclotetrasiloxane, methyl tert-butyl ether, toluene, trifluoroacetic acid and sodium sulfate were purchased from Chimmed, Moscow, Russia. Potassium persulfate, styrene, γ -methacryloxypropyltrimethoxysilane, Karstedt's catalyst and trimethylchlorosilane were purchased from Sigma-Aldrich, St. Louis, MA, USA. Styrene was purified from the stabilizer with a 5% aqueous solution of sodium hydroxide, washed with water until neutral pH, dried over calcium chloride and distilled twice in vacuum. Methyl methacrylate was purified from stabilizers by distillation at normal pressure in the presence of 0.2 wt.% hydroquinone. All other reagents were used as received.

2.2. Syntheses

All syntheses were carried out in an argon atmosphere.

Synthesis of α,ω -dipropylmethacrylatepolydimethylsiloxane with the number of repeating siloxane units $n = 20$ (I-SAM)

Synthesis of α,ω -dipropylmethacrylatepolydimethylsiloxane with the number of repeating siloxane units $n = 20$ (I-SAM) was carried out according to the procedure given in [40]. The reaction scheme, synthesis procedure and ^1H NMR spectrum are given in Supplementary Materials (Figure S1).

The ^1H NMR (400.13 MHz, CDCl_3): d, ppm; -0.05 – 0.2 (m, CH_3 , 3H); 0.45 – 0.68 (m, CH_2 , 2H); 1.6 – 1.8 (m, CH_2 , 2H); 1.87 – 2.03 (m, CH_3 , 3H); 4.0 – 4.22 (m, CH_2 , 2H); 5.45 – 5.68 (m, $\text{CH}_2 = \text{C}$, 1H); and 6.03 – 6.22 (m, $\text{CH}_2 = \text{C}$, 1H).

Synthesis of branched γ -methacryloxypropyl containing dimethylsiloxane oligomer (b-SAM)

A total of 0.4 g of the catalyst (CT-175 sulfonic acid resin) was added to a mixture of 16.7 g of octamethylcyclotetrasiloxane (D4) and 3.5 g of γ -methacryloxypropyltrimethoxysilane. The reaction was carried out at $T = 65^\circ\text{C}$ for 15 h. Then, the temperature was raised to 145°C and held for 3 h in order to get rid of the catalyst (decomposed), and then, the low-boiling components were distilled off. The structure of the obtained compound was confirmed by the data of ^1H NMR spectroscopy (Figure S2).

The ^1H NMR (400.13 MHz, CDCl_3): d, ppm; 0.1 – 0.2 (s, SiCH_3 , 3H); 0.65 – 0.85 (s, SiCH_2CH_2 , 1,89H); 1.6 – 1.8 (s, $\text{CH}_2\text{CH}_2\text{CH}_2$, 2,07H); 1.87 – 2.03 (s, C-CH_3 , 3,03H); 3.45 – 3.55 (m, O-CH_3 , 0,17H); 4.0 – 4.22 (s, $\text{O-CH}_2\text{CH}_2$, 2H); 5.45 – 5.68 (s, $\text{C-C}=\text{CH}_2$, 1H); and 6.03 – 6.22 (s, $\text{C-C}=\text{CH}_2$, 1H).

Synthesis of oligo-(γ -methacryloxypropyl)silsesquioxane (s-SAM).

A total of 5 g (0.020 mol) of γ -methacryloxypropyltrimethoxysilane and 22.8 g (0.20 mol) of trifluoroacetic acid were stirred at 120 °C for 2 h; after which, methyl tert-butyl ether was added and washed with 10% sodium sulfate solution in water and distilled water until neutral pH. The resulting solution was kept for 12 h over sodium sulfate, filtered out. The resulting solution was added to a mixture of 3.3 g (0.03 mol) of trimethylchlorosilane and 2.4 g (0.03 mol) of pyridine, the reaction mass was refluxed, then washed with water until neutral pH and kept for 12 h over sodium sulfate. The target product was isolated by distillation of the volatiles on a rotary evaporator, followed by evacuation at 50 °C/1 mm Hg. The yield of the product, a colorless viscous liquid, was 88%. The structure of the obtained compound was confirmed by the data of ^1H NMR spectroscopy (Figure S3).

The ^1H NMR (400.13 MHz, CDCl_3): d, ppm; 0.1–0.2 (s, SiCH_3 , 2,5H); 0.65–0.85 (s, SiCH_2CH_2 , 1,89H); 1.6–1.8 (s, $\text{CH}_2\text{CH}_2\text{CH}_2$, 2,07H); 1.87–2.03 (s, C- CH_3 , 3,03H); 3.45–3.55 (m, O- CH_3 , 0,17H); 4.0–4.22 (s, O- CH_2CH_2 , 2H); 5.45–5.68 (s, C-C= CH_2 , 1H); and 6.03–6.22 (s, C-C= CH_2 , 1H).

2.3. Characterization

Particle size distribution of the polymer suspension was measured using a photon analyzer “Zetasizer Nano ZS” (Malvern Instruments Ltd, Malvern, Great Britain). The ^1H NMR spectra were recorded on a Bruker WP250 SY spectrometer, and the solvent was CDCl_3 . The spectra were processed on a computer using the ACDLABS program. The colloidal-chemical properties of organosilicon SAMs (surface and interfacial tension) were studied by tensiometry using a semi-automatic digital tensiometer “K9” (KRÜSS company, Hamburg, Germany). Kinetic studies of the polymerization of vinyl monomers in the presence of SAMs were carried out by the dilatometric method. For polymerization experiments, we chose the volume ratio of the SAM monomer solution–water equal to 1:9, potassium persulphate concentration 1 mass% (in the monomer) and polymerization temperature was 80 ± 0.5 °C. SAM concentration varied from 1 to 1.5 mass% (in the monomer). The morphology of the microparticles was studied using a scanning electron microscope (SEM) “Versa 3D DualBeam” (FEI, Hillsboro, USA) in high vacuum mode. Separation of the copolymer into different fractions was carried out on a preparative high-performance liquid chromatography unit with an automatic dispenser and fraction collector “LC-20” (Shimadzu, Kyoto, Japan). Programming and registration of chromatograms were carried out using proprietary Shimadzu software (LabSolutions LCGC).

3. Results

Colloidal Characteristics of Organosilicon Surface-Active Polymerizable Oligomers

Series of samples were prepared to measure the interfacial tension at the interface toluene solution of SAM/water. The first sample was a toluene solution, and the subsequent samples were an SAM solution in toluene with an SAM concentration in the range from 0.25 to 1.0 wt.%. Isotherms of interfacial tension were plotted against the surfactant concentration in the toluene solution. These data were used to calculate the surface activity (G , $\text{mJ}\cdot\text{m}/\text{mol}$), the maximum Gibbs adsorption (H_{max} , mol/m^2), the area occupied by the surfactant molecule (S_0 , m^2) and the thickness of the interfacial layer formed by surfactant molecules (δ , m).

The isotherms of the interfacial tension at the interface toluene solution of SAM/water are shown in Figure 2. The character of the isotherms is similar to the isotherms obtained by measuring the interfacial tension of typical hydrocarbon surfactants.

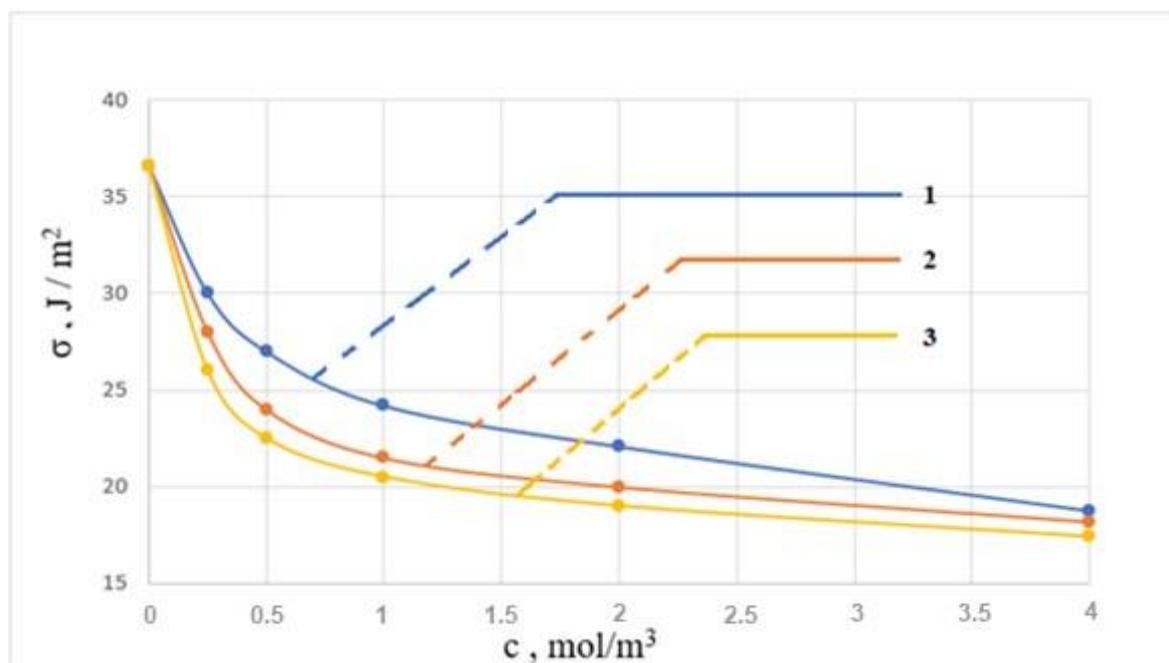


Figure 2. Interfacial tension at the border toluene solution of the organosilicon oligomers/water: 1—toluene solution of l-SAM/water; 2—toluene solution of b-SAM/water; and 3—toluene solution of s-SAM/water.

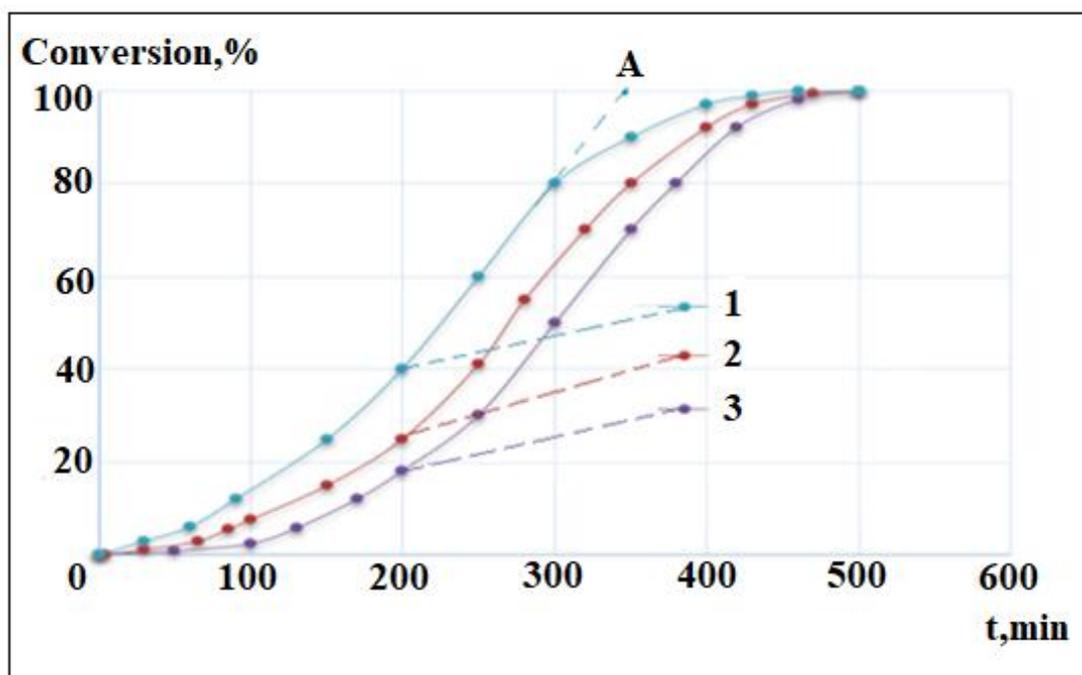
As can be seen from Figure 2 and Table 1, all three organosilicon SAMs are surface-active, and despite significant differences in molecular architecture (linear, branched and “spherical”), they have similar colloidal-chemical characteristics. It is worth mentioning that values of the surface activity and maximum adsorption increase in the series l-SAM < b-SAM < s-SAM. It is also noteworthy that the measured adsorption layer thicknesses vary in order l-SAM > b-SAM > s-SAM; however, for all three SAMs, the layer thickness is >10 nm, which significantly differs from water-soluble surfactants (~2–5 nm) [52] and exceeds the contour length not only of the spherical and branched SAM, but also of the linear SAM. This indicates the polymolecular nature of adsorption, i.e., the tendency to form “thick” adsorption layers at the oil–water interface. This structure of the adsorption layers can probably explain the relatively small differences in the colloidal-chemical characteristics of these SAMs as well as the similarity of the colloidal-chemical characteristics as compared to some other water-insoluble oligomers (dimeric, comb-type, etc.) [40,53].

Table 1. Colloidal-chemical characteristics of l-SAM, b-SAM and s-SAM.

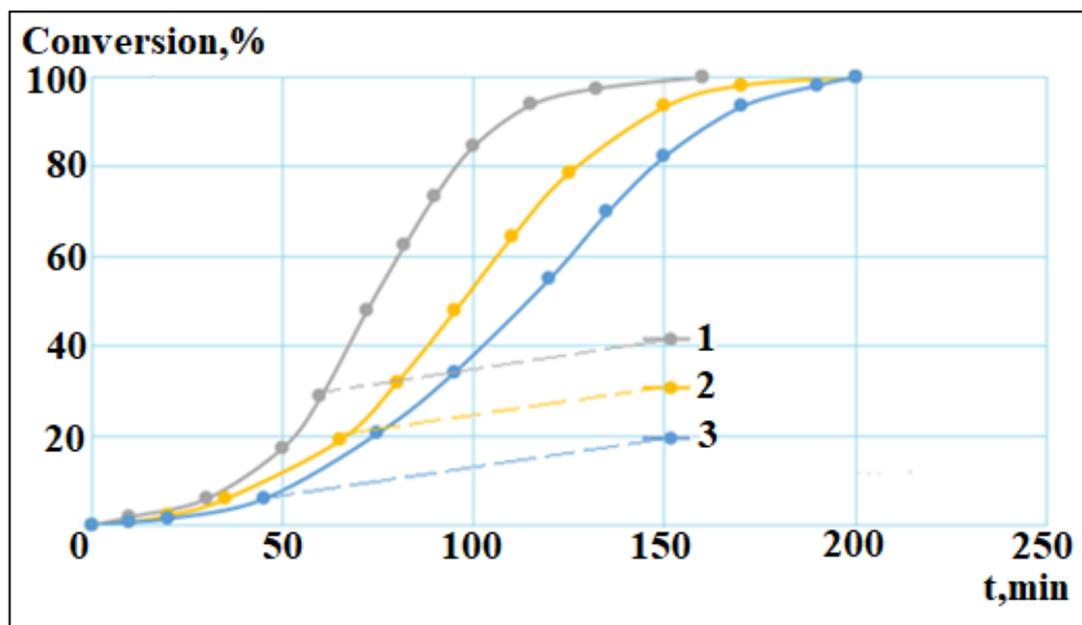
Substance	σ_{12} , min mJ/m ²	Area Occupied by mol. $S_0 \cdot 10^{20}$ m ²	Layer Thickness, $\delta \cdot 10^9$ m	Surface Activity G, mJ·m/mol	Adsorption $H_{\max} \cdot 10^6$, mol/m ²
l-SAM	18.7 (±0.1)	23.0	14.1	1.7	7.2
b-SAM	18.2 (±0.1)	22.3	11.6	1.81	7.4
s-SAM	17.4 (±0.1)	21.4	10.1	1.89	7.8

The polymerization was carried out under the following conditions: the monomer/water volume ratio was 1/9, respectively; the concentration of potassium persulfate (PSP) used as initiator was 1 wt.% per monomer; the temperature was 80 ± 0.5 °C; and the SAM concentration was varied from 1 to 1.5 wt.% per monomer, which corresponds to the concentration of saturated interfacial layer in the studied toluene–water model system.

The conversion–time curves of kinetics of polymerization of styrene and methyl methacrylate in presence of SAMs are shown in Figure 3a and Figure 3b, respectively.



(a)



(b)

Figure 3. (a) Conversion–time curves of styrene polymerization with (1) 1 wt.% l-SAM; (2) 1 wt.% b-SAM; and (3) 1 wt.% s-SAM; p.A—the intersection of the extrapolation of the constant rate section with a line parallel to the abscissa axis corresponding to 100% conversion (b) Conversion–time curves of methyl methacrylate polymerization with (1) 1 wt.% l-SAM; (2) 1 wt.% b-SAM; and (3) 1 wt.% s-SAM.

It can be seen that the kinetic curves are S-shaped, which is typical for heterophase radical polymerization of styrene and methyl methacrylate. The initial section of the kinetic curves is characterized by a low reaction rate and, according to the literature, is called the induction period [10,40,49]. Then, the rate of polymerization grows and changes to

constant up to high monomer conversions (70–80%)—a constant rate section. At last, the rate slows down. The intersection of the extrapolation of the constant rate section with a line parallel to the abscissa axis corresponding to 100% conversion (Figure 3a, point A) and similar intersection points on other kinetic curves not shown in Figure 3b are taken in this work as the time of the polymerization completion.

Figure 4 shows the values of the induction periods, the constant rates and the total conversion times for styrene and methyl methacrylate polymerization in the presence of the SAMs studied. For styrene, although the values of the constant rates were almost the same, the duration of the induction periods decreased consistently in order s-SAM > b-SAM > l-SAM.

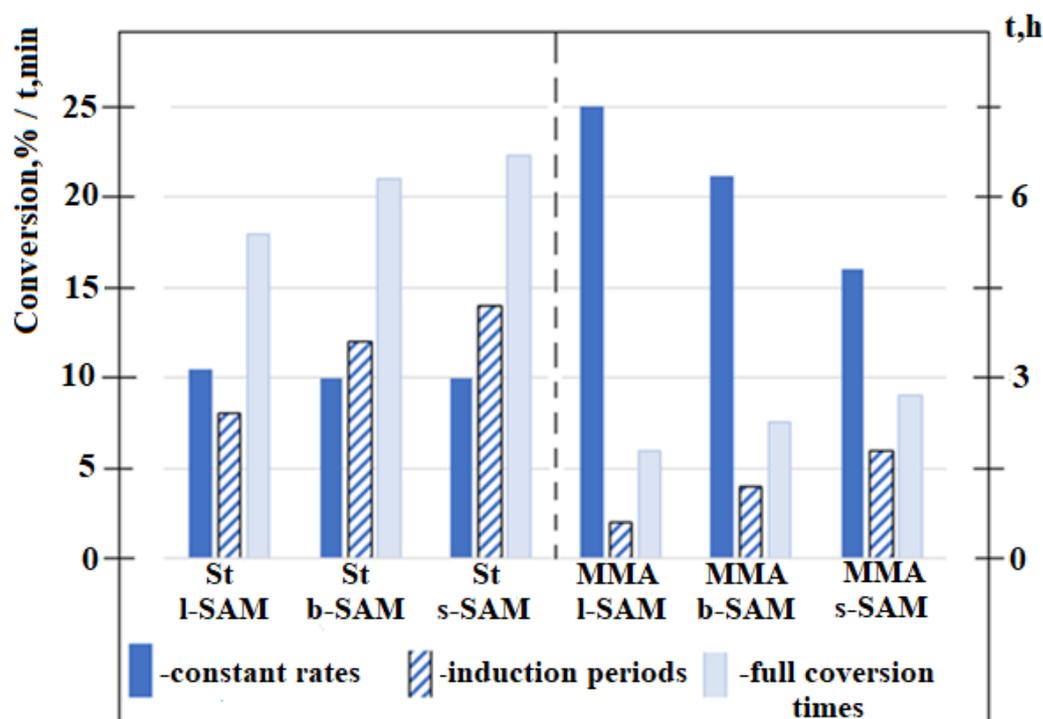


Figure 4. The values of the induction periods of the constant polymerization rates and of the full conversion times for polymerization of styrene (left) and methyl methacrylate (right) in the presence of the SAMs.

Approximately the same results are noticed in the polymerization of methyl methacrylate. The induction periods decrease in the same order. However, the values of the constant rates decrease markedly in the series l-SAM > b-SAM > s-SAM.

As it was shown in [46], stability of the adsorption layer on the interphase monomer droplet—water is additionally increased if the forming polymer is incompatible with the surface-active oligomers (organosilicon macromers of various structures)—is shown. Incompatibility of organosilicon oligomers of different structures with polystyrene and poly(methyl methacrylate) was shown experimentally in [54]. Therefore, this factor also additionally contributes to the high stability of the adsorption layers in the studied systems. In fact, 1 wt.% used SAM per monomer was sufficient for providing high stability of the reaction system without coagulum.

And finally, the one more factor facilitating stability of the adsorption layers and formation of strong shell on the polymer–monomer particles is copolymerization of the surfactants (SAMs) with the main monomers. In order to prove that the comonomer enters into a copolymerization reaction, the following experiment was carried out. The product of the styrene polymerization in the presence of SAM was separated by preparative chromatography into three fractions: low molecular weight, medium molecular weight and high molecular weight. All fractions were characterized by NMR spectroscopy. The molar

mass of the SAM was about 1000 g/mol, and the molar mass of the resulting copolymer was over 30,000 g/mol. The presence of the SAM was observed in the high molecular weight fraction (Supplementary Materials, Figure S4), which suggests that the SAM was chemically bonded to the polymer.

This reaction also provides binding of the surfactant and makes the process ecologically benign, without contamination of the waste water. The absence of the residual surfactant is confirmed with the value of the surface tension of the aqueous phase after the completion of polymerization ($\sigma = 72 \text{ mJ/m}^2$) equal to the value of pure water.

From Figure 3a,b and Figure 4, one can see that all three SAMs act as effective (good) colloidal stabilizers of heterophase radical polymerization providing by 1.5–2 high values and prolonged period of the constant polymerization rates as compared to polymerization of those monomers in presence of hydrocarbon and other water-soluble surfactants [42,43]. The efficiency of those SAMs is rather similar but increases in the order s-SAM < b-SAM < l-SAM, despite the fact that the values of the interfacial tension and of the surface activity are decreased in the that order. But, at the same time, the series of the polymerization efficiency of the SAMs corresponds to the values in the series of the adsorption layer thickness (see Table 1). This fact indicates that the flexible molecule of l-SAM builds up the better protecting adsorption layer than more rigid b-SAM and s-SAM.

The duration of the constant rate section up to high conversion values (~80%) additionally indicates the formation of strong interfacial adsorption layers from the early stages of polymerization. In heterophase polymerization, the rate of polymerization is proportional to the number of particles. A constant polymerization rate indicates that the process proceeds with a constant number of stable particles, i.e., there are no processes of flocculation and coalescence of particles. The systematic increase in the constant rates during the polymerization of MMA requires a separate study, but it can be assumed that the differences in the constant rates is related to the structure of the formed layers and differences in the compatibility of SAMs with the formed polymer.

It should be noted that the suspensions obtained are stable during storage for three months and in weak electrolyte solutions.

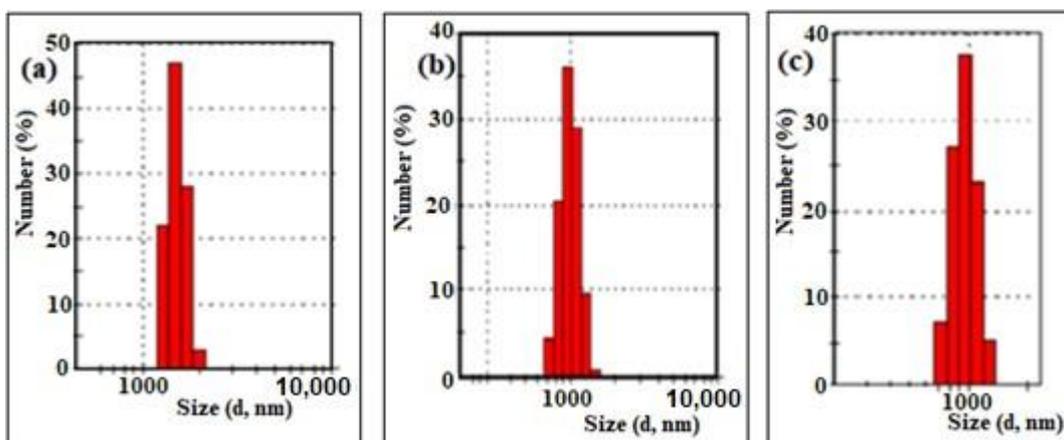
These data support the hypothesis that polymerizable oligomers are involved in the stabilization of the surface layers of polymer–monomer particles.

The characteristics (average particle diameter and particle size distribution) of polystyrene and poly(methyl methacrylate) suspensions obtained in the presence of the studied SAMs were evaluated by photon correlation spectroscopy. Particle distribution histograms of polymer suspensions obtained in the presence of l-SAM, b-SAM and s-SAM are shown in Figure 5A,B. Figure 6 shows scanning electron microscopic photographs of polystyrene dispersions obtained in the presence of 1 wt.% SAMs. These results illustrate the data presented in Table 2 indicating a narrow size distribution of the spherical particle.

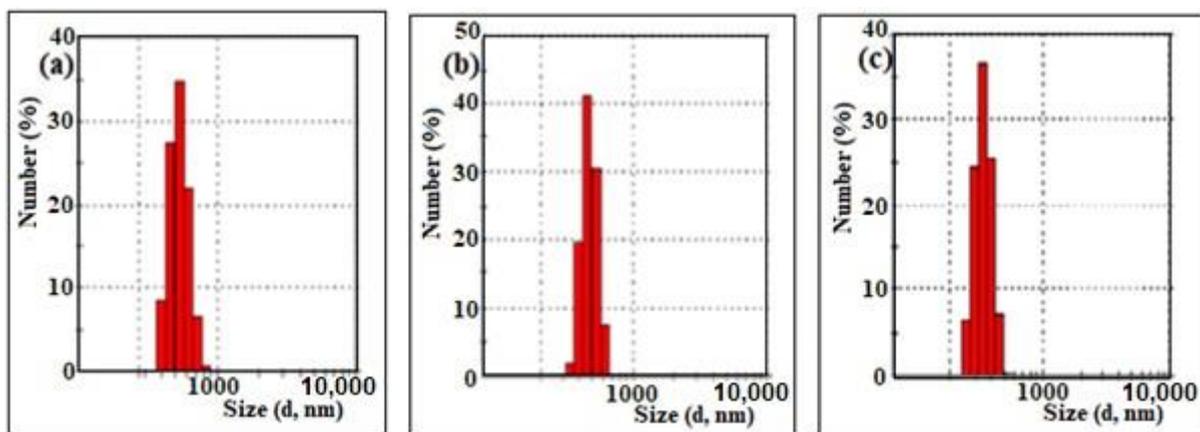
Table 2. Characteristics of polymer suspensions obtained in the presence of surface-active macromers.

SAM/Monomer	SAM, %	d_{av} , nm	d_w/d_n
l-SAM/St	1	1600	1.01
l-SAM/MMA	1	530	1.03
b-SAM/St	1	1100	1.05
b-SAM/MMA	1	490	1.02
s-SAM/St	1	970	1.04
s-SAM/MMA	1.5	430	1.02

d_{av} —average particle diameter by size, and d_w/d_n —polydispersity index (d_w —weight average particle diameter, and d_n —number average particle diameter).



(A)



(B)

Figure 5. (A) Histograms of the size distribution of polystyrene particles (by number) obtained in the presence of l-SAM (a), b-SAM (b) and s-SAM (c). (B) Histograms of the size distribution of poly(methyl methacrylate) particles (by number) obtained in the presence of l-SAM (a), b-SAM (b) and s-SAM (c).

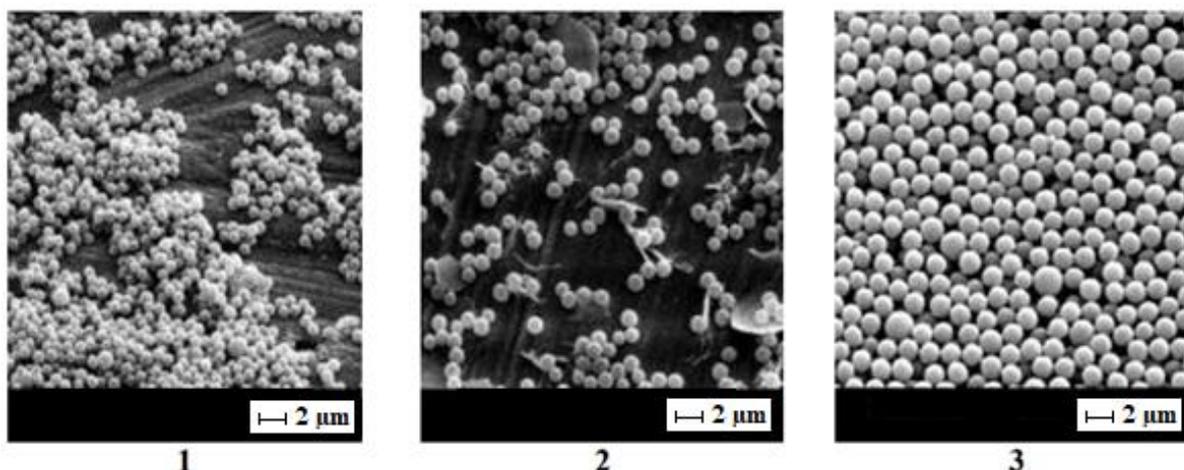


Figure 6. Scanning electron microscope photographs of the polystyrene particles, obtained in the presence of s-SAM (1), b-SAM (2) and l-SAM (3).

The results shown in Figure 5A,B and Table 2 show that the use of all three SAMs allows the synthesis of large polymeric (polystyrene and poly(methyl methacrylate)) particles with a narrow size distribution ($d_w/d_n \sim 1.01\text{--}1.05$) via one-step synthesis. It means that in each of the polymer suspensions, about 90% of the particles have diameters differing within some 10%. As an example, the numerical data of the distribution of the diameters of the polystyrene particles obtained in the presence of I-SAM measured by the photon correlation spectroscopy are given in Table S1 in the Supplementary Materials. In all cases, these particles have sizes approximately an order of magnitude larger than those obtained in the presence of hydrocarbon surfactants in the same conditions [41].

4. Conclusions

Thus, the results obtained in this work confirm the assumption that the use of water-insoluble and incompatible with the forming polymer colloidal stabilizers of oil–water emulsions leads to the formation of strong adsorption layers at the interface with the aqueous phase and, thus, provides a one-stage production of large polymer particles with a narrow size distribution via the radical heterophase polymerization in these systems. The high thickness of these multimolecular adsorption layers leads to a leveling effect of the chemical structure and molecular architecture of the surfactants on their measurable colloidal-chemical characteristics. This conjecture may provide a plausible explanation to the experimental facts that the use of few other oligomers with quite different molecular structures [40,41], which are water-insoluble and polymer-incompatible as colloidal stabilizers in heterophase radical polymerization, enables to produce polymer dispersions with large (~ 1 μm) particles and narrow particle size distribution via one-step simple process. The use of polymerizable surfactants additionally strengthens the outer shell of the resulting particles. A wide choice of the surfactants in these syntheses allows to vary the surface properties of the resulting polymer particles, which may be very useful for the further application of thus-obtained dispersions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/physchem4010006/s1>, Figure S1: ^1H NMR spectrum of α , ω - dipropyl methacrylate polydimethylsiloxane ($n = 20$); Figure S2: ^1H NMR spectrum of branched γ -methacryloxypropyl containing dimethylsiloxane oligomer; Figure S3: ^1H NMR spectrum of oligo-(γ -methacryloxypropyl)silsesquioxane; Figure S4: ^1H NMR spectrum of high molecular weight fraction of the styrene polymerization product in the presence of SAM; Table S1: The numerical data of the distribution of the diameters of the polystyrene particles obtained in the presence of I-SAM.

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