Silicon (2015) 7:217–227
DOI 10.1007/s12633-014-9265-4

ORIGINAL PAPER

Novel Approach to Synthesis of Monodisperse Polymeric Microspheres: Heterophase Polymerization of Styrene and Methyl Methacrylate in Presence of Water-Insoluble Functional PDMSs

Denis I. Shragin · Inessa A. Gritskova ·
Victor M. Kopylov · Elena V. Milushkova ·
Liubov A. Zlydneva · Sergey M. Levachev

Received: 30 April 2014 / Accepted: 24 November 2014 / Published online: 17 December 2014

Abstract Water-insoluble polydimethylsiloxanes (PDMSs) with functional organic substituents at the silicon atom are promising surface-active substances for the synthesis of monodisperse polymeric microspheres. In this regard a number of PDMS oligomers bearing different functional chain ends (amino, carboxylic and epoxy groups) were synthesized by conventional approaches. Solubility of PDMS in both the monomers (styrene (St) or methyl methacrylate (MMA)) and water as well as their surface-active properties at the water-toluene interface were investigated. Heterophase polymerization of St and MMA was carried out in the presence of functional PMDS and the resulting suspensions of polymeric microspheres were characterized using scanning electron microscopy (SEM). It was shown that the polymeric suspensions obtained have a very narrow particle size distribution and high stability in electrolyte solutions. The mechanism of the interfacial layer formation which explains the observed results is proposed.

Keywords Polystyrene · Polymethyl methacrylate · Radical polymerization · Functional polydimethylsiloxane · Surface-active substances · Monodisperse functional latexes

1 Introduction

Over the recent years monodisperse functional polymeric microspheres have been extensively studied and widely used as the protein carriers for the development of immunodiagnostic assays; the insoluble supports in solid-phase peptide synthesis; in nanotechnology as building blocks for the new types of materials, including solid spatially periodic structures with nonlinear optical properties; as the stationary phases for chromatography and catalysis and so forth [1–4].

The particles for immunological studies should meet the following requirements: a definite particle size, a low polydispersity index, a definite surface structure and functionality, high stability in saline [5]. Over the past three decades considerable attempts have been made in the synthesis of such microspheres. Different methods were applied to obtain monodisperse polymeric particles including the seed polymerization [6] the two-stage swelling method [7], the modified suspension polymerization with the use of Shirasu Porous Glass [8, 9], the dynamic monomer swelling method [10] *etc* [11, 12].

However, these approaches are technologically complicated, time-consuming and difficult to reproduce. From this point of view, heterophase polymerization is a very attractive method for the synthesis of functional polymeric suspensions with a narrow particle size distribution[13].

I. A. Gritskova · V. M. Kopylov · E. V. Milushkova · L. A. Zlydneva
M. V. Lomonosov Moscow State University of Fine Chemical Technologies, Prospect Vernadskogo, 86, Moscow 119571, Russia

D. I. Shragin
N.S. Enikolopov Institute of Synthetic Polymeric Materials, Foundation of the Russian Academy of Sciences, Profsoyuznaya St., 70, Moscow, 117393 Russia

D. I. Shragin (✉)
A.N. Nesmeyanov Institute of Organoelement Compounds, Foundation of the Russian Academy of Sciences, GSP-1, V-334, Vavilova St., 28,, Moscow 119991, Russia
e-mail: dshragin@mail.ru

S. M. Levachev
Chemistry Department, M. V. Lomonosov Moscow State University, GSP-1, Leninskie gory, Moscow, 119991 Russia

The literature review has revealed that such suspensions can be prepared in the presence of water-insoluble surfactants, forming an emulsion of the oil-in-water type. This group of surfactants includes monoalkyl phthalates, di-(p-tolyl)-carbalkoxyphenylcarbinol [14], oligomeric peroxyesters [15] and carboxyl-containing monofunctional PDMS [16].

It was shown that the main features of polymeric suspensions obtained in the presence of the aforesaid surfactants are high stability and a narrow particle size distribution. However, the synthesis of these surfactants was quite sophisticated and could be conducted only on a laboratory scale [14–16].

For the further development of the synthesis of monodisperse polymeric suspensions, we suggested using PDMS containing different functional organic substituents at the terminal silicon atoms of the polysiloxane chain. We chose these oligomers because of their structural similarity to the Gemini type organic surfactants exhibiting a much higher surface activity than the conventional organic surfactants [17] and a simple synthetic technique for producing such oligomers. The surfactant functional groups provide the possibility of a direct synthesis of functional polymeric microspheres in the presence of surfactant. Thus, further reactions with polymeric particles can be carried out without any modification of the particle surface.

In the present study three types of PDMS oligomers bearing different functional chain ends, i.e. amino, carboxylic and epoxy groups were synthesized by the conventional approaches. Also, the surface-active properties of these substances as well as the heterophase polymerization of St and MMA in the presence of functional PDMSs were investigated.

2 Materials and Experimental Methods

2.1 Materials

Octamethylcyclotetrasiloxane (Penta-91), 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (Penta-91), hexamethyldisilazane (Dow Corning), allyl glycidyl ether (Aldrich), toluene were distilled before use. Methylhydrogen terminated polydimethylsiloxane DC-1-8114 (Dow Corning), α, ω bis(tetramethyl-ammoniumoxy) polydimethylsiloxane (TMAS) (Penta-91), Karstedt catalyst – platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane com plex (Aldrich), undecanoic acid (Aldrich), potassium persulfate (Aldrich), azobisisobutyronitrile (AIBN), trifluoroacetic acid (Aldrich), PDMS-PEG (Penta-91) were used as received. St and MMA (reagent grade) were purchased from Aldrich, distilled under reduced pressure and preserved in the refrigerator until use. Cation resin CT175 (Purolite) was dried at 80°C/3 mbar for 3 h before use. Deionized water was distilled twice before use.

2.2 Methods

^{1}H and ^{29}Si NMR spectra were recorded on a Bruker AM-360 spectrometer operating at 360.1 and 71.6 MHz, respectively, 303 K using $CDCl_3$ as a solvent. Chemical shifts are reported in ppm and referenced to the residual nondeuterated solvent frequency. $Cr(AcAc)_3$ was added to reduce the ^{29}Si spin-lattice relaxation times.

The content of amino groups in PDMS-amino, carboxy groups in PDMS-carboxy and epoxy groups in PDMS-epoxy was determined by titrimetric analysis with the use of 0.1 n HCl, NaOH or HBr respectively.

Kinematic viscosity measurements at 20° C were performed using a glass capillary viscometer ВПЖ-2 (Labteh, Russia) with a capillary diameter of 2.37 mm.

The particle size and particle size distribution were measured using a scanning electron microscope (SEM) (HITACHI S-570, Hitachi LTD., Japan).

Interfacial tension measurements were performed by the ring method with a K-9 tensiometer (Kruss, Germany).

The solubility of PDMSs in monomers was determined by dropwise addition of surfactant to monomer until the solution turned turbid.

The molecular weights of PS and PMMA were calculated from the Mark-Houwink equation. Typical viscosities of polymer solutions in toluene were measured in a capillary viscometer Ubellode at 20° C.

The polydispersity indices (Dw/Dn) and zeta potential ξ were determined using a Zetasizer Nano ZS -90 instrument (Malvern Instruments, UK).

The colloidal stability of the suspensions was evaluated as follows. The round-bottomed microplate was loaded with the polymeric suspension and then 0.1 M- 0.25 M water solution of NaCl was added to it. Afterwards, the suspension was allowed to stay for 24 h until water completely evaporated. The suspension was considered to be stable if the polymer was a compact piece at the bottom of the round-bottomed microplate.

The type of the emulsion, which formed in the presence of the silicone surfactant, was determined by two methods:

1) by measuring the conductivity of the emulsion using conductivity meter OAKON con 5 (PRC);
2) by staining the continuous phase using the dye Congo red [18].

2.3 Synthesis

2.3.1 α, ω-bis(3-aminopropyl)polydimethylsiloxane (PDMS-amino)

Into a 500 mL two–neck flask, fitted with a condenser and a mechanical stirrer, was placed 30.1 g (0.121 mol) of 1,3-bis(3-aminopropyl) -1,1, 3,3-tetramethyldisiloxane, 270.0 g (0.91 mol) of octamethylcyclotetrasiloxane and 0.3 g of catalyst - TMAS polydimethylsiloxane (0.95 wt. % of nitrogen). The flask was immersed in an oil bath and stirred at 100-105° C for 10 h. Then the reaction mixture was heated at 140° C for 3 h to decompose the catalyst followed by a distillation of volatile by-products at 150° C /3 mm Hg for 2 h to give 275.0 g(91 % yield) of PDMS-amino. The content of nitrogen was 0.97 wt. %, the content of volatile compounds was 5.0 wt.%.

2.3.2 Methylhydrogen terminated polydimethylsiloxane (MHS-30)

Into a 250 mL two–neck flask, fitted with a condenser and a mechanical stirrer, was placed 50 g (0.075 mol) of methylhydrogen terminated polydimethylsiloxane DC-1-8114 (the active hydrogen content is 0.30 wt. %)127.7 g (0.431 mol) of octamethylcyclotetrasiloxane and 5.3 g sulfocationic resin Purolite CT175. The flask was immersed in an oil bath and stirred at 70-75° C for 12 h. The reaction mixture was then filtered to remove the catalyst. Volatile by-products were distilled off at 100° C /3 mm Hg for 2 h to give 160.0 g (90 % yield) of methylhydrogen terminated polydimethylsiloxane with an average chain length equal to 30 units and the active hydrogen content – 0.080 wt. %.

2.3.3 α, ω-bis(3-glycidoxypropyl)polydimethylsiloxane (PDMS-epoxy)

Into a 250 mL two–neck flask, fitted with a condenser and a mechanical stirrer, was placed 50.0 g (0.075 mol) of methylhydrogen terminated polydimethylsiloxane MHS-30 (the active hydrogen content is 0.080 wt. %) and 5.0 g (0.044 mol) of allyl glycidyl ether. The flask was immersed in an oil bath and stirred at 70° C for 15 min followed by addition of 0.2 ml of a toluene solution of Karstedt catalyst (1 mg Pt/ml). In 10 minutes the temperature increased up to 80° C. After that the reaction mixture was stirred at 80-85° C for 12 h until the conversion of SiH groups reached 95 %. Then volatile by-products were distilled off at 130° C / 3 mm Hg for 2 h to give 52.3 g (95 % yield) of PDMS-epoxy with the content of epoxy groups - 3.26 wt. %.

2.3.4 α, ω-bis-(10-carboxydecyl)polydimethylsiloxane (PDMS-carboxy)

Undecanoic acid trimethylsilyl ether was synthesized according to synthetic procedure described in [19].

Into a 250 mL two–neck flask, fitted with a condenser and a mechanical stirrer, was placed 50.0 g (0.075 mol) of methylhydrogen terminated polydimethylsiloxane MHS-30 (the active hydrogen content is 0.080 %) and 11.3 g (0.004 mol) of undecanoic acid trimethylsilyl ether. The flask was immersed in an oil bath and stirred at 70 ° C for 15 min followed by addition of 0.2 ml of a toluene solution of Karstedt catalyst (1 mg Pt/ml). In 10 minutes the temperature increased up to 82° C. After that the reaction mixture was stirred at 100-105° C for 12 h until the conversion of SiH groups reached 95 %. Then volatile by-products were distilled off at 130° C / 3 mm Hg for 2 h. The protective group was removed by treatment of the reaction mixture with 10 g of water. Afterwards, water and hexamethyldisiloxane were distilled off to give 57.8 g (96 % yield) of PDMS-carboxy with the content of carboxy groups -2.85 wt. %.

2.3.5 Synthesis of polymeric microspheres

A typical recipe and method of heterophase polymerization is given below.

The synthesis of polystyrene (PS) and polymethyl methacrylate (PMMA) microspheres was carried out in a dilatometer. The dilatometer was loaded with the 0.0109 g of siloxane surfactant and 0.0109 g of initiator. 10.8 ml of phosphate buffer (pH=7.0) and 1.2 ml of the monomer were degassed prior to loading into the dilatometer and then the monomer was rapidly added to the dilatometer and stirred during 1 minute. Afterwards, the water phase was added to the other reactants and the dilatometer was immediately immersed in a water bath adjusted to 60° C. Polymerization was considered to be completed when the volume of the polymerizing system ceased to change. A monomer conversion was calculated using the following expression:

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

ΔH – the change of dilatometric height at time t, ΔH_{max} – the change of dilatometric height at a complete conversion

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

V_m– the monomer volume, ρ_m–the monomer density, ρ_n–the polymer density, S – the capillary cross-section area.

The degree of completion of the polymerization was also confirmed gravimetrically by measuring the value of the solids at the H_{max} point. Solids content was determined as the residue of the sample of suspension thermostated at 70 °C until the mass of the sample ceased to change. In all experiments the solids content agreed well with the dilatometric data.

3 Results and Discussion

3.1 Synthesis of α,ω carbofunctional PDMSs

A common method of the preparation of the carbofunctional polysiloxanes is the catalytic equilibration reaction of cyclic siloxane, e.g. octamethylcyclotetrasiloxane (D_4) with carbofunctional disiloxanes, which is carried out in acidic or alkaline media [20]. Another method is hydrosilylation of α, ω-dihydrosiloxanes by a special organic molecule, containing both a double bond and the desired functional group.

α,ω-bis(3-aminopropyl) PDMS was synthesized by anionic copolymerization of (D_4) and 1,3-bis(3-aminopropyl) tetramethyldisiloxane (as a chain terminating agent) in the presence of TMAS according to scheme 1.

The obtained oligomer will be subsequently referred to as PDMS-amino.

The reaction was carried out at a reactant ratio 7.5:1. The polymerization mixture was allowed to equilibrate for 8 hours at 100° C followed by decomposition of the initiator and the removal of the volatiles by a high vacuum distillation.

Synthesis of epoxy- and carboxy-containing PDMS was conducted in two steps.

At the first stage, an oligomer with an average number of siloxane units equal to 30 was synthesized by a catalytic rearrangement of α,ω-dihydropolydimethylsiloxane and octamethylcyclotetrasiloxane in the presence of sulfocationic resin (Scheme 2).

Then, at the second stage, the resulting SiH-terminated oligomer was hydrosilylated by allyl glycidyl ether or trimethylsilyl ether of undecenoic acid in the presence of Karstedt catalyst (Scheme 3).

The obtained products were denoted by PDMS-carboxy and PDMS-epoxy, respectively. Afterwards, the trimethylsilyl protective group was removed by hydrolysis. The conversion of SiH-groups was, at least, 94.0 %. Low molecular weight volatiles were removed by a high vacuum distillation. The structure of all synthesized oligomers was confirmed by ^{1}H and ^{29}Si NMR spectroscopy.

Thus, three types of functional PDMSs were obtained. Their properties are given in Table 1. Also, a polyoxyethylene-polysiloxane block copolymer having the average formula $HO(CH_2CH_2O)_9(CH_2)_3Si(CH_3)_2O[(CH_3)_2SiO]_7Si(CH_3)_2(CH_2)_3(OCH_2CH_2)_9OH$ (PDMS-PEG) was investigated in this study.

Table 1 Properties of the synthesized α, ω-carbofunctional PDMSs

PDMS	Density, d_4^{20}	η^{20}, cSt	Functional groups, wt.%		
			theory	exp*	exp **
“PDMS-amino”	0.965	137	1.30	1.28	1.26
“PDMS-carboxy”	0.969	173	3.30	2.85	2.85
PDMS-epoxy	0.979	153	3.37	3.26	3.30
PDMS-PEG	0.971	142	-	-	-

*- titrimetric analysis

**- ^{1}H NMR data

3.2 Colloidal properties of functional PDMSs

All α,ω-carbofunctional PDMSs are soluble in St and MMA and insoluble in water (Table 2). Also, vinyl monomers in the presence of functional PDMS form the emulsion of the oil-in-water type (Fig. 1).

Figure 1 shows an image of the aqueous styrene emulsion containing silicone surfactant. It can be seen that the continuous phase of the emulsion (dispersion medium) is colored red, therefore the water soluble dye Congo red is immobilized in an aqueous phase. This experiment allows one to visualize the structural features of the resulting emulsions and classify them as a direct emulsion.

Another method for determining the emulsion type based on measuring the electrical conductivity of the system showed the value of this parameter was equal to 0.9 $\cdot 10^{-4}$ S/m. The initial aqueous phase had the conductivity equal to 1.0 $\cdot 10^{-4}$ S/m, the conductivity of the styrene was 1.2 $\cdot 10^{-10}$ S/m. The electrical conductivity of the test emulsion sample was close to the conductivity of the water.

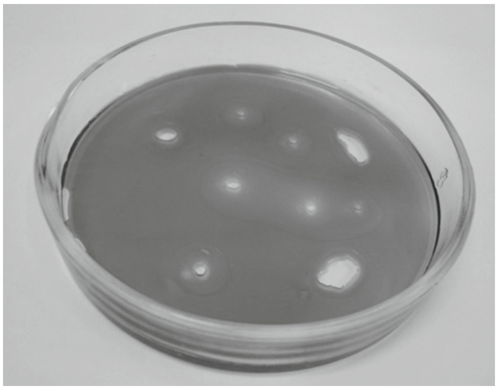
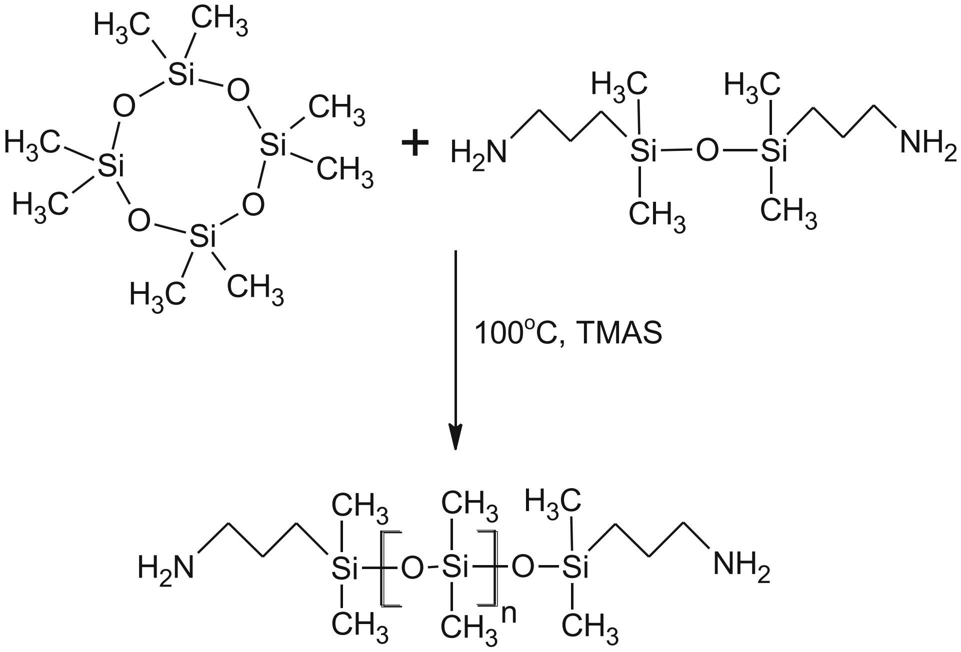


Fig. 1 Congo red water solution/solution of PDMS-carboxy in St

Scheme 1

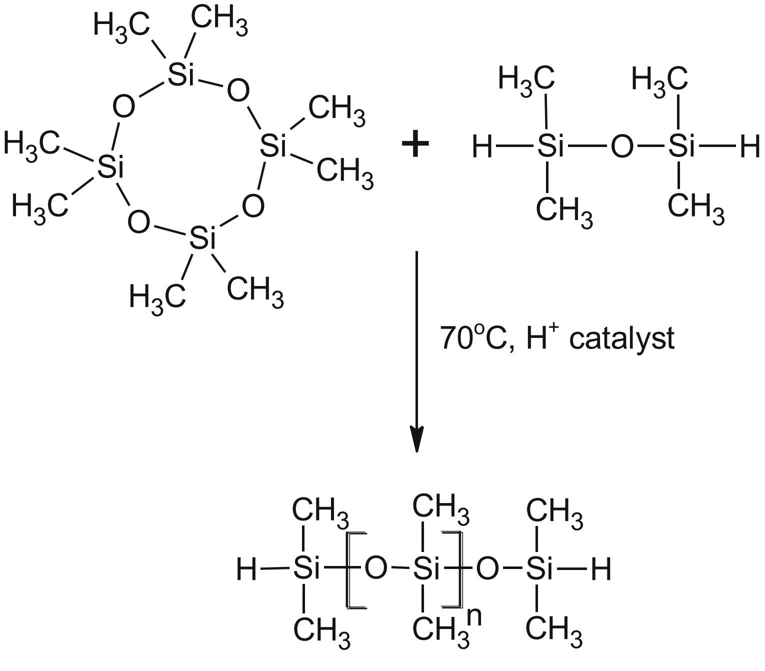


Therefore, it is possible to classify the investigated emulsion as a direct emulsion. Presumably, a slight drop in the conductivity of the emulsion relative to the pure aqueous phase is due to the influence of the volumetric proportion of the nonpolar liquid in the overall electrical system.

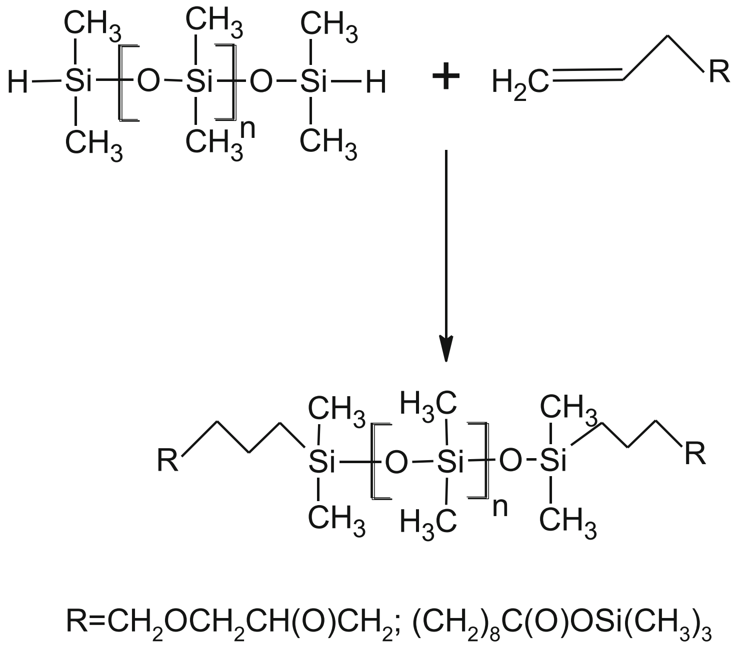
A distinctive feature of the synthesized functional PDMSs is their incompatibility with PS and PMMA resulting in a phase separation in the emulsion droplets and the formation of core-shell structures. The shell of such composite particles exclusively consists of PDMS.

Surface-active properties play an important role in the physical and chemical behavior of the reaction system. In the initial stage of polymerization this system represents PDMS dissolved in St (or MMA) droplets, which are dispersed in water, whereas at the end of the process the emulsion is transformed into a dispersion of polymeric microspheres.

Scheme 2



Scheme 3



$R=CH_2OCH_2CH(O)CH_2$; $(CH_2)_8C(O)OSi(CH_3)_3$

The interfacial tension and interfacial characteristics of the adsorption layer formed at the toluene solution of a surfactant / water interface were chosen as the main colloid chemical properties of surfactants which affect the size of the droplets in the initial monomer emulsion.

To get these characteristics we have obtained the interfacial tension isotherms. Three series of parallel measurements of interfacial tension for each concentration of silicone surfactant were carried out. The deviation from the medium value of $\sigma_{1,2}$ was no more than 0.5 mJ/m^2. Subsequently, the adsorption layer parameters of each studied surfactant were calculated accordingly to [18].

Table 2 proves that the PDMS-amino and PDMS-PEG have the highest surface activity. Moreover, their interfacial tensions exhibit close minimum values - 1.0 and 0.3 mJ/m^2 respectively.

The effect of the chemical structure of a polar group in the surfactant molecule becomes apparent when considering the maximum adsorption magnitude at the interface. Thus, PDMS-amino has the lowest adsorption equal to $0.77 \cdot 10^{-6}$ mol/m^2 and the interfacial layer with 1.97 nm thickness, whereas PDMS-epoxy and PDMS-carboxy are characterized by nearly twice the values of both the adsorption maximum and the interfacial layer thickness as compared to those for PDMS-amino. In addition, the former surfactants decrease the interfacial tension less effectively than PDMS-amino does. Thus, the interfacial tension values are 17.8 mJ/m^2 for PDMS-epoxy and 15.8 mJ/m^2 for PDMS-carboxy. PDMS-PEG exhibits the lowest values ofinterfacial tension and a fourfold higher

Table 2 Colloidal properties of the surfactants

PDMS	$\sigma_{1.2}$, mJ/m^2	$\Gamma_\infty \cdot 10^6$, mol/m^2	G, mJ · m/mol	S_0, Å^2	$\delta \cdot 10^9$,m	Solubility, wt. % (t= 20° C)		
						Water	St	MMA
PDMS-amino	1.0	0.77	5.40	215	2.0	-	16	infinite
PDMS-carboxy	15.8	1.34	10.40	124	3.8	-	18	infinite
PDMS-epoxy	17.5	1.47	4.33	113	3.7	-	24	infinite
PDMS-PEG	0.3	2.98	4.35	56	4.1	5	80	infinite

$^*\sigma_{1.2}$ – minimum value of interfacial tension; Γ_∞ - maximum adsorption by the Langmuir equation ($\Gamma = \Gamma_\infty$ Kc / (1 + Kc)); G - the surface activity in the Rebinder equation (G = lim (dσ / dc) for c → 0); S_o - the area per molecule at the interface at the maximum adsorption ($S_o = 1/\Gamma_\infty$); δ - thickness of the adsorbed layer at the maximum adsorption ($\delta = \Gamma_\infty \cdot M/\rho$, where M molecular weight of the surfactant, ρ - the density of the surfactant).

maximum absorption magnitude ($2.98 \cdot 10^{-6}$ mol /m^2) as compared to PDMS-amino, whereas the thickness of its interfacial layer is close to that observed for PDMS-epoxy and PDMS-carboxy

Thus, investigation of the colloid-chemical properties of the synthesized oligomers showed that these properties strongly depend on the chemical nature of the PDMS chain ends. The obtained values of the interfacial tensions and the adsorption layer thickness make it possible to conclude that the synthesized surfactants may be used as stabilizers of direct emulsions whose effectiveness is determined by the chemical structure of the terminal groups (Fig. 2).

3.3 Heterophase polymerization of St and MMA

It is well known that the formation of the monomer - polymer particles (MPPs) during the heterophase polymerization of poorly water-soluble monomers can proceed according to different mechanisms: 1) in the presence of water-soluble surfactant - from surfactant micelles and microdroplets of the monomer; 2) without surfactant – by the mechanism of homogeneous nucleation, which leads to the formation of polymeric suspension with a wide particle size distribution.

Previously it was shown that in the presence of water-insoluble surfactants the MPPs are formed from the monomer microdroplets [14, 15]. These MPPs have a narrow particle size distribution provided that a hard interfacial layer on the particle surface is formed.

Polymerization of St and MMA was initiated by potassium persulfate (PP). It is known [21] that the oligomeric surfactants are formed in the aqueous phase when the polymerization of hydrophobic monomers is initiated by PP. These oligomeric molecules are involved in the formation of the interfacial layer on the MPP surface. So, to determine the effect of oligomeric surfactants on the interfacial layer formation, the results obtained when using PP were compared with surfactant-free heterophase polymerization and the polymerization initiated by hydrocarbon - soluble initiator-AIBN.

The kinetic curves of St and MMA polymerization initiated by either PP or AIBN in the presence of silicone surfactant at a monomer /water ratio 1:9 (v/v) are shown in Fig. 3 as well as the kinetic curves of surfactant-free and “bulk” polymerization.

The kinetic curves of St and MMA polymerization are typical of heterophase polymerization. When using PP as an initiator a complete monomer conversion is achieved in 5 h for St and in 1 h for MMA at 80° C, whereas at 60° C St and MMA can be completely converted into polymers in 25 h and 2 h respectively. If the polymerization is initiated by AIBN a complete monomer conversion is achieved in 35 h for St and in 5 h for MMA at 60° C. Stable dispersions of either PS or PMMA with a narrow particle size distribution are formed upon completion of the polymerization process (Table 3).

Depending on the PDMS type initiator and the polymerization temperature particles of different diameters ranging from 0.4 to 0.8 microns and ξ- potential values from -18 to -46 mV were synthesized.

In the surfactant-free polymerization of St and MMA a suspension with a wide particle size distribution (D_w / D_n =1.3-1.4) was formed. Also, changing the nature of the initiator significantly affects both particle size and particle size distribution.

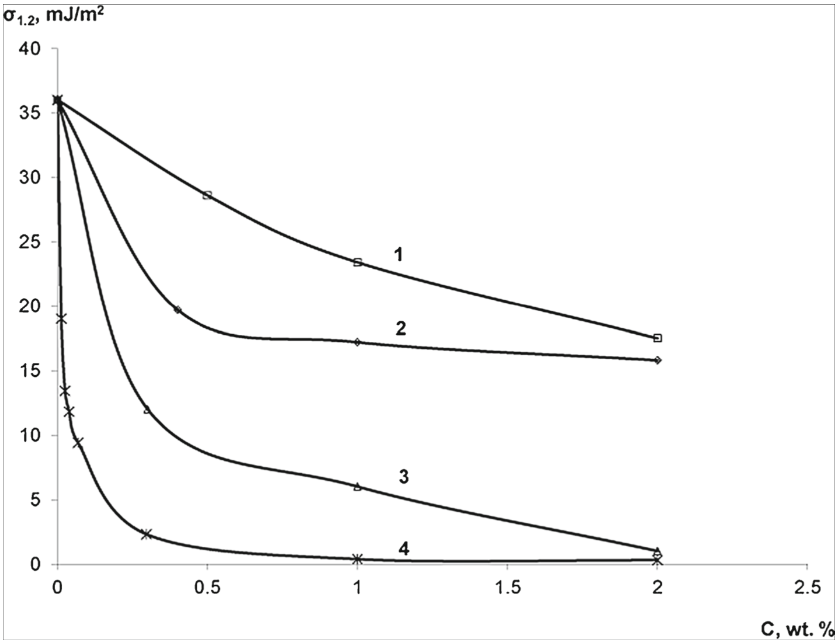


Fig. 2 Surface tension isotherms of PDMS at the toluene/water interface 1 - PDMS-epoxy; 2 - PDMS-carboxy; 3 - PDMS-amino; 4 - PDMS- PEG

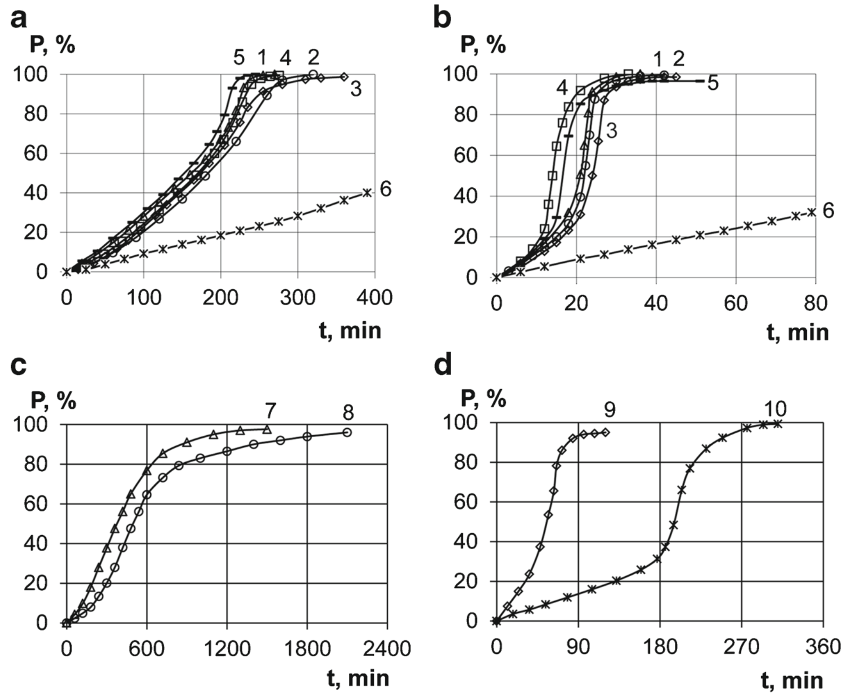


Fig. 3 Time-conversion curves of St (**a**) and MMA (**b**) polymerization initiated by PP in the presence of: 1 – PDMS-epoxy; 2 – PDMS-amino; 3 – PDMS-carboxy; 4 – PDMS-PEG (monomer:water =1:9 v/v, = 80 ±0.5° C, pH = 7, PP and PDMS concentrations are 1 wt. % per monomer), 5–surfactant-free polymerization; 6–"bulk" polymerization. St polymerization (**c**) in the presence of PDMS-carboxy initiated by: 7–PP, 8–AIBN; MMA polymerization (**d**) in the presence of PDMS-amino initiated by: 9–PP and 10–AIBN (monomer:water =1:9 v/v, = 60 ±0.5° C, pH =7, PP and PDMS concentrations are 1 wt. % per monomer)

The narrow particle size distribution of the obtained suspensions indicates the formation of a hard interfacial layer on the MPP surface in the presence of the organosilicone surfactant.

Table 3 Properties of PS and PMMA suspensions obtained in the presence of functional PDMS surfactants (monomer:water =1:9 v/v, ⊤ = 80 ± 0.5° C, pH = 7, PP and PDMS concentrations are 1 wt. % per monomer (a), ⊤ = 60 ± 0.5° C (b); ⊤ = 60 ± 0, 5° C, AIBN 1 wt. % per monomer (c))

	PDMS	d, μm	ξ, mV	D_w/ D_n	$M_\eta \cdot 10^{-5}$	Stability in NaCl, M
	St polymerization					
a	PDMS-epoxy	0.7	-347	1.02	3.1	0.25
	PDMS-carboxy	0.05	-367	1.01	4.2	0.25
	PDMS-amino	0.4 and 2.0	-22.6	Bimodal distribution	6.4	0.25
	PDMS-PEG	0.5	-43.5	1.03	2.4	0.20
	Without surfactant	0.4	-18.3	1.32	3.9	0.10
b	PDMS-carboxy	0.7	-35.0	1.03	6.8	0.20
c	PDMS-carboxy	0.7	-19.3	1.03	4.2	0.20
	MMA polymerization					
a	PDMS-epoxy	0.4	-46.3	1.01	9.3	0.25
	PDMS-amino	0.8	-27/8	1.01	1.0	0.20
	PDMS-carboxy	0.4	-31.6	1.02	7.3	0.25
	PDMS-PEG	0.4	31.6	1.02	15.0	0.20
	Without surfactant	0.6	-20.1	1.41	3.7	0.10
b	PDMS-amino	0.8	-27.0	1.03	6.4	0.15
c	PDMS-amino	0.4	-18.0	1.03	5.3	0.15

The negative value of the zeta potential is apparently due to the usage of PP as an initiator, which upon decomposition forms charged anion radicals, causing the charge on the particles of the polymeric slurry.

Since the number of anions formed during the decay of PP was significantly greater than the number of functional groups in the silicone surfactant (even in the case of an amino-PDMS), the value of zeta potential is mainly determined by the amount of PP used.

The PS suspension obtained in the presence of PDMS-amino had a bimodal particle size distribution with the particles 0.4 and 2.0 μm in diameter, while the PMMA suspensions are characterized by a unimodal particle size distribution with the particles 0.8 μm in diameter (Fig. 4).

The formation of two particle sets in the case of St polymerization in the presence of amino-functional surfactant can be explained as follows. PP decomposes forming sulfate ions, which subsequently react with the amino group of PDMS-amino to give - α,ω-bis(3-aminopropyl)polydimethylsiloxane sulfate. This surfactant is characterized by higher hydrophilicity than the initial PDMS-amino molecule. Apparently, its formation during the early stages of polymerization leads to the monomer which is dispersed more effectively. This, in turn, results in the formation of superfine particle fractions in the polymeric suspension. The formation of MPPs of large diameters can be attributed to the fact that as PDMS-amino interacts with

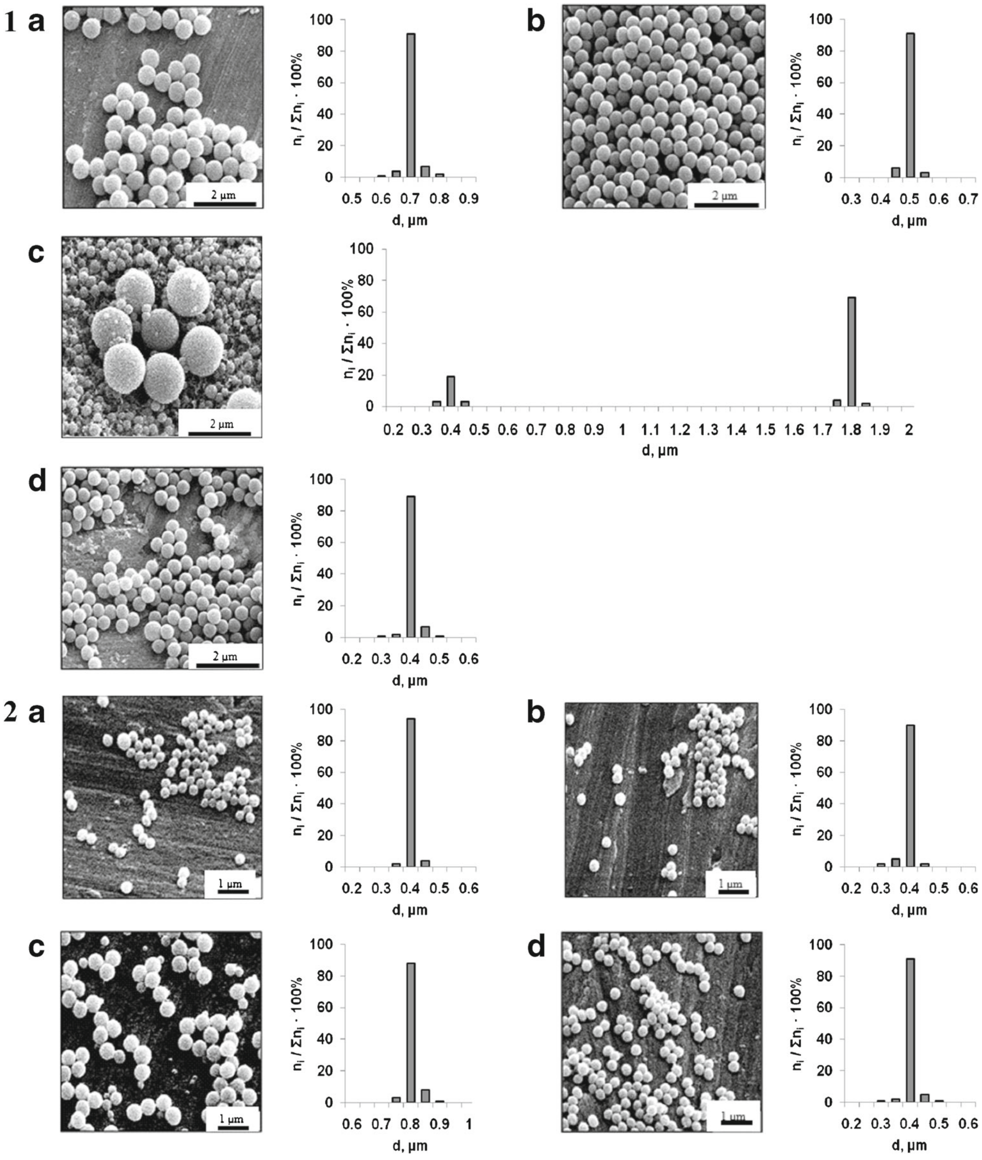


Fig. 4 Microphotographs of PS (**1**) and PMMA (**2**) particles and size distribution histograms: **a**) PDMS-epoxy, **b**) PDMS-carboxy **c**) PDMS-amino, **d**) PDMS-PEG (monomer:water =1:9 v/v, $T = 80 \pm 0.5°$ C, pH = 7, PP and PDMS concentrations are 1 wt. %, per monomer)

sulfate ions of the initiator, the PDMS-amino content in the particle volume goes down and the monomer is dispersed less effectively.

By monitoring the diameter changes of polymeric particles during the polymerization of St and MMA in the presence of PDMS-carboxy (Table 4) we found that stable suspensions of polymeric microspheres with a narrow particle size distribution are formed at the early stages of the polymerization process. Note that with increasing monomer conversion the particle diameters remain virtually the same.

The fact that the particles have a narrow size distribution at the early stages of the polymerization is indicative of the formation of a hard interfacial layer on the MPP surface. The ability of the interphase layer forming during initiation to stabilize MPPs so as to prevent monomer droplets from further dispersion is a common property of all studied surfactants. Thus, MPPs formed at the early stages of the polymerization maintain the same size throughout a dispersion process i.e. the polymerization proceeds in a discrete volume of MPPs. An average size of the MPPs remains the same throughout the polymerization, because the interfacial adsorption layers prevent MPPs both from coagulation and isothermal distillation.

To explain the results obtained, we propose the following mechanism of the interfacial layer formation on the MPP surface. This mechanism differs from that of the interfacial layer formation in the presence of water-soluble surfactants.

Table 4 Changes in diameters and monomer conversion during the polymerization of St and MMA in the presence of PDMS-carboxy (monomer:water =1:9 v/v, $T = 80 \pm 0.5^\circ$ C, pH = 7, PP concentration is 1 wt. % per monomer)

Monomer	Monomer conversion, %	d, μm	D_w/D_n	ξ, mV	Stability in NaCl, M
St	10	0.3	1.03	-41.8	0.15
	20	0.3	1.04	-39.0	0.15
	30	0.4	1.03	-37.1	0.20
	50	0.4	1.01	-36.5	0.20
	100	0.5	1.01	-36.1	0.25
MMA	10	0.3	1.04	-42.7	0.15
	20	0.3	1.04	-38.3	0.15
	30	0.3	1.03	-35.9	0.20
	50	0.4	1.03	-31.4	0.20
	100	0.4	1.02	-27.9	0.25

It is known [20] that all elementary reactions during heterophase polymerization proceed in the adsorption layers of MPPs. Hence, the resulting polymer is not uniformly distributed in the particle volume. At the very beginning of the polymerization its concentration is higher near the MPP surface. The formation of the PS molecules favors the displacement of organosilicone surfactant onto the interface. When a critical concentration of PDMS in PS is reached, a phase separation occurs and MPPs of a core-shell structure are formed.

The shell is formed as a result of the following. At first, initiation takes place on the surface of monomer microdroplets; then, a high molecular weight PS (PMMA) is formed and subsequently precipitates onto the particle surface, since water serves as a polymer precipitator. The organosilicone surfactant displaced by the polymer from the MPP volume forms a liquid-crystal film which possesses all the necessary rheological properties to create a Rebinder structural-mechanical barrier at the interface.

The formation of a liquid-crystal film on the MPP surface provides a smooth transition from the solid phase of a hydrophobic polymer to the aqueous dispersion medium. The chemical structure of the diphilic organosilicone surfactant together with the high flexibility of the siloxane chain significantly contributes to this transition. These properties allow the surfactant to acquire a conformation which provides the highest concentration of the methyl groups near the particle surface whereas the hydrophilic groups are oriented toward the aqueous phase.

In addition, such an orientation of the surfactant molecules provides a high concentration of functional groups capable of further modification on the surface of polymeric microspheres.

The duration of the interfacial layer formation on the MPP surface in the presence of organosilicone surfactant is a distinctive feature of the proposed mechanism. The interfacial layer starts to form at the very beginning of the polymerization as a result of a phase separation in the MPP volume and displacement of the surfactant onto the MPP surface because of its incompatibility with an organic polymer. This process continues until nearly complete monomer conversion when all surfactant molecules are concentrated in the interfacial layer.

The structure of the interfacial layer formed on the MPP surface in the presence of the water-soluble surfactant differs from that of the interfacial layer formed by the water-insoluble surfactant.

If the interfacial layer is formed in the presence of a water-soluble surfactant then there is a sharp division into a hydrophobic layer created by a hydrocarbon chain and a hydrophilic one formed by the polar groups of a surfactant molecule. Alternatively around, if the interfacial layer is created in the presence of an organosilicone surfactant, no division into hydrophilic and hydrophobic regions occurs. In this case, the interfacial layer with 2-4 nm thickness is formed, and a smooth transition from hydrophilic to hydrophobic region (which contains both organic functionalities and a siloxane main chain) is observed that ultimately determines a high stabilizing ability of the interfacial layer.

4 Conclusions

In this research the possibility of the synthesis of monodisperse polymeric microspheres with the use of α, ω-functional PDMSs as surfactants with different functional organic substituents at the siloxane chain ends was evaluated. It was shown that polymeric suspensions obtained in the presence of functional PDMSs irrespective of the monomer type (St, MMA) are characterized by a narrow particle size distribution. Furthermore, it was assumed that the creation of a Rebinder structural-mechanical barrier in the interfacial adsorption layer occurs at the very beginning of the polymerization process. In turn, the formation of a hard interfacial layer provides high stability of MPPs during the synthesis and a narrow particle size distribution.

Acknowledgments We acknowledge the financial support provided by the Russian Foundation of Fundamental Research, Project 13-03-12251.

References

1. Pellach M, Margel S (2014) Photochem and Photobiol 90:952–956

2. Ryu J-H, Lee Y-H, Suh K-D (2008) J Appl Polym Sci 107:102–108
3. Kuehne AJC, Gather MC, Sprakel J (2012) Nat Commun, doi:10.1038/ncomms2085
4. Horák D, Kučerová J, Korecká L, Jankovičová B, Palarčík J, Mikulášek P, Bílková Z (2012) Macromol Biosci 12:647–655
5. Prokopov NI, Gritskova IA, Cherkasov VR, Chalykh AE (1996) Russ Chem Rev 65:167–180
6. Omer-Mizrahi M, Margel S (2010) Polymer 51:1222–1230
7. Ugelstad J, P C Mørk, Kaggerud KH, Ellingsen T, Berge A (1980) Adv Colloid Interface Sci 13:101–140
8. Omi S, Katami K, Yamamoto A, Iso M (1994) J Appl Polym Sci 51:1–11
9. Omi S, Matsuda A, Imamura K, Naga M, Ma G-H (1999) A: Physiochemical Eng Asp 153:373–381
10. Okubo M, Shiozaki M, Tsujihiro M, Tsukuda Y (1991) Colloid Polym Sci 269:222–226
11. Gao Zh, Grulke EA, Ray AK (2007) Colloid Polym Sci 285:847–854
12. Senuma Y, Hilborn JG (1999) Mat Res Innovat 3:42–49
13. Kawaguchi S, Ito K (2005) Adv Polym Sci 175:299–328
14. Gritskova IA, Adebayo GB, Krasheninnikova YG, Kaminsky VA (1998) Colloid Polym Sci 276:1068–1077
15. Yanul' Yu B (1992) Synthesis of functional polymeric suspensions in the presence of oligomeric peroxyesters. PhD thesis, Moscow
16. Gritskova IA, Zhdanov AA, Chirikova OV, Schegolikhina OI (1994) Dokl Akad Nauk (Russ Ed) 334:57–59
17. Holmberg K, Jönsson B, Kronberg B, Lindman B (2003) Surfactants and polymers in aqueous solution, 2nd edn. Wiley, New York
18. Adamson AW, Gast AP (1997) Physical chemistry of surfaces. Wiley interscience publication. New York, p. 808
19. Kopylov VM, Kovjazin VA, Ivanov VV, Markuze IYu (2007) Organosilicon carboxylates of rare-earth elements as thermal stabilizers of polydiorganosiloxane liquids and a method for preparation thereof. Pat Russian Federation No. 2291877
20. Yilgor I, McGrath JE (1988) Adv in Polym Sci 89:1–86
21. Khomikovskii PM (1958) Rus Chem Rev (Russ Ed) 27:1025–1055