J Inorg Organomet Polym (2012) 22:564–576
DOI 10.1007/s10904-011-9605-4

Synthesis and Characterization of Hybrid Core–Shell Systems Based on Molecular Silicasols

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Received: 15 July 2011 / Accepted: 26 September 2011

Abstract New hybrid "rigid inorganic core–soft organic shell" systems based on molecular silicasols were synthesized by applying different synthetic schemes. Inorganic core was composed of molecular silicasols, which were synthesized from hyperbranched polyethoxysiloxane and tetraethoxysilane by polymer chemistry methods. Different organic modifiers were used to form soft shell of the hybrid particles. Obtained compounds were characterized by elemental analysis, GPC, IR and NMR spectroscopy. These systems will be designated for use as model objects for investigation of nanoparticles–polymer matrix interactions in polymer nanocomposites.

Keywords Hyperbranched polyethoxysiloxane · Molecular silicasol · Molecular silica nanoparticles · Hybrid organic–inorganic polymers · Nanogels · Nanocomposites

1 Introduction

Creation of hybrid materials is one of the most promising areas of the contemporary polymer materials science. The transition from simple filled compositions to the formation of hybrid materials gave rise to the new independent field of composite materials. Its main difference from the prevalent methods of composite production was that instead of the filler its precursor was introduced into polymer system. Professor Mark has been being one of the pioneers and main players in this field for many years. His approach of in situ formation of inorganic phase [1–5] resulted in dramatic increase of the efficiency of the introduction of inorganic phase to the polymer composition. These results attracted many successors inspired by the idea of creating hybrid systems that would fully combine advantages of organic polymer matrixes and inorganic networks generated directly during the formation of hybrid material.

Publications at the turn of the century demonstrated a huge potential of hybrid systems and set main directions of the field development, most importantly, improvement of the technology of hybrid materials formation and effective control over conversion of functional groups.

Another approach, which also induced creation of hybrid materials, dealt with formation of nanocomposites based on organic polymer matrixes and inorganic nanosized fillers, most of which were products of hydrolysis of silicon, aluminium or titanium alkoxides. Both approaches needed effective controlling sol–gel processes during the formation of inorganic filler.

The main problem concerning creation of nanocomposite materials is incompatibility of the nanofiller with polymer matrix causing aggregation of nanoparticles, which is usually hard to avoid [6, 7]. High values of the surface energy at the nanoparticle–polymer interface make aggregation, which impairs basic operational characteristics of composite materials, thermodynamically beneficial [8].

One of the efficient approaches to solve this problem is chemical modification of the filler surface. Examples of such approach can be found elsewhere [9–13], although

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every type of filler needs creation of its own modifying agent. Development of polymer nanoobjects that are polymer molecules possessing nanoparticle properties and synthesis of their numerous modifications demonstrated that polymer chemistry has a huge potential for synthesis and modification of nanoobjects [13–17]. Application of polymer chemistry methods to synthesis and chemical modification of nanofillers can be very efficient for solving the problem of regulating the compatibility in the system nanofiller–polymer matrix.

Among widespread fillers for polymer composition, silica is most prevalent. Different methods of silica synthesis, i.e. in the form of silicic acid, silica gel, etc. are summarized in Ref. [18].

One of well-known approaches to silica synthesis is hydrolytic polycondensation of tetraalkoxysilanes. Properties of the silica particles obtained by this method depend on synthetic conditions. Most of published research is devoted to the synthesis of colloidal silica particles by means of hydrolysis of tetraethoxysilane (TEOS) in alcohol–water–ammonia medium [19, 20]. Colloidal silica particles could be modified with various organic compounds, including oligomers and polymers. Modification allows to improve the compatibility of the filler with specific polymer matrix as well as to change properties of the particles themselves [13, 21–26].

"Polymeric" approach to the synthesis and modification of hybrid organic–inorganic nanoobjects based on molecular silicasols [27] allowed not only to obtain new series of hybrid nanoobjects, but also to observe for the first time gradual qualitative changes occurring in "hard inorganic core–soft organic shell" systems upon increase of the core size and rigidity [28]. The results obtained from the investigation of how the core structure influences the properties of core–shell particles give rise to further research and comparison of the nanoparticles of the same composition, but formed by means of different methods. Hyperbranched polyethoxysiloxanes and their derivatives are perfect model systems for such an investigation, because they allow to easily produce a wide variety of modified silica particles with different surface layers [29]. Qualitative differences in properties of these nanoobjects are very important, from both basic and applied points of view, for the creation of polymer-based nanocomposites.

The goal of this particular work was to synthesize hybrid nanoparticles of inorganic core–polar organic shell type and to characterize them as macromolecular systems. Various approaches to the synthesis of hybrid molecular systems are considered in this paper, while the objective is not to optimize the synthesis, but rather to obtain model objects for further investigation of fundamental aspects of structure–properties relationship for a hybrid nanoparticle–polymer matrix system.

2 Materials and Methods

2.1 Materials

Methoxyacetic acid (98%), ethylene glycol monomethyl ether (99%), diethylene glycol monomethyl ether 99%), triethylene glycol monomethyl ether (99%), terephthaloyl chloride (99%) were supplied from Fluca Chemie GmbH (Switzerland), THF, DMSO, toluene, dioxane, hexane, Py, AcCl, AllBr, AcOH, TEOS, $(ClMe)Me_2SiCl$, HMe_2SiCl, platinum catalyst PC 072, Na_2CO_3, NaOH, NaCl, $(NH_4)_2CO_3$, Na metal, silica were supplied from ACROS (Russia).

2.2 Syntheses of Molecular Silicasols Modified with Ethylene Oxide Derivatives

2.2.1 Syntheses of Mono-, Di- and Tri(Ethylene Oxide) Derivatives of Molecular Silicasols Based on Hyperbranched Polyethoxysiloxane

2.2.1.1 Synthesis of Ethylene Glycol Allyl Methyl Ether Metallic Na (7.67 g, 0.3340 mol) was added slowly to ethylene glycol monomethyl ether (25.36 g, 0.3340 mol) solution in dioxane (100 mL) at stirring at 60 °C. The process was being carried out for 6 h until Na dissolved completely. As viscosity increased, dioxane (2 × 30 mL) was added gradually. Thereafter, AllBr (40.4 g, 0.3340 mol) was added to the reaction mixture. The mixture was stirred for 9 h at 70 °C. The formed precipitate was filtered out and the filtrate was evaporated at 40 °C, 100 mbar. The pure product (30.80 g) was obtained by vacuum distillation at 83 °C, 200 mbar (yield 79%).

^1H NMR (250 MHz, $CDCl_3$): δ ppm, 5.84–5.99 (m, $CH_2{=}CH$, 1H), 3.52–3.60 (m, CH_2CH_2O, 4H), 4.00–4.03 (m, $CH_2{=}CHCH_2O$, 2H), 5.15–5.30 (m, $CH_2{=}CH$, 2H), 3.38 (s, $O{-}CH_3$, 3H).

Syntheses of both di- and tri(ethylene glycol) allyl methyl ethers were carried out using similar chemical schemes. The mole ratios were the same. As a result there were obtained.

2.2.1.2 Di(Ethylene Glycol) Allyl Methyl Ether (27.60 g) obtained by vacuum distillation at 45 °C, 1 torr (yield 69%). $n_D^{20} = 1.4271$.

^1H NMR (250 MHz, $CDCl_3$): δ ppm, 3.38 (s, OCH_3, 3H), 3.54–3.69 (m, CH_2CH_2O, 8H), 4.01–4.03 (d, $CH_2{=}CHCH_2O$, 2H), 5.14–5.31 (m, $CH_2{=}CH$, 2H), 5.84–5.99 (m, $CH_2{=}CH$, 1H).

2.2.1.3 Tri(Ethylene Glycol) Allyl Methyl Ether (27.80 g), obtained by vacuum distillation at 76 °C, 1 torr (yield 76%).

^{1}H NMR (250 MHz, $CDCl_3$): δ ppm, 3.36 (s, OCH_3, 3H), 3.51–3.66 (m, CH_2CH_2O, 12H), 3.99–4.02 (d, CH_2=CHCH_2O, 2H), 5.14–5.29 (m, CH_2=CH, 2H); 5.82–5.98 (м, CH_2=CH,1H).

2.2.2 Syntheses of Mono-, Di- and Tri(Ethylene Oxide) Derivatives of Molecular Silicasols

were carried out by hydrosilylation reaction of dimethyl hydride derivatives of molecular silicasols obtained according to ref [25] with mono-, di- and tri(ethylene glycol) allyl methyl ethers respectively.

2.2.2.1 Synthesis of Mono(Ethylene Oxide) Derivative of Molecular Silicasol A solution of ethylene glycol allyl methyl ether (19.37 g, 0.1667 mol) in dioxane (10 mL) and platinum catalyst PC 072 (250 μL) were added to dimethyl hydride derivative of molecular silicasol (15.70 g, 0.08074 mol) under Ar. The reaction mixture was stirred for 5 days at 40 °C. Thereafter, the catalyst was filtered out and the filtrate passed through a silica gel column. The pure product (28.14 g) was obtained and fractionated by fractional precipitation into hexane from a solution in toluene (yield 79%).

^{1}H NMR (250 MHz, $CDCl_3$): δ ppm, 0.05–0.10 (m, SiCH_3), 0.46–0.60 (m, Si–CH_2, 2H), 1.52–1.67 (m, $CH_2CH_2CH_2$, 2H), 3.36–3.53 (m, OCH_2CH_2OCH_2, OCH_3, 9H).

IR: cm^{-1}, 3400–3600, 2850–2900, 1400, 1100–1050.

2.2.2.2 Synthesis of Di(Ethylene Oxide) Derivative of Molecular Silicasol was carried out analogously by the reaction of di(ethylene glycol) allyl methyl ether (3.33 g, 0.0208 mol), dimethyl hydride derivative of molecular silicasol (2.00 g, 0.0104 mol) in the presence of platinum catalyst PC 072 (15 μL). The reaction mixture was stirred in toluene (13 mL) for 10 days at 40 °C. There were obtained 3.1 g of the pure caramel-like product (yield 58%).

^{1}H NMR (250 MHz, $CDCl_3$): δ ppm, 0.08–0.33 (m, SiCH_3, 6H), 0.49–0.65 (m, CH_2Si, 2H), 1.54–1.63 (m, $CH_2CH_2CH_2$, 2H), 3.39 (m, OCH_3, 3H), 3.56–3.64 (m, OCH_2, 10H).

IR: cm^{-1}, 3400–3600, 2850–2900, 1400, 1250, 1100–1050.

2.2.2.3 Synthesis of Tri(Ethylene Oxide) Derivative of Molecular Silicasol was carried out analogously by the reaction of tri(ethylene glycol) allyl methyl ether (4.20 g, 0.02056 mol), dimethyl hydride derivative of molecular silicasol (1.98 g, 0.01028 mol) in the presence of platinum catalyst PC 072 (15 μL). The reaction mixture was stirred in toluene (13 mL) for 10 days at 40 °C. There were obtained 3.6 g of the pure viscous product (yield 58%).

^{1}H NMR (250 MHz, $CDCl_3$): δ ppm, 0.07–0.22 (m, SiCH_3, 6H), 0.51–0.60 (m, CH_2Si, 2H), 1.54–1.65 (m, $CH_2CH_2CH_2$, 2H), 3.38 (m, OCH_3, 3H), 3.55–3.67 (m, OCH_2, 14H).

IR: cm^{-1}, 3400–3600, 2850–2900, 1400, 1250, 1100–1050.

2.2.3 Syntheses of Di- and Tri(Ethylene Oxide) Derivatives of Molecular Silicasols Based on Molecular Silicasol

2.2.3.1 Synthesis of 4,7,10-Trioxyundecyldimethylchlorosilane Platinum catalyst PC 072 (18 μL) was added to di(ethylene glycol) allyl methyl ether (17.90 g, 0.11 mol) under Ar. Thereafter, dimethylchlorosilane (9.60 g, 0.11 mol) was added. The reaction mixture was stirred for 3 h. The pure product (24.18 g) was obtained by vacuum distillation at 97 °C, 1 torr (yield 85%). $n_D^{20} = 1.4425$.

^{1}H NMR (250 MHz, $CDCl_3$): δ ppm, 0.41 (s, SiCH_3 6H), 0.81–0.88 (t, SiCH_2, 2H), 1.64–1.76 (quin, CH_2 CH_2CH_2, 2H), 3.39–3.68 (m, OCH_2, OCH_3, 13H).

2.2.3.2 Synthesis of 4,7,10,13-Tetraoxytetradecyldimethylchlorosilane Platinum catalyst PC 072 (18 μL) was added to tri(ethylene glycol) allyl methyl ether (30.06 g, 0.14 mol) under Ar. Thereafter, dimethylchlorosilane (15.26 g, 0.14 mol) was added. The reaction mixture was stirred for 3 h. The pure product (32.15 g) was obtained by vacuum distillation at 130–131 °C, 3 torr (yield 73%). $n_D^{20} = 1.4473$.

^{1}H NMR (250 MHz, $CDCl_3$): δ ppm, 0.41 (s, SiCH_3 6H), 0.81–0.88 (t, SiCH_2, 2H), 1.53–1.76 (quin, $CH_2CH_2CH_2$, 2H), 3.38–3.67 (m, OCH_2, OCH_3, 17H).

2.2.3.3 Synthesis of 4,7,10-Trioxyundecyldimethylacetoxysilane 4,7,10-trioxyundecyldimethylchlorosilane (23.8 g, 0.09 mol) was being added to a mixture of CH_3COOK (8.67 g, 0.09 mol) and MTBE (104 mL) for 20 min. The reaction mixture was stirred at reflux for 12 h. Thereafter, the formed precipitate of KCl was filtered out. The pure product (17.82 g) was obtained by vacuum distillation at 96 °C, 3 torr (yield 68%). $n_D^{20} = 1.4726$.

^{1}H NMR (250 MHz, $CDCl_3$): δ ppm, 0,27 (s, SiCH_3, 6H), 0.71–0.78 (t, SiCH_2, 2H), 1.58–1.78 (quin, $CH_2CH_2CH_2$, 2H), 2.04 (s, OCH_3, 3H), 3.38–3.67 (m, OCH_2, OCH_3, 13H).

2.2.3.4 Synthesis of 4,7,10,13-Tetraoxytetradecyldimethylacetoxysilane 4,7,10,13-tetraoxytetradecyldimethylchlorosilane (30.95 g, 0.096 mol) was being added to a mixture of CH_3COOK (10.05 g, 0.11 mol) and MTBE (150 mL) for 20 min. The reaction mixture was stirred at reflux for 12 h. Thereafter, the formed precipitate of KCl was filtered out. The pure product (21.82 g) was obtained by vacuum distillation at 136.5–137 °C, 3 torr (yield 71%). n_D^{20} =1.4765.

^{1}H NMR (250 MHz, CDCl$_3$): δ ppm, 0,26 (s, SiCH_3, 6H), 0.70–0.77 (t, SiCH_2, 2H), 1.58–1.72 (quin, $CH_2$$CH_2$$CH_2$, 2H), 2.04 (s, O$CH_3$, 3H), 3.38–3.66 (m, O$CH_2$, O$CH_3$, 17H)

2.2.3.5 Modification of Molecular Silicasol with 4,7,10-Trioxyundecyldimethylacetoxysilane

4,7,10-trioxyundecyldimethylacetoxysilane (8.87 g, 0.0318 mol), acetic acid (52.00 g), a solution of molecular silicasol (1.84 g, 0.0106 mol) in THF (47 mL) and $CH_3C(O)Cl$ were mixed up. The reaction mixture was stirred at reflux for 30 h. Thereafter, acetic acid was removed by washing with toluene (2 × 100 mL). The reaction mixture was filtered. Most of volatile products were removed by vacuum distillation at 50 °C, 1 torr. The pure product (4.74 g) was obtained and fractionated by fractional precipitation into hexane from a solution in toluene (yield 76%).

IR: cm^{-1}, 3400–3600, 2850–2900, 1400, 1250, 1100–1050.

El. Anal.: %, C 51.83; H 9.84; Si 13.37 (MM 1000).

2.2.3.6 Modification of Molecular Silicasol with 4,7,10,13-Tetraoxytetradecyldimethylacetoxysilane

4,7,10,13-tetraoxytetradecyldimethylacetoxysilane (13.12 g, 0.0407 mol), acetic acid (65.00 g), a solution of molecular silicasol (2.33 g, 0.0133 mol) in THF (47 mL) and $CH_3C(O)Cl$ were mixed up. The reaction mixture was stirred at reflux for 30 h. Thereafter, acetic acid was removed by washing with toluene (2 × 100 mL). The reaction mixture was filtered. Most volatiles were removed by vacuum distillation at 50 °C, 1 torr. The pure product (2.42 g) was obtained and fractionated by fractional precipitation into hexane from toluene solution (yield 27%).

IR: cm^{-1}, 3400–3600, 2850–2900, 1400, 1250, 1100–1050.

2.2.4 Syntheses of Di- and Tri(Ethylene Oxide) Derivatives of Molecular Silicasols Based on Hydrolytic Polycondensation of TEOS

Polycondensation of TEOS (2.29 g, 0.011 mol) was carried out in acetic acid (20.61 g, 0.34 mol) at 80 °C for 10 h. Thereafter, 4,7,10-trioxyundecyldimethylacetoxysilane (12.24 g, 0.044 mol) and $CH_3C(O)Cl$ (0.05 g) were added. The reaction mixture was stirred at reflux for 12 h. After adding of toluene (100 mL) the reaction mixture was washed with water until neutral medium was observed, dried with Na_2SO_4, vacuumized. After fractionating by preparative GPC 1.97 g of the liquid viscous product were obtained. (yield 61%).

IR: cm^{-1}, 3400–3600, 2850–2900, 1400, 1250, 1100–1050.

El. Anal.: %, C 44.75; H 8.34; Si 19.78 (MM 2700).

In accordance with the foregoing technique by using the mole ratios being the same there were synthesized 3.60 g of molecular silicasol modified with 4,7,10,13-tetraoxytetradecyldimethylacetoxysilane (yield 30%).

IR: cm^{-1}, 3400–360, 2850–2900, 1400, 1250, 1100–1050.

El. Anal.: %, C 48.89; H 9.34; Si 13.35 (MM 2400); C 48.06; H 9.21; Si 14.73 (MM 3200)

2.3 Synthesis of Molecular Silicasols Modified with Acetoxy Derivatives

2.3.1 Synthesis of (Acetoxymethyl)Dimethylacetoxysilane

A solution of chloromethyldimethylchlorosilane (43.66 g, 0.3051 mol) in dioxane (50 mL) was added to a suspension of CH_3COOK (60.61 g, 0.6175 mol) in dioxane (150 mL). The reaction mixture was stirred at reflux for 3 days. The precipitate was filtered out and dioxane was removed by vacuum evaporation. The product (21.98 g) including 86% of (acetoxymethyl)dimethylacetoxysilane according to GC-data was obtained by vacuum distillation at 41–44 °C, 1 torr (yield 33%).

^{1}H NMR (250 MHz, CDCl$_3$): δ ppm, 0.34 (s, SiCH_3, 6H), 2.05 (s, OC(O)CH_3, 6H), 3.86 (s, CH_2Si, 2H).

2.3.2 Synthesis of Acetoxy Derivative of Molecular Silicasol

A solution of molecular silicasol (6.99 g, 0.03986 mol) in THF (240 mL) was added to (acetoxymethyl)dimethylacetoxysilane (30.34 g, 0.1594 mol). The reaction mixture was stirred at reflux for 15 h. The pure product (10.09 g) was obtained and fractionated by fractional precipitation into hexane from a solution in THF (yield 58%).

^{1}H NMR (250 MHz, CDCl$_3$): δ ppm, 0.14–0.23 (m, SiCH_3, 6H), 2.03–2.09 (m, OC(O)CH_3, 3H), 3.69–3.73 (m, SiCH_2, 2H).

IR: cm^{-1}, 3500, 2900–2750, 1750, 1400, 1300, 1240, 1050.

El. Anal.: %, C 21.84; H 4.41; Si 32.06 (MM 28000–75000); C 23.37; H 4.88; Si 31.84 (MM 16000); C 24.89; H 4.59; Si 30.79 (MM 7000); C 31.55; H 6.02; Si 25.67 (MM3200).

2.4 Synthesis of Molecular Silicasols Modified with (Methoxyacetyl)Oxy Derivatives

2.4.1 Synthesis of Potassium Methoxyacetate

Potassium methoxyacetate was obtained by mixing a solution of $(NH_4)_2CO_3$ (65.57 g, 0.4744 mol) in H_2O

(250 mL) with a solution of methoxyacetic acid (85.47 g, 0.9488 mol) in H_2O (70 mL). The reaction mixture was stirred until CO_2 stopped to evolve. The precipitate was filtered out and the filtrate was evaporated. Thereafter, toluene was added and the reaction mixture was dried by azeotropic distillation for 3 days. After vacuumization at 50 °C, 1 torr there were obtained 116.85 g of the product (yield 96%).

2.4.2 *Synthesis of [(Methoxyacetyl)Oxymethyl] Dimethyl(Methoxyacetyl)Oxysilane*

A solution of chloromethyldimethylchlorosilane (26.92 g, 0.1881 mol) in dioxane (20 mL) was added dropwise to a suspension of potassium methoxyacetate (48.24 g, 0.3763 mol) in dioxane (200 mL). The reaction mixture was stirred at reflux for 5 days. The precipitate was filtered out and dioxane was removed by vacuum evaporation. The product (30.33 g) was obtained by vacuum distillation at 116–122 °C, 1 torr (yield 64%).

^{1}H NMR (250 MHz, $CDCl_3$): δ ppm, 0.39 (s, SiCH_3, 6H), 3.42 (s, OCH_3, 6H); 3,98 (s, OCH_2C(O), 4H), 4.04 (s, CH_2Si, 2H).

2.4.3 *Synthesis of [(Methoxyacetyl)Oxymethyl] Dimethylsilanol*

A solution of [(methoxyacetyl)oxymethyl]dimethyl(methoxyacetyl)oxysilane (15.30 g, 0.0611 mol) in THF (180 mL) was added dropwise to a mixture of $(NH_4)_2CO_3$ (33.50 g, 0.3486 mol), THF (400 mL) and H_2O (6.40 g, 0.3551 mol) at 0 °C. The fraction (4.40 g) including 43% of the product in accordance to GC-data was obtained by vacuum distillation at 89–92 °C, 1 torr (yield 17%).

^{1}H NMR (250 MHz, $CDCl_3$): δ ppm, 0.18 (s, SiCH_3, 6H), 3.42 (c, OCH_3, 3H), 3.84 (s, OCH_2C(O), 2H), 4.01–4.03 (d, OCH_2Si, 2H).

2.4.4 *Synthesis of Bis(Chloromethyl) Tetramethyldisiloxane*

Pyridine (23.03 g, 0.2961 mol) and H_2O (2.62 g, 0.1456 mol) were added to a solution of chloromethyldimethylchlorosilane (41.67 g, 0.2912 mol) in THF (100 mL) at 5 °C. The reaction mixture was stirred at ambient temperature for 1 h. The precipitate was filtered out. The pure product (28.83 g) was obtained by vacuum distillation at 88–90 °C, 20 mbar (yield 86%).

^{1}H NMR (250 MHz, $CDCl_3$): δ ppm, 0.21 (s, SiCH_3, 12H), 2.73 (s, ClCH_2Si, 4H).

2.4.5 *Synthesis of Bis[(Methoxyacetyl)Oxy] Tetramethyldisiloxane*

Bis(chloromethyl)tetramethyldisiloxane (24.39 g, 0.2320 mol) was added to a suspension of potassium methoxyacetate (29.73 g, 0.2330 mol) in DMSO (60 mL). The reaction mixture was stirred at 90 °C for 10 h. The precipitate was filtered out. The pure product (32.52 g) was obtained by vacuum distillation at 135–138 °C, 1 torr (yield 91%).

^{1}H NMR (250 MHz, $CDCl_3$): δ ppm, 0.13 (s, SiCH_3, 12H), 3.41 (s, OCH_3, 6H), 3.77 (s, OCH_2Si, 4H), 4.01 (s, OCH_2C(O), 4H).

2.4.6 *Synthesis of Molecular Silicasols Modified with (Methoxyacetyl)Oxy Derivatives*

TEOS (20.01 g, 0.09606 mol) was added to methoxyacetic acid (180.09 g, 1.9992 mol) at 40 °C. The condensation was carried out for 1 h. Thereafter, bis[(methoxyacetyl)oxy]tetramethyldisiloxane (32.52 g, 0.09606 mol) and $CH_3C(O)Cl$ (2 mL) were added at once. The reaction mixture was stirred at 90 °C for 28 h. 21.22 g of the product were obtained after vacuumization at 50 °C, 1 torr (yield 89%).

^{1}H NMR (250 MHz, $CDCl_3$): δ ppm, 0.21 (m, SiCH_3, 12H), 3.41 (m, OCH_3, 6H), 3.80 (m, OCH_2Si, 4H), 4.00 (m, OCH_2C(O), 4H).

El. Anal.: %, C 34.31; H 6.02; Si 19.85 (MM 12000); C 34.07; H 6.09; Si 22.55 (MM 2400).

2.5 Characterization Techniques

^{1}H-NMR spectra were measured on Bruker WP-200 SY spectrometer operating at 200, 13 MHz and recorded at 25 °C using $CDCl_3$ as a solvent. The tetramethylsilane was used as internal standard. The weight–average molecular weight (M_w) was determined by GPC (Czech Republic) with Phenogel-75 KD columns, by using THF eluent (1.0 mL min^{-1}), polystyrene standards and RIDK-102 refractive index detector. The infrared spectra were measured on Brucker Equinox 55/S. Characteristic viscosities were measured on SHOTT ViscoSystem®-AVS370.

3 Results and Discussion

3.1 Molecular Silica Systems Modified with Ethylene Oxide Derivatives

For synthesis of molecular silica particles with ethylene oxide groups in outer layer hyperbranched polyethoxysiloxanes (HPEOS) and molecular silicasols were used. Molecular silicasols by-turn were produced by means of hydrolitical polycondensation of HPEOS as well as from tetraethoxysilane (TEOS).

3.1.1 Synthesis of Hybrid Molecular Particles with Ethyleneoxide Surface Layer from HPEOS

Synthetic scheme (Scheme 1) includes two steps: first, polycyclization (i.e. molecular silicasol formation) with simultaneous functionalization of HPEOS with dimethyl hydride siloxane groups and, second, hydrosilylation of (alpha)methyl-(omega)allyl ethers of di- and triethylene glycols.

The first step is monitored with ^{1}H NMR spectroscopy. Completeness of the reaction is indicated by the absence of the ethoxy proton signals in NMR spectra. GPC curves of initial HPEOS and its dimethyl hydride derivative are shown on Fig. 1.

From the comparison of the curves one can see, that the curve pattern remains almost unchanged. That fact indicates that interaction between modified molecules can be neglected.

Hydrosilylation was carried out in presence of platinum catalyst (zero-valent platinum) in small excess ($\sim$5%) of modifying agent in 60% dry toluene solution. Completeness of the reaction was controlled by means of 1H NMR (absence of hydride silyl (4.711 ppm) and methylene (5.176 ppm, 5.838 ppm) protons signals). In all cases conversion of hydride silyl groups exceeded 90%. A typical spectrum of the sample taken from the reaction mixture at the ending of the modification process is shown on Fig. 2.

Residual hydride silyl groups can be neglected, because they are strongly screened. Purification of the product from unreacted methylallyl ethers of ethylene glycols was conducted in different ways. In the case of mono(ethylene oxide) derivative 6 high-molecular fractions of modified molecular silicasol were isolated by precipitation from 50% toluene solution into hexane. Their GPC curves are shown in Fig. 3. The residual product from mother solution had broad molecular mass distribution similar to that before precipitation. Despite the efficiency of synthetic scheme, fractionation results could not be regarded as satisfactory, because of low influence of modification on the properties of hybrid system. Thereupon these samples were not investigated further.

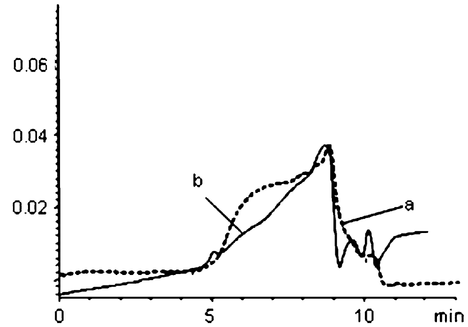


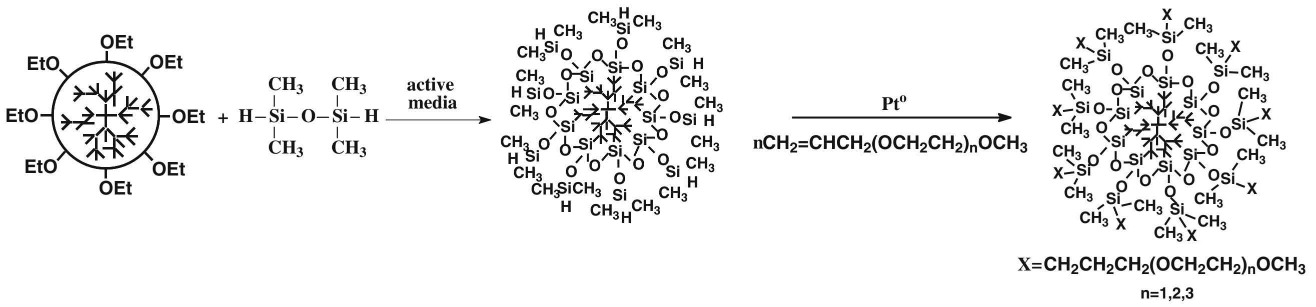
Fig. 1 GPC- curves of initial HPEOS (*a*) and dimethylhydride derivative of molecular silicasol (*b*)

Figure 4 shows GPC-curves of di(ethylene oxide) derivative of molecular silicasol, which was fractionated by means of preparative GPC. Two fractions, low-molecular (7% yield, Fig. 4b) and high-molecular (60% yield, Fig. 4c) were isolated. Tri(ethylene oxide) derivative was precipitated from water–alcohol solution into water. Two fractions were isolated: low-molecular ($\sim$80% yield, Fig. 5b) and high-molecular (12% yield, Fig. 5c).

After fractionation all investigated samples were transparent colorless viscous liquids. Molecular masses and hydrodynamic radii of the particles obtained were determined by means of GPC using universal calibration method, proposed for systems with complicated molecular structure [28]. Some characteristics of low- and high-molecular fractions of di- and tri(ethylene oxide) derivatives of molecular silicasols obtained from HPEOS are summarized in Table 1.

3.1.2 Synthesis of Hybrid Molecular Particles with Ethylene Oxide Surface Layer from Molecular Silicasol

Modification scheme for molecular silicasol is shown below (Scheme 2). Chemical operation consisted in



Scheme 1 Synthesis of hybrid molecular particles with mono-, di-, and tri(ethylene oxide) surface layer

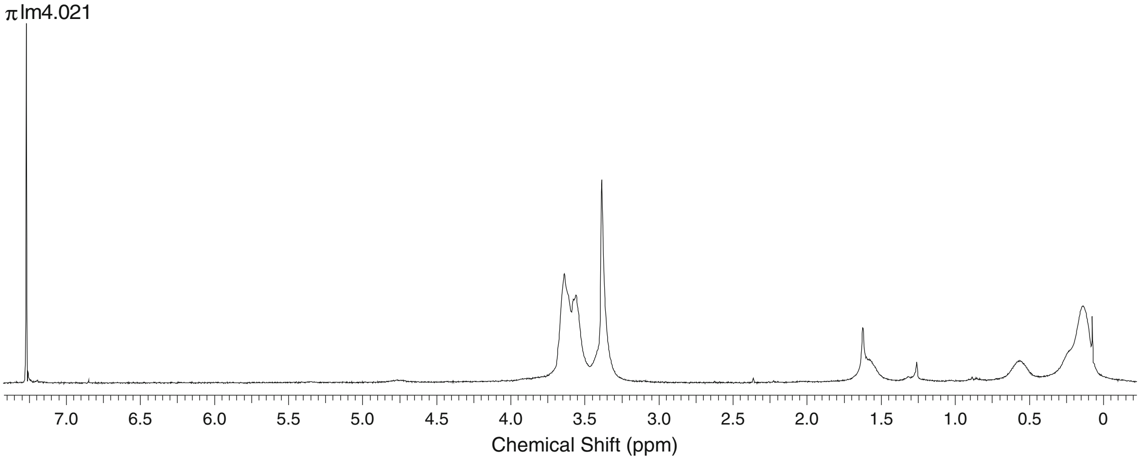


Fig. 2 ^{1}H NMR ($CDCl_3$) spectrum of molecular silicasol with ethylene oxide surface layer

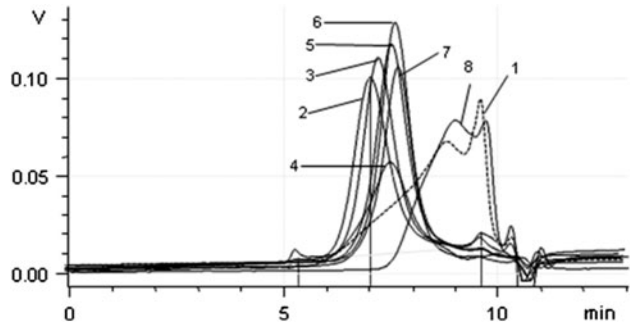


Fig. 3 GPC-curves of molecular silicasol modified with mono (ethylene oxide) derivative (*1*) and its fractions: (*2*) MM = 70000, (*3*) MM = 40000, (*4*) MM = 37000, (*5*) MM = 32000, (*6*) MM=25000, (*7*) MM = 24000, (*8*) residual product from mother solution

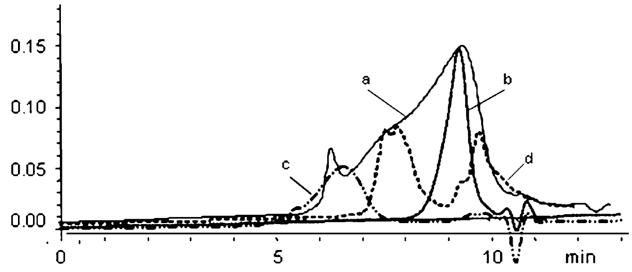


Fig. 4 GPC-curves of di(ethylene oxide) derivative of molecular silicasol (*a*) and its fractions: (*b*) low-molecular fraction, (*c*) high-molecular fraction, (*d*) intermediate fraction

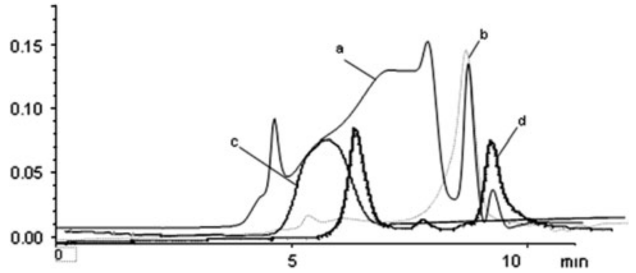


Fig. 5 GPC-curves of tri(ethylene oxide) derivative of molecular silicasol (*a*) and its fractions: (*b*) low-molecular fraction, (*c*) high-molecular fraction, (*d*) intermediate fraction

refluxing of acetoxy derivatives of methyl ethers of di- and triethylene glycols with 4.2% solution of molecular silicasol in THF for 8 h.

Condensation was carried out in acetic acid with catalytic quantity of acetyl chloride added. Molar ratio of modifying agent to OH-groups of silicasol was 3:1. Efficiency of blocking reaction was controlled by sampling and samples analysis by means of IR and ^{1}H NMR spectroscopy. Ratio of the intensity of proton signals of functional groups and chemical shifts of corresponding protons were in good agreement with the calculated values. As an example ^{1}H NMR spectrum of molecular silicasol with methoxy diethylene oxide propyl dimethyl silyl groups in outer layer is shown on Fig. 6.

IR spectra of modified products contain absorption bands between 3400 and 3600 cm^{-1}, corresponding to valence vibrations of OH-groups, that indicates incomplete blocking process. However the low intensity of absorption in this area, as well as the stability of the products upon storage qualitatively argues for a rather high conversion of modification process.

Fractionation of obtained products conducted by precipitation from toluene solution into hexane gave quite narrow fractions of corresponding di- and tri(ethylene oxide) derivatives. GPC curves of some fractions and initial tri(ethylene oxide) derivative are presented in Fig. 7.

Table 1 Modified molecular silica nanoparticles

Modified silica nanoparticles	Initial molecular nanoparticles	Modifying agent	MM of the fractions, (GPC)[a]	Yield[b], %	$[\eta]^{25}$, dL/g	R_h, nm	Ratio Si_{core}/Si_{shell}
Mono(ethylene oxide) derivatives	HPEOS	Ethylene glycol allyl methyl ether	70000	79			
			40000				
			37000				
			32000				
			25000				
			24000				
Di(ethylene oxide) derivatives	HPEOS	Di(ethylene glycol) allyl methyl ether	500000	58	0.05	2.36(GPC)	2.14
			1100		0.03	0.77(GPC)	0.39
	Molecular silicasols	4,7,10-trioxyundecyldimethylacetoxysilane	10500	76			
			1800				
	TEOS	4,7,10-trioxyundecyldimethylacetoxysilane	2700	61	0.02	0.99(GPC)	0.82
Tri(ethylene oxide) derivatives	HPEOS	Tri(ethylene glycol) allyl methyl ether	500000	58	0.05	2.79(GPC)	2.05
			1100		0.03	0.78(GPC)	0.96
	Molecular silicasols	4,7,10,13-tetraoxytetradecyldimethylacetoxysilane	25000	27			
			16000				
			10500				
	TEOS	4,7,10,13-tetraoxytetradecyldimethylacetoxysilan	3200	30	0.03	1.12(GPC)	0.82
			2200		0.02	0.94(GPC)	0.74
Acetoxy derivatives	Molecular silicasols	(Acetoxymethyl)dimethylacetoxysilane	75000-28000	58			2.14
			22000				
			16000		0.03	1.98(GPC)	1.90
			10000				
			7000		0.03	1.46(GPC)	1.66
			5500				
			3400				
			3200		0.02	1.01(GPC)	0.74
(Methoxyacetyl) oxy derivatives	Molecular silicasols	Bis[(methoxyacetyl)oxy]tetramethyl disiloxane	12000	89	0.04	2.04(η) 2.62(GPC)	0.48
			4700				
			2400		0.03	1.02(η) 0.97(GPC)	0.68

[a] MM was determined at the maximum of the peaks

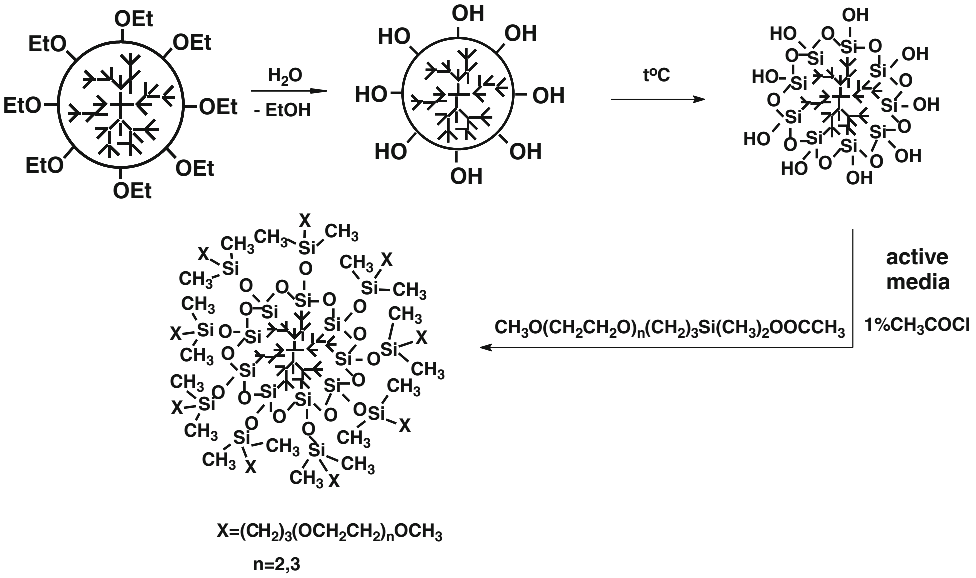
[b] Yield before fractionation

3.1.3 Synthesis of Hybrid Molecular Particles with Ethylene Oxide Surface Layer from TEOS

Another option of obtaining molecular silica systems with di- and tri(ethylene oxide) shell was synthesis of silica particles through hydrolytic polycondensation of TEOS in active media and their modification with acetoxy silyl derivatives of methyl ethers of di- and triethylene glycols (Scheme 3).

It is known that hydrolysis of TEOS in acetic acid and water media gives silica which has the density close to that of crystalline SiO_2 [28]. This way of producing dense silica was further improved in following ways: (1) removal of water from reagents list turned acetic acid from solvent into active media (according to "active media" concept water is generated in interaction of alkoxysilanes with acetic acid [30]). (2) at the particular stage of the reaction hexamethyldisiloxane as a precursor of blocking agent along with catalytic quantities of acetyl chloride was introduced into the system. This method, described in detail in work [30], is based on the idea that blocking of functional groups at different phases of growth allows one to govern molecular mass and size of the particles produced.

Scheme 2 Modification of molecular silicasols with acetoxy derivatives of methyl ethers of di- and triethylene glycols



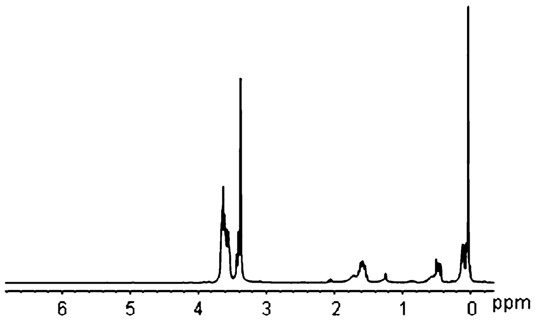


Fig. 6 ^{1}H-NMR spectrum of di(ethylene oxide) derivative of molecular silicasol

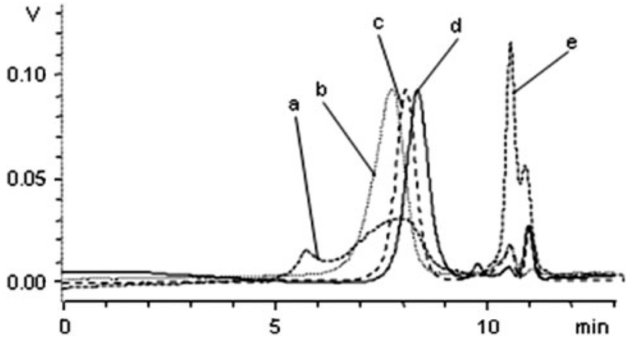


Fig. 7 GPC-curves of tri(ethylene oxide) derivative of molecular silicasol (*a*) and its fractions: (*b*) MM = 25000, (*c*) MM = 16000; (*d*) MM = 10500; (*e*) MM = 1000

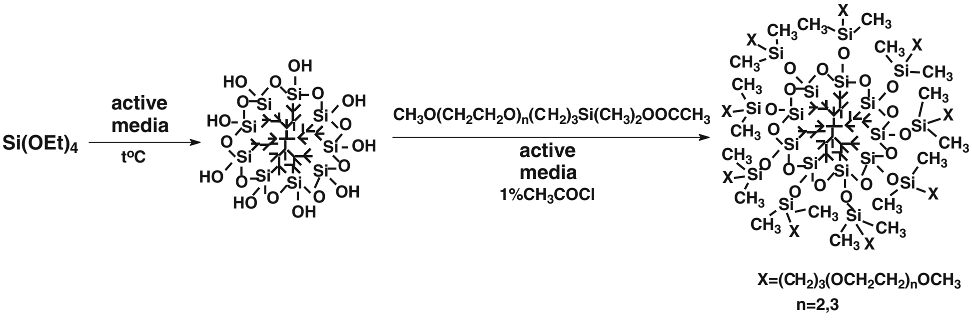
Here blocking stage of the known scheme was modified as shown in Scheme 3: acetoxy(dimethyl)propyl derivatives of methyl ethers of di- and triethylene glycols were used as blocking agents. Preliminary investigation showed that depending on reaction time physical properties of obtained products differ significantly. For the condensation time below 13 h the product was liquid, from 13 till 18.5 h—gum-like amorphous substance, and from 18.5 till 22.5 h—crystal-like solid powders. Comparison of GPC curves of different samples demonstrates that elution time shifts to low values indicating increase of size and molecular mass of obtained particles with increase of the reaction time.

Because low-molecular silica particles have better compatibility with polymer matrix, while used as nanofillers for polymer composites, experimental conditions which allow obtaining low-molecular silica particles were selected for further investigation.

Synthesis of modified molecular silica particles was conducted at 80 °C. First stage of the process is condensation of TEOS in acetic acid by refluxing of the mixture for 10 h. It was followed by modification of molecular silicasol obtained at first stage with fourfold excess of acetoxy derivatives of corresponding ethers and catalytic amount of acetyl chloride. Modification lasted 12 h. Completeness of the condensation and blocking reactions was determined from ^{1}H NMR spectra data, comparing integral intensities of signals of trimethylsilyl and ethoxyl protons at silicon (Fig. 8). Typical IR spectrum of obtained product is shown on Fig. 9. Molecular silicasols had yield 78% and 85% in case of di- and triethylene oxide derivatives respectively.

Fractionation of the hybrid systems obtained was done by means of preparative GPC. Besides target fractions one low-molecular fraction was isolated, which was identified (from ^{1}H NMR data) as bis(2,4,7-trioxaundecyldimethyl)disiloxane—the product of interaction between blocking agent

Scheme 3 Synthesis of hybrid systems by condensation in active media



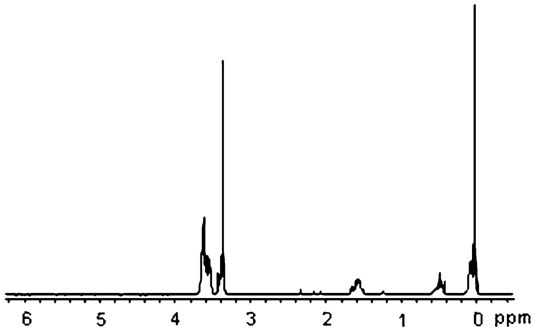


Fig. 8 ^{1}H-NMR ($CDCl_3$) spectrum of di(ethylene oxide) derivative of molecular silicasol

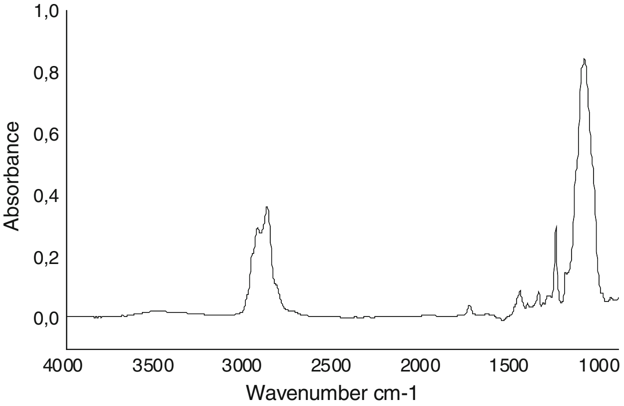


Fig. 9 IR spectrum of di(ethylene oxide) derivative of molecular silicasol

molecules. Based on the material balance blocking degrees of molecular silica particles with 2,4,7-trioxa undecyl dimethyl acetoxysilane and 2,4,7,11-tetraoxa tetradecyl acetoxysilane were 85 and 88% respectively. That is higher than blocking degrees of molecular silicasols obtained by hydrolytic polycondensation of HPEOS. This was confirmed also by ^{1}H NMR data: according to NMR spectrum presented on Fig. 10 content of residual ethoxy groups in modified silicasols does not exceed 10%.

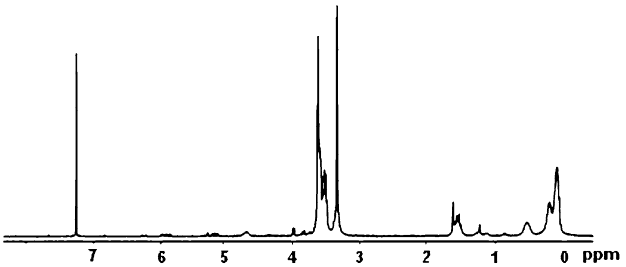


Fig. 10 ^{1}H-NMR spectrum of tri(ethylene oxide) derivative of molecular silicasol

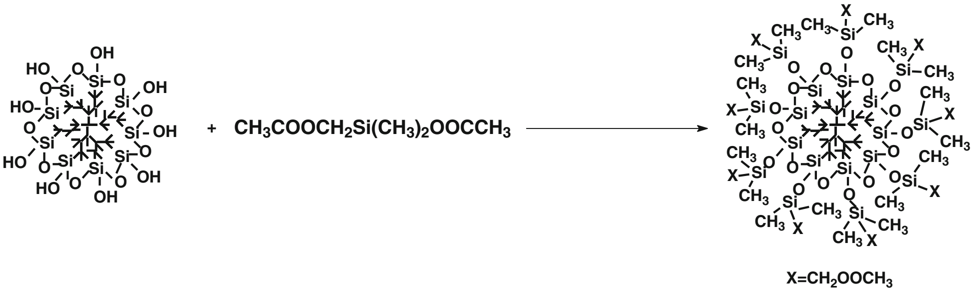
3.2 Synthesis of Molecular Silica Systems Modified with Acetoxy(Dimethyl)Silyl Methyl Ether of Acetic Acid

Target compounds were obtained from molecular silicasols in the similar way as described in Sect. 3.1.2 (Scheme 4).

Reaction was conducted in THF, it was controlled through sampling and investigation of the samples by IR and 1H NMR spectroscopies. For IR spectra reduction of the intensity of absorption between 3400 and 3600 cm^{-1} corresponding to valence vibrations of OH-groups was observed. Reaction was carried on till there were no changes in IR spectra of the samples. Yield of the product was 58%, its IR-spectra still had the absorption bands between 3400 and 3600 cm^{-1} indicating incomplete blocking process. Most probably this is due to steric factors that influence reaction progress under these conditions.

Figure 11 presents GPC curve of molecular silicasol with ester groups in outer layer. Rate of the curve indicates broad molecular-mass distribution of molecular silicasol with ester groups in outer layer.

The reason for certain increase in polydispersity of this product versus polydispersity of initial silicasol is possible intermolecular interaction between silicasol molecules during the modification process. At the same time absence of gelation for this highly functional system indicates that number of intermolecular side-reactions during blocking



Scheme 4 Synthesis of hybrid systems with ester groups in outer layer

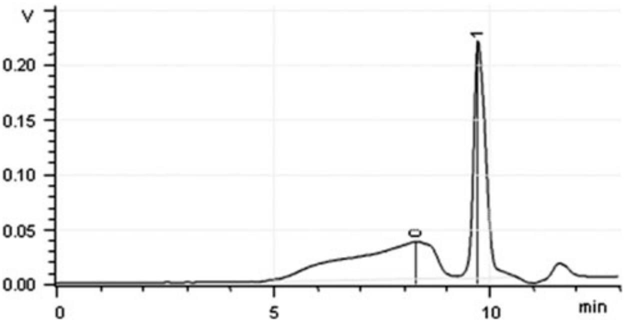


Fig. 11 GPC-curve of molecular silicasol with ester groups in outer layer

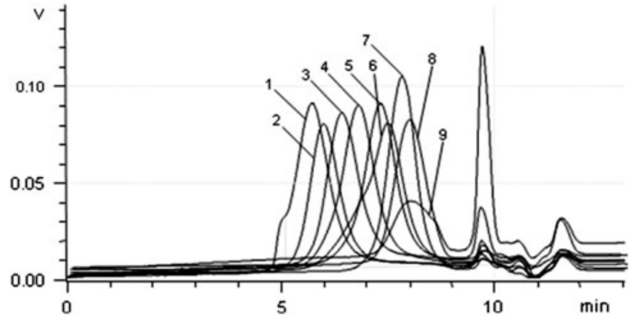
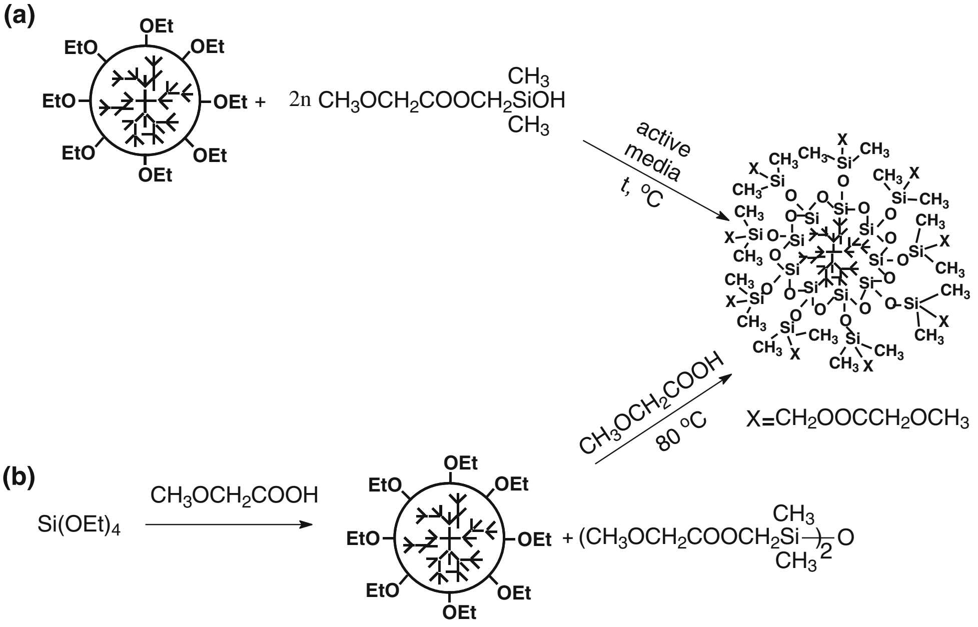


Fig. 12 GPC-curves of obtained fractions of molecular silicasol with ester groups in outer layer: (*1*) MM = 75000–28000, (*2*) MM = 22000, (*3*) MM = 16000, (*4*) MM = 10000, (*5*) MM = 7000; (*6*) MM = 5500, (*7*) MM = 4000, (*8*) MM = 3400, (*9*) MM = 3200

process is low. Though broadening of molecular mass distribution is indeed undesired, it allowed us to obtain multiple fractions by precipitation from THF solution into hexane. GPC curves of nine fractions obtained are presented in Fig. 12.

Fractions obtained were hard white powders (fractions 1–6), transparent gum-like substance (fraction 7) or viscous liquids, containing significant amount of corresponding disiloxane (fractions 8–9).



Scheme 5 Synthesis of hybrid silica particles with 2,5-dioxa-3-on-hexy(dimethyl)silyl groups in outer layer

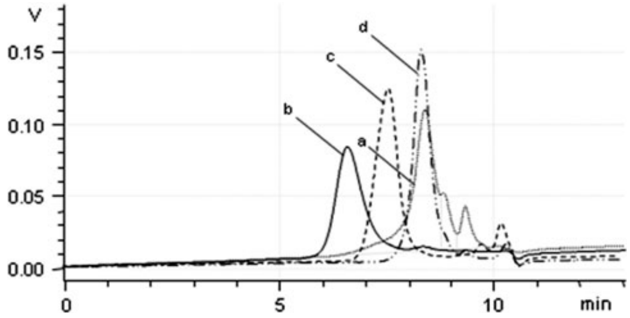


Fig. 13 GPC-curves of molecular silicasol with methoxyacetoxy ester groups in outer layer (*a*) and its fractions: (*b*) MM = 12000, (*c*) MM = 4700, (*d*) MM = 2400

3.3 Synthesis of Molecular Silica Systems Modified with Functional Silane Containing Methoxyacetic Acid Groups as a Part of Organic Substituents

Further complication of the structure of ester group in modifier required appropriate follow-up in modifying reagents synthesis. Upon synthesis of methoxyacetic acid ester of silyl-substituted methanol isolation of target silanol failed, because of its aptitude for homocondensation. Result of the synthesis was always a mixture of silanol and the product of its condensation—1,3-bis-(2,5-dioxa-3-on-hexyl)tetramethyldisiloxane. Content of 2,5-dioxa-3-on-hexyl(dimethyl)silanol in the sample after vacuum distillation was 42% according to GLC data. That is why two schemes were used to obtain hybrid derivative (Scheme 5).

In the first variant hydrolytic condensation of HPEOS (MM ~ 3000) with the mixture of silanol and disiloxane was carried out in acetic acid at reflux for 12 h (Scheme 5a). Target product was isolated by precipitation, but had very low yield (17%) and broad molecular mass distribution as was indicated by GPC. In this connection synthetic scheme was improved in following way (Scheme 5b): hydrolytic polycondensation of TEOS in acetic acid analogous to one described in Sect. 3.1.3 was chosen as a basis for synthesis of silica core. On the one hand this option provides production of densest silica particles and on the other hand it is closest to the option of carrying out blocking processes in active media [31]. To avoid possible interesterification processes with acetic acid, polycondensation of TEOS was conducted in methoxyacetic acid at 40 °C for 1 h followed by blocking reaction with bis-(methoxyacetoxymethyl)tetramethyldisiloxane at 80 °C for 6 h. Yield of modified polymer was 87%, it was viscous liquid. Polymer was fractionated (and disiloxane removed) by precipitation from THF solution into hexane (high-molecular fraction) and by preparative GPC (intermediate and low-molecular fractions). GPC curves of the polymer and its fractions are presented on Fig. 13.

Figure 14 represents ^{1}H-NMR spectrum of obtained polymer.

4 Conclusions

Among different characteristics of hybrid particles summarized in Table 1, one should first of all give attention to viscosity data. Viscosity values for almost all particles indicate that these hybrid systems behave in a similar way as model systems thoroughly investigated in work [31]. This means that their behavior can be described in terms of a “molecule-particle” model, though for a more specific attribution, especially for fractionated samples, detailed thermomechanical investigations are required.

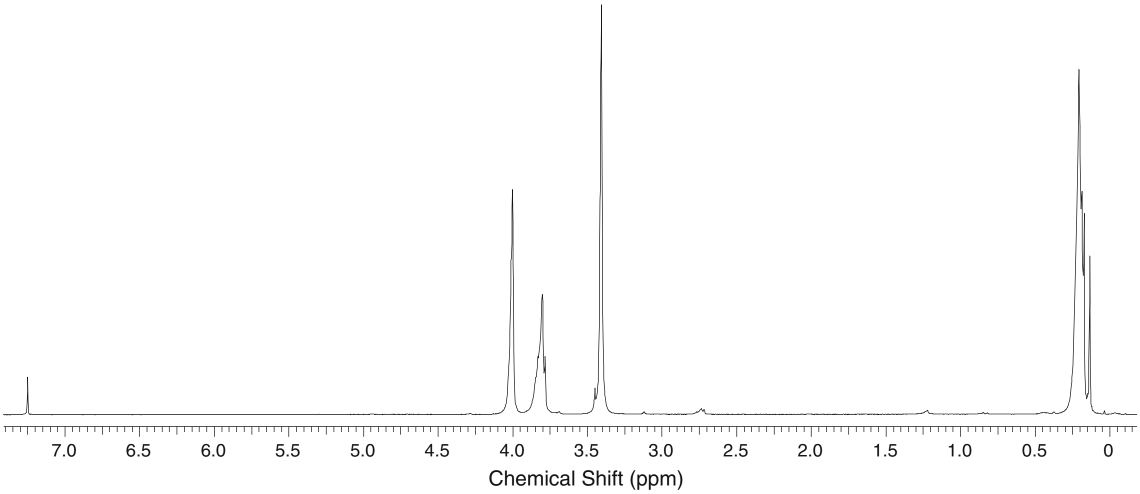


Fig. 14 ^{1}H-NMR spectrum of molecular silicasol with methoxyacetoxy ester groups in outer layer

Fractionated samples are ready-made models for investigations of interactions in their compositions with different polymer matrixes from PEO and PMMA to PLA, PVAc and other polar polymer systems.

Comparing different options for synthesis of hybrid particles allowed us to conclude that the third method, based on polycondensation of TEOS in active media with further blocking of particle growth and simultaneous formation of outer layer, is the most universal and simple. However, another two methods are also valuable, especially when there are some limitations in choosing functional groups of modifier.

The results presented are only part of the basis for comprehensive research on polymer–nanoparticle interactions for wide selection of polymer matrixes. Further plans include investigating the obtained object by means of X-Ray scattering and thermomechanical analysis, as well as synthesis of new hybrid particles with functional shell using described approach.

Acknowledgments This work was supported by Russian Foundation for Basic Research (grant 11-03-01083-a).

References

1. C.-C. Sun, J.E. Mark, Polymer **30**, 103–106 (1989)
2. J.E. Mark, Polym. Eng. Sci. **36**, 2905 (1996)
3. J.E. Mark, P.D. Calvert, J. Mats. Sci. C **1**, 159 (1994)
4. D.W. McCarthy, J.E. Mark, D.W. Schaefer, J. Polym. Sci., Polym. Phys. Ed. **36**, 1167 (1998)
5. D.W. McCarthy, J.E. Mark, S.J. Clarson, D.W. Schaefer, J. Polym. Sci., Polym. Phys. Ed. **36**, 1191 (1998)
6. K.J. Klabunde, J. Habdas, G. Cardenas-Trivino, Chem. Mater. **5**, 481–483 (1989)
7. Y.-Q. Hua, Y.-Q. Zhang, L.-B. Wu, Y.-Q. Huang, G.-Q. Wang, J. Macromol. Sci. B Phys. **44**, 149–159 (2005)
8. E.D. Schukin, A.V. Pertsov, E.A. Amelina, *Kolloidnaya khimiya* (Vysshaya shkola, Moscow, 2004), pp. 295–296
9. Y.K. Takahara, S. Ikeda, S. Ishino, K. Tachi, K. Ikeue, T. Sakata, T. Hasegawa, H. Mori, M. Matsumura, B. Ohtani, J. Am. Chem. Soc. **127**, 6272–6275 (2005)
10. S.-W. Zhang, S.-X. Zhou, Y.-M. Weng, L.-M. Wu, Langmuir **21**, 2124–2128 (2005)
11. V. Monteil, J. Stumbaum, R. Thomann, S. Mecking, Macromolecules **39**, 2056–2062 (2006)
12. Y. Yang, Y. Dan, Colloid Polym. Sci. **281**, 794–799 (2003)
13. I. Sondi, T.H. Fedynyshyn, R. Sinta, E. Matijevic, Langmuir **16**, 9031–9034 (2000)
14. E.V. Getmanova, A.S. Tereshchenko, G.M. Ignat′eva, E.A. Tatarinova, V.D. Myakushev, A.M. Muzafarov, Rus. Chem. Bull., Int. Ed. **53**(1), 137 (2004)
15. A.V. Bystrova, E. Parshina, E.A. Tatarinova, M.I. Busin, L.A. Ozerina, A.N. Ozerin, A.M. Muzafarov, Nanotechnol. Russ. **2**(1–2), 83–89 (2007)
16. N.A. Shumilkina, V.D. Myakouchev, E.A. Tatarinova, M.O. Gallaymov, A.P. Khokhlov, M.I. Busin, A.M. Muzafarov, Doklady Chem. **403**(2), 159 (2005)
17. J.M.J. Frechet, D.A. Tomalia, *Dendrimers and other dendritic polymers* (Wiley, New York, 2001)
18. R.K. Iler, *The chemistry of silica* (Wiley, New York, 1979)
19. W. Stober, A. Fink, E. Bohn, J. Colloid Interface Sci. **26**, 62–69 (1968)
20. V.A. Blaaderen, V.J. Geest, A.J. Vrij, J. Colloid Interface Sci. **154**, 481–501 (1992)
21. T.E. von Werne, G. Patten, J. Am. Chem. Soc. **121**, 7409–7410 (1999)
22. K. Bridger, B. Vincent, Eur. Polym. J. **16**, 1017–1021 (1980)
23. J. Buitenhuis, Z. Zhang, Scientific Report (2004/2005)
24. Y. Shen, S. Zhu, R. Pelton, Macromolecules **34**, 5812–5818 (2001)
25. H. Sertchook, D. Avnir, Chem. Mater. **15**, 1690–1694 (2003)
26. X.M. Sang, X.J. Yang, Z.D. Cui, S.L. Zhu, J. Sheng, J. Macromol. Sci. B Phys. **44**, 237–248 (2005)
27. V.V. Kazakova, E.A Rebrov, V.D. Myakushev, T.V. Strelkova, A.N. Ozerin, L.A. Ozerina, T.B. Chenskaya, S.S. Sheiko, E.Yu. Sharipov, A.M. Muzafarov, ACS Symposium Book Series 729, **34**, pp. 503–513 (2000)
28. N.V. Voronina, I.B. Meshkov, V.D. Myakouchev, N.V. Demchenko, T.V. Laptinskaya, A.M. Muzafarov, Nanotechnol. Russ. **3**(5–6), 321–329 (2008)
29. I.B. Meshkov, V.V. Kazakova, O.B. Gorbatcevich, N.V. Voronina, V.D. Myakouchev, A.M. Muzafarov, Polym. Prep. **47**(2), 1152 (2006)
30. E.V. Egorova, N.G. Vasilenko, N.V. Demchenko, E.A. Tatarinova, A.M. Muzafarov, Doklady Chem. **424**(1), 15–18 (2009)
31. N.V. Voronina, I.B. Meshkov, V.D. Myakushev, T.V. Laptinskaya, V.S. Papkov, M.I. Buzin, M.N. Il'ina, A.N. Ozerin, A.M. Muzafarov, J. Polym. Sci. **48**, 4310–4322 (2010)