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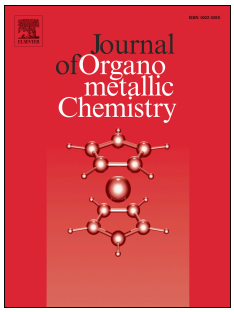

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Sodiumoxy(aminopropyl)alkoxysilanes - AB2 type monomers for the synthesis of hyperbranched poly(aminopropyl)alkoxysiloxanes and their derivatives

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Abstract

Based on commercially available aminopropyltrialkoxysilanes, new monosodium salts of organoalkoxysilanes (sodiumoxoaminopropyldialkoxysilanes) with two types of chemically independent functional -ONa and -OAlk groups at the silicon atom were synthesized and characterized. The sodiumoxoaminopropyldialkoxysilanes obtained can be regarded as AB_2-type monomers - promising reagents for providing controlled polycondensation and production of functional organosilicon polymers with controlled molecular architectures. Subsequently, polyaminopropylsiloxanes with hyperbranched molecular architectures were obtained by heterofunctional polycondensation of the corresponding AB_2-type monosodiumoxoorganodialkoxysilanes. The structures synthesized were characterized using ^{29}Si NMR, ^{1}H NMR, GPC and elemental analyses. The hyperbranched polymer matrices obtained containing aminopropyl organic radicals showed the ability to stabilize silver nanoparticles.

Keywords

Aminopropyltrialkoxysilane; Sodiumoxoaminopropyldialkoxysilane; Hyperbranched, Heterofunctional polycondensation; AB_2-type monomer.

1. Introduction

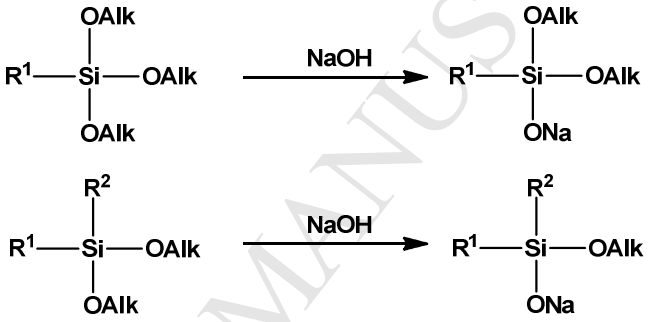
The majority of methods for the synthesis of polysiloxane compounds provide a statistical distribution of products, both in structure and composition. Therefore, from the perspective of the basic "structure-properties" relationship paradigm in polymer chemistry, the development of selective methods that allow the molecular structures of the polymers formed to be controlled is a very important task. The following synthetic approaches that allow synthesizing siloxane polymers with controlled structures can be noted: non-equilibrium polymerization [1], heterofunctional condensation reactions [2, 3], exchange decomposition reactions [4] and the Pierce-Rubinstein reaction [5] which has become very popular and has led to the synthesis of a significant number of well-defined structures. Furthermore, the use of monosodium salts of alkoxysilanes (sodiumoxyalkoxysilanes) also known as Rebrov salts became one of the simplest versatile ways to obtain siloxane structures with controlled molecular architecture [6]. Over the past quarter century, many such siloxane structures have been synthesized with the use of monosodiumoxoalkoxysilanes [7]. The other compounds that should be mentioned include branched oligosiloxanes and polyorganosiloxanedendrimers [8],

hyperbranchedpolyethoxysiloxanes [2, 3], linear polyorganosilsesquioxanes [9], as well as unique forms of polyorganosilsesquioxanes [10].

The known methods for the preparation of monosodiumoxoalkoxysilanes include the synthesis from the corresponding alkoxysilanes in reactions with alkali metals [11]. The multistage nature of this process due to the need for isolation of the corresponding organoalkoxysilanol, as well as the usage of unstable alkali metals in these reactions make this method ineffective.

A much more facile one-step process for the production of monosodiumoxyalkoxysilanes is to synthesize them from the corresponding alkoxysilanes in reactions with alkali metal hydroxides (Fig. 1), [12, 13].

A method for synthesizing a number of monosodiumoxoorganoalkoxysilanes (Fig. 1) based on a direct reaction of organoalkoxysilanes with sodium hydroxide was studied in detail and optimized [6, 14].

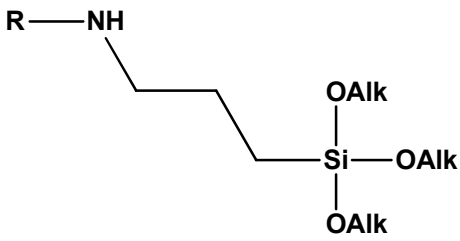


$R^{1,2}$ = -CH_3, -$CH{=}CH_2$; -C_6H_5; Alk = -CH3, -CH_2CH_3) -$CH(CH_3)_2$, -$CH_2(CH_2)_2CH_3$

Figure 1. Sodiumoxyorganoalkoxysilanes obtained in [6].

In fact, methods for the preparation of various sodiumoxoorganodialkoxysilanes have been developed based on a number of organotrialkoxysilanes [6] (Fig. 1). Within the framework of the Flory theory [15], sodiumoxoorganodialkoxysilanes can be considered as AB_2-type monomers that are promising reagents for controlled polycondensation and production of polymers with controlled molecular architecture.

In turn, there are no studies on the characterization and preparation of monosodium salts based on commercially available aminopropyltrialkoxysilanes (Fig. 2).



R = -H, -$CH_2CH_2NH_2$; Alk = -CH3, -CH_2CH_3

Figure 2. Commercially available aminopropylalkoxysilanes.

In view of the fact that, due to the high coordination ability of the amino groups, amino-containing polymer matrices are widely used in the development of agents for metal ion coordination and stabilization of metal nanoparticles [16], adsorption of inorganic nanoparticles [17], encapsulating agents for the transport of drug substances [18], and taking into consideration the widespread use of aminopropylalkoxysilanes and aminopropyl-containing polysiloxanes as binders and hardeners [19] in the manufacture of copolymeric materials [20], special purpose coatings [21], water-soluble organosilicon systems [22], etc., the development and creation of a new class of amino-containing organosilicon monomer and polymer structures are promising tasks.

Thus, the purpose of this work was to expand the range of monosodium organoalkoxysilane salts by development of synthetic methods for the production of new monosodium salts and evaluation of the prospects of these compounds in the creation of new amino-containing polyorganosiloxane structures with controlled molecular architecture.

In this work, commercially available aminopropyltrialkoxysilanes were employed to prepare new mono-sodium salts of organoalkoxysilanes. Based on the latter, the corresponding polyaminopropylsiloxanes with controlled hyperbranched structures were then synthesized. The polymer matrices thus obtained were then used for the production and stabilization of metallic silver nanoparticles.

2. Experimental section

2.1 Materials

Starting reagents were purchased from Acros or Aldrich. All solvents were of reagent grade and dried and distilled before use according to standard procedures.

2.2 Methods

NMR spectra in solutions were acquired using a Bruker Avance AV-300 spectrometer (300 MHz for ^{1}H; 77.5 MHz for ^{13}C; 59.6 MHz for ^{29}Si). Chemical shifts are reported in ppm and referred to the residual non deuterated solvent frequencies (δ = 7.25 ppm) for ^{1}H NMR; deuterated chloroform (δ = 77.00 ppm) for ^{13}C NMR; tetramethylsilane (δ = 0.00 ppm) for ^{29}Si NMR; ammonia (δ = 0.00 ppm) for ^{15}N NMR, sodium chloride (δ = 0.00 ppm) for ^{23}Na NMR.

High resolution mass spectra were measured with a Bruker Microtof II instrument with electrospray ionization (ESI) (Germany)

GLC analysis was performed on a Chromatech Analyst-5000 chromatograph (Russia) with a catharometer detector, helium as the carrier gas, and a 2 m x 3 mm column. The stationary phase SE-30 (5%) was applied on Chromaton-H-AW.

GPC analysis was conducted in a chromatographic system consisting of a STAYER series II high-pressure pump (Aquilon, Russia), a RIDK 102 refractive index detector (Czech Republic), and a

JETSTREAM 2 PLUS column oven (KNAUER, Germany). The thermostating temperature was 40 °C (+ / -0.1 °C). Toluene was used as the eluent, and the flow rate was 1.0 ml/min. A 300 x 7.8 mm column was filled with Phenogel sorbent (Phenomenex, USA) with a particle size of 5 µm and a pore size of 10^3 Å (passport range separation of up to 75,000 D). Recording and data counting were performed using a Multichrom 1.6 GPC program (Ampesand, Russia). Calibration of GPC data was conducted by the Polysterene Standard Calibration Kit for Liphophilic GPC (E. Merck, Darmstadt, F.R. Germany).

Ultraviolet absorption (UV) spectra of the samples (in methanol and acetonitrile solutions, in cells with 1 cm light path) were recorded using a Shimadzu UV 2501 PC spectrophotometer.
DLS measurements for particle sizing were conducted with a Zetatrac dynamic light scattering spectrometer (Microtrac, USA) using Microtrac V 10.5.3 software.

TEM analysis was provided with a JEM-1011 Transmission Electron Microscope (JEOL Ltd., Japan) equipped with a Gatan Erlangshen ES500W digital camera, using Digatal Micrograph v.3 software (Gatan) for the camera control and image processing.

2.3 Synthetic procedures

2.3.1 Trialkylsilanols

2.3.1.1 Synthesis of trimethylsilanol

200 ml of 0.1 M HCl solution was slowly added (in 1 hour) to hexamethyldisilazane (0.683 mol) with stirring. The mixture was stirred at room temperature for 1 hour. GLC data showed the absence of initial hexamethyldisilazane. The resulting solution was washed from the excess of HCl acid and then dried with $CaCl_2$. According to GLC data, the yield of the target compound was 95 %.

2.3.1.2 Synthesis of vinyldimethylsilanol

Vinyldimethylchlorosilane (0.221 mol) was slowly added (in 1 hour) to a two-phase system consisting of $(NH_4)_2CO_3$ (0.132 mol) aqueous solution (100 ml) and diethyl ether (100 ml). The mixture was stirred at room temperature for 3 hours. The resulting solution was extracted 3 times with 75 ml of diethyl ether and the combined extracts were washed with a saturated aqueous NaCl solution and then dried with $CaCl_2$. Diethyl ether was evaporated. According to GLC data, the yield of the target compound was 60 %.

2.3.2 Monosodium salts of aminopropylalkoxysilanes

2.3.2.1 Synthesis of monosodium salts of aminopropylalkoxysilanes

The typical procedure for the preparation of monosodium salts from the corresponding aminopropylalkoxysilanes is shown in Scheme 1.

A mixture of the corresponding aminopropyltrialkoxysilane (0.05 mol)) and sodium hydroxide (0.05 mol) was stirred in boiling THF (40 ml) for 20 min under argon. After cooling, the resulting solution was evaporated under reduced pressure and vacuumed at 1 mBar for 30 min at 50 °C. Products were obtained as colorless liquids in quantitative yields.

(*Product characterization for this and other reactions is given in supporting information*).

2.3.2.2 Termination of monosodium salts of aminopropylalkoxysilanes with trimethylchlorosilane

The procedure for the termination of the corresponding sodiumoxoaminopropylalkoxysilanes is described in Scheme 2.

Trimethylchlorosilane (0.022 mol) in dry THF (5 ml) was added to a solution of the corresponding sodiumoxoaminopropyldialkoxysilanes (0.022 mol) and pyridine (0.024 mol) in dry THF (15 ml) at –30 ° C. The mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure, and the mixture was diluted with dry hexane and filtered. Hexane was removed under reduced pressure, and the product was distilled under vacuum (1 mBar). The product was obtained as colorless liquid in 80-90% yield.

2.3.3 Hyperbranched polyaminopropylalkoxysiloxanes

2.3.3.1 Synthesis of hyperbranched polyaminopropylalkoxysiloxanes

The typical procedure for the preparation of hyperbranched aminopropylalkoxysiloxanes is presented in Scheme 4.

To a solution of the corresponding sodiumoxoaminopropylalkoxysilane obtained previously (0.022 mol) with additionally 20 ml toluene, an equimolar amount of acetic acid (0.022 mol) was rapidly added at room temperature. The solution was left overnight with stirring. Next day, the resulting solution was centrifuged, decanted from the precipitate, evaporated under reduced pressure and vacuumed at 1 mBar for 2 hours at 50 °C. The products were obtained as colorless viscous liquids in quantitative yields.

2.3.3.2 Termination of amino groups in hyperbranched polyaminopropylalkoxysiloxanes with phenyl isocyanate

The procedure for the termination hyperbranched polyaminopropylalkoxysiloxanes amino groups is given in Scheme 6.

To the corresponding hyperbranched polyaminopropylalkoxysiloxane (2.3 mmol) dissolved in a mixture of 10 ml THF and 5 ml toluene, phenyl isocyanate (2.4 mmol in the case of polyaminopropylethoxysiloxane or 4.7 mmol in the case of polyethylenediaminopropylmethoxysiloxane) was added under argon at room temperature. The solution was left overnight with stirring. Next day, the solvent was evaporated under reduced pressure and the product was vacuumed at 1 mBar for 2 hours at 50 °C. The products were obtained as white powders in quantitative yields.

2.3.3.3 Termination of hyperbranched polyaminopropylalkoxysiloxanes with trimethylchlorosilane and vinyldimethylchlorosilanes

The procedures for the termination of the corresponding hyperbranched polyaminopropylalkoxysiloxane is shown in Schemes 7 and 8.

To the corresponding hyperbranched polyaminopropylalkoxysiloxane (0.017 mol) dissolved in 15 ml toluene, a solution of trimethylsilanol (0.0253 mol) or vinyldimethylsilanol (0.0253 mol) in toluene (15 ml), or a mixture of trimethylsilanol (0.0101 mol) and vinyldimethylsilanol (0.0152) was added in 30 min. The solution was left overnight with stirring. Next day, the solvent was evaporated under reduced pressure and the product was vacuumed at 1 mBar during 1 hour at 50 °C. The products were obtained as colorless viscous liquids in quantitative yields.

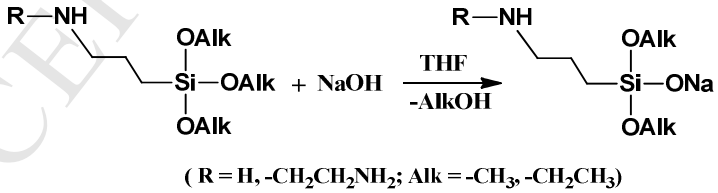
2.3.3.4 Synthesis and stabilization of Ag nanoparticles with hyperbranched polyaminopropyl-siloxane matrices

To a solution of the corresponding hyperbranched polyaminopropylsioxane (3.3 mmol) or aminopropyltrialkoxysilane (3.3 mmol) in 40 ml CH_3OH or CH_3CN, $AgBF_4$ (1.1 mmol) was added. Three flasks with the reaction mixture were stirred both in the light and in the dark for 3 days and irradiated for 30 min with a 125 watt mercury UV lamp. After that, the solvent was evaporated and the product was vacuumed at 1 mBar. The products were obtained as brown or dark orange gels in quantitative yields.

3. Results and Discussion

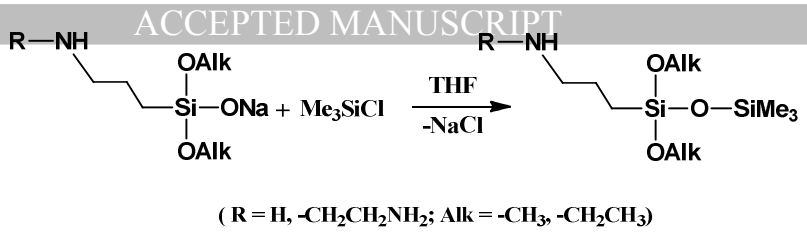
3.1 Monosodium salts of aminopropylalkoxysilanes

Monosodium salts of aminopropylalkoxysilanes were synthesized by providing a reaction between the corresponding aminopropyltrialkoxysilanes and sodium hydroxide (Scheme 1).



Scheme 1. Synthetic scheme for monosodiumoxyaminopropyldialkoxysilanes

The quantitative yields and purity of the monosodiumoxoaminopropyldialkoxysilanes thus obtained were determined directly by means of ^{1}H-, ^{13}C-, ^{15}N-, ^{29}Si NMR and mass spectroscopy methods, as well as indirectly, by analyzing the products of monosodium salts thus obtained, capped with trimethylchlorosilanes (Scheme 2), by means of GPC, ^{1}H, ^{13}C, ^{15}N, ^{29}Si NMR and mass spectroscopy.



(R = H, -$CH_2CH_2NH_2$; Alk = -CH_3, -CH_2CH_3)

Scheme 2. Termination reactions of monosodiumoxoaminopropylalkoxysilanes

Reactions between alkoxysilanes and sodium hydroxide represent nucleophilic substitution of the alkoxy group at the silicon atom with a hydroxide ion. Since replacement of one alkoxy group in the molecule of the starting organoalkoxysilane by an electron-donor NaO- group significantly reduces the reactivity of the silicon atom towards secondary nucleophilic substitution reactions [23] (Fig. 3), the corresponding monosodiumoxoorganoalkoxysilane is formed as the main product under certain conditions.

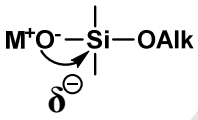


Figure 3. Inductive electron effect in sodiumoxolalkoxysilane molecules.

In contrast to the reactions of NaOH with a number of organotrialkoxysilanes (where the organic radical R = -CH_3 or -CH=CH_2) that occur at room temperature with a significant exothermic effect and require optimization and thermal control for the reaction process and for prevention of possible side reactions [6], reactions of aminopropyltrialkoxysilanes with NaOH under standard conditions occur very slowly and elevated temperatures are needed. Such a decrease in the reactivity of organoalkoxysilanes in nucleophilic substitution reactions on transition towards aminopropyl organic substituents at the silicon atom can result from the participation of the amino group in the complex rearrangement during the formation of a transition complex, and can also be associated with the steric effect of the aminopropyl group. At the same time, the coordination ability of amino groups can also lead to the prevention of side reactions that often occur with a number of various organoalkoxysilanes [6].

3.2 Hyperbranched polyaminopropylalkoxysiloxanes

Monosodium salts of organoalkoxysilanes that have two types of chemically independent functional groups are promising reagents for the creation of polyorganosiloxane structures with controlled molecular architecture of the polymeric backbone (well-defined polysiloxane structures).

Previously, based on a number of monosodium salts of alkoxysilanes $(C_2H_5O)_3SiONa$ [4] and organoalkoxysilanes $RSi(OC_2H_5)_2ONa$ (R = CH_3-, CH_2 = CH-) [6], the possibility to synthesize the corresponding polysiloxanes and polyorganosiloxanes with hyperbranched structures was demonstrated. Similarly, in this work, based on the synthesized monosodium salts of aminopropyltrialkoxysilanes, the possibility to prepare hyperbranched polyaminopropylsiloxanes by controlled polycondensation was studied and demonstrated.

Monosodiumoxoorganodialkoxysilanes are AB_2-type monomers (Fig. 4).

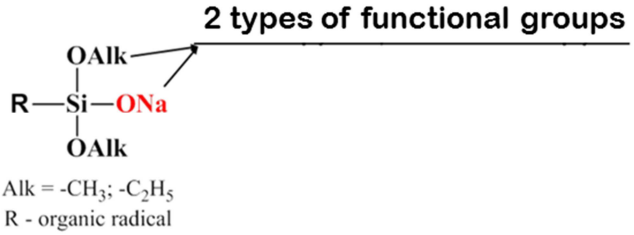
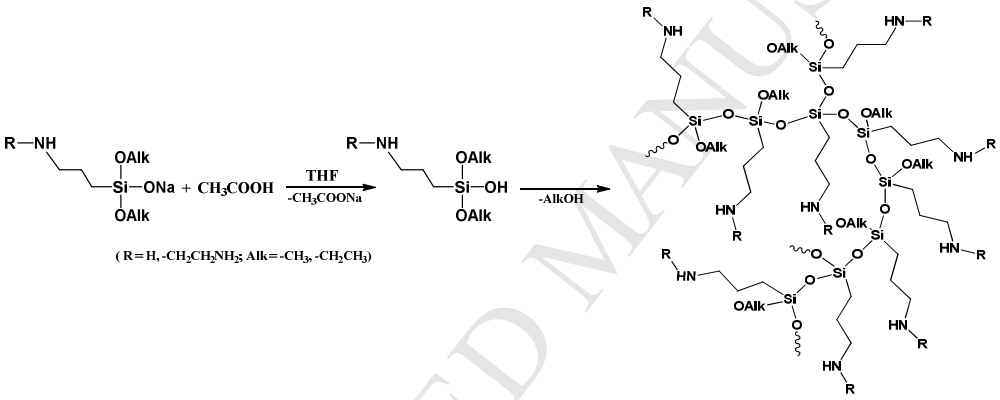


Figure 4. Monosodium salts of organotrialkoxysilanes - AB_2-type monomers

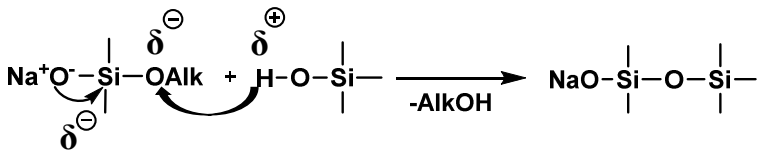
In accordance with the Flory condition [15], due to which totally acyclic polymers with hyperbranched structures can be synthesized without the risk of gelation in heterofunctional polycondensation of a monomer containing more than two functional groups of different chemical nature, polycondensation of the corresponding sodiumoxoaminopropyldialkoxysilanes was provided (Scheme 4).



Scheme 4. Synthetic scheme for hyperbranched polyaminopropylalkoxysilanes

The polycondensation was carried out in accordance with the method known as "silanol" method [2,3], in which a sodiumoxoorganodialkoxysilane solution undergoes neutralization with an equimolar amount of acetic acid, thus forming hydroxyorganodiethoxysilane, which undergoes an in-situ heterofunctional condensation to give the corresponding hyperbranched polyorganoalkoxysiloxane.

This method is based on the previously discovered effect of activation of alkoxy groups in sodiumoxoalkoxysilane molecules due to the positive inductive effect of NaO- groups towards the reagents with mobile protons (such as, for example, silanols) (Scheme 5) [6].



Scheme 5. Mechanism of heterofunctional condensation of sodiumoxyalkoxysilane and silanol.

A number of NMR spectroscopy methods such as ^{1}H, ^{29}Si, ^{13}C, and ^{15}N NMR spectroscopies were used for characterization and estimation of the molecular structures of the polymers thus obtained.

It follows from the ratio of the integral intensities of ^{1}H NMR proton signals (Fig.5) of polyaminopropylalkoxysiloxanes that the condensation of sodiumoxyorganodiethoxysilanes in the presence of acetic acid is a heterofunctional process that occurs solely as a reaction between the alkoxy and hydroxy groups generated in the neutralization of the corresponding sodium salts, and thus this process obeys the Flory rule.

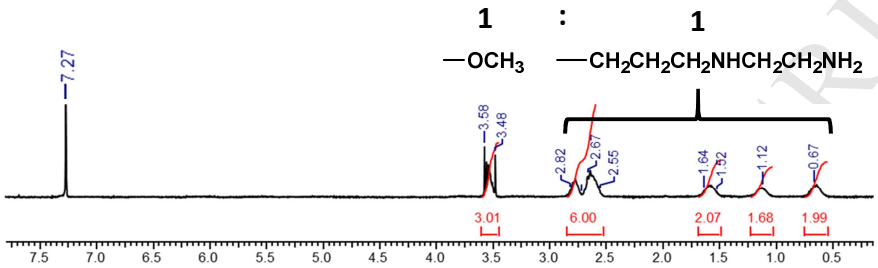


Figure 5. ^{1}H NMR spectra ($CDCl_3$) of polyethylenediaminopropylmethoxysilane

A ^{29}Si NMR study (Fig. 6) of the resulting hyperbranched polyvinylethoxysiloxanes with addition of paramagnetic chromium(III) acetylacetonate serving as a relaxation accelerator [24] allowed us to obtain data on the ratio of different siloxane units in the structures of the polymers synthesized.

As a rule, molecules of hyperbranched polymers obtained from the AB_2 type monomers consist of linear (L) units with one unreacted functional group; dendritic (D) units without functional groups, and terminal (T) units with two unreacted functional groups.

To provide a quantitative relationship between different units in the structure of hyperbranched polymers and thus obtain a description of their molecular structures, it is worthwhile to use the appropriate equation for calculating the degree of branching, DB: DB = (D + T) / (D + L + T) [24].

While the degree of branching of an ideal dendrimer equals 1, it usually does not exceed 0.5 for hyperbranched polymers with less-perfect structures obtained from AB_2-type monomers and possessing a considerably broader polydispersity index [25]. The degree of branching found from the previous equation was 0.43 for the polyaminopropylethoxysiloxane synthesized and 0.49 for the polyethylenediaminopropylmethoxysiloxane.

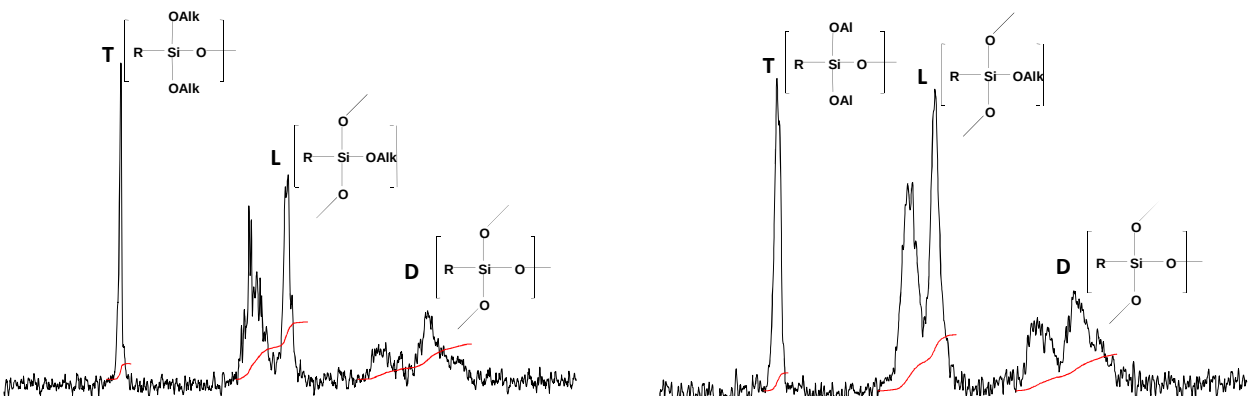
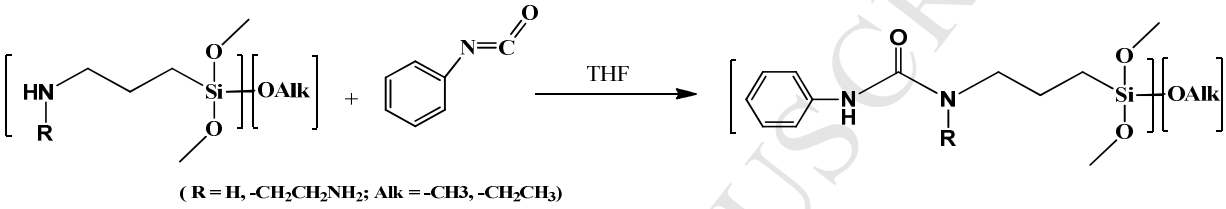


Figure 6a. ^{29}Si NMR spectra of polyaminopropylethoxysilane

Figure 6b. ^{29}Si NMR spectra of polyaminopropylethoxysilane

The molecular weights and molecular weight distribution of the amino-containing polyalkoxysiloxanes obtained were determined indirectly by GPC analysis of the products obtained upon termination of the polymers with phenyl isocyanate (Scheme 6).



Scheme 6. Synthetic scheme of termination of amino groups in hyperbranched polyaminopropylalkoxysiloxane (HBPAPES) with phenyl isocyanate.

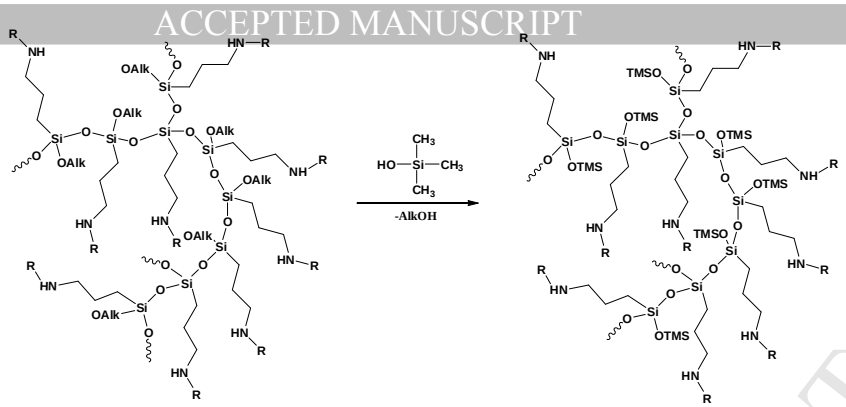
The need to convert amino groups by means of additional capping reactions is due to the complexity of studies of amino-containing polymers with standard GPC techniques due to the specific interactions of amino groups with GPC column fillers, which lead to the adsorption of such polymers on the column, and thus making them impossible to detect and determine their molecular weight characteristics [26].

The GPC curves obtained for capped polymers correspond to the average mass molecular weights in the range from 900 to 1200 kDa in polystyrene standards, corresponding to M_w = 500 - 900 kDa for the initial samples.

Thus, polycondensation of the monosodium salts of aminopropylalkoxysilanes by the above method leads to the production of hyperbranched polymers with relatively small molecular weights corresponding to polyorganosiloxane structures with ≤10 repeating organoalkoxysiloxane units.

The large number of residual alkoxy groups in polymer structures allows its further chemical modification. At the same time, the presence of a large number of basic amino groups in the polyaminopropylalkoxysiloxanes obtained makes these systems highly reactive and easily condensable through the residual alkoxy groups, thus permitting the modification of such polymers without the use of any additional catalysts.

To obtain more chemically stable terminated derivatives of polyaminopropylsiloxanes, their residual alkoxy groups were converted in to trimethylsiloxy groups. This chemical conversion was carried out by hydrolytic condensation between polyaminopropylalkoxysiloxanes and trimethylsilanol autocatalyzed by the own amino groups of the polymers (Scheme 7).



Scheme 7. Synthetic scheme of termination of hyperbranched polyaminopropylalkoxysilanes with trimethylsilanol.

Due to the heterofunctional mechanism of the condensation reactions of silanol and alkoxy groups catalyzed by amines and accompanied by the formation of the corresponding alcohols as by-products [26] and the absence of homofunctional condensation processes which could lead to H_2O formation in the system, the termination of polyaminopropylsiloxanes does not involve side reactions of intra- as well as intermolecular "cross-linking" of polymers. It occurs quantitatively and with preservation of their initial hyperbranched polymer architectures. The completeness of the termination reactions was estimated by ^{1}H NMR spectroscopy (Fig. 7).

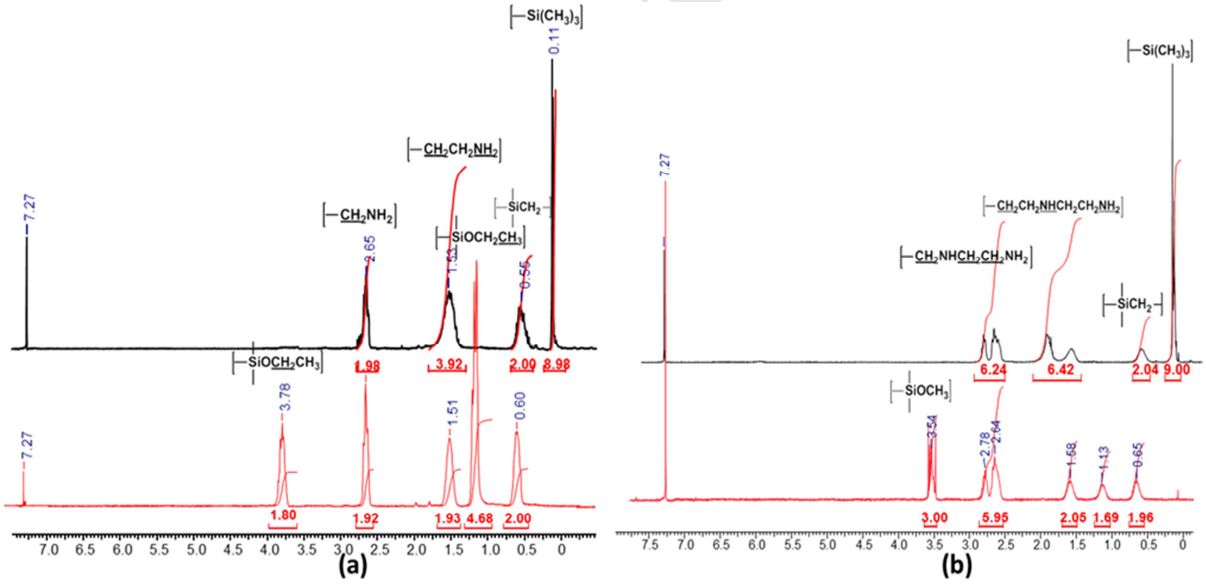
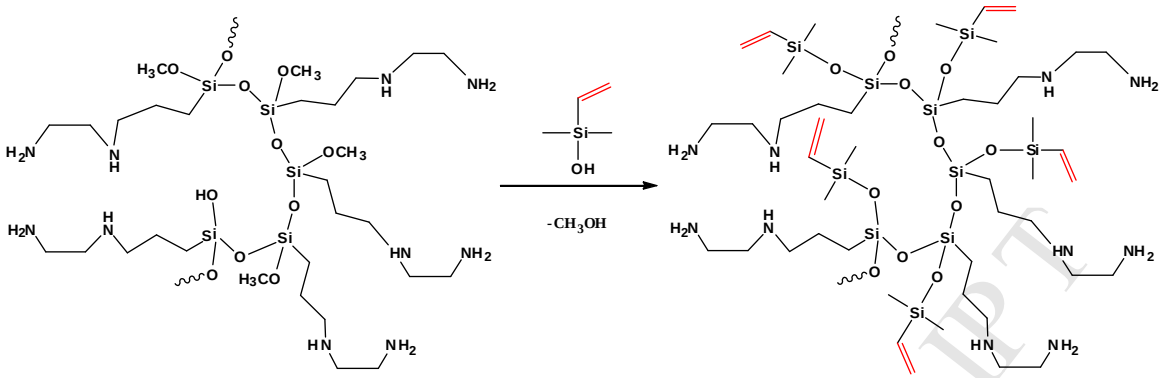


Figure 7. ^{1}H NMR spectra ($CDCl_3$) of polyaminopropylethoxysiloxane (a) and polyethylenediaminopropylmethoxysiloxane (b) before (—) and after (—) the termination with trimethylsilanol.

By varying the type of the blocking agent, the method developed allows one to perform polymer-analogous transformations of the resulting polymers through their residual alkoxy groups, thus making it possible to obtain structures with different organic radicals and functional groups in the polymer structures. In fact, when dimethylvinylsilanol was used as the blocking agent, latent reactive vinyl groups were introduced into the structure of

hyperbranched polyethylenediaminopropylmethoxysilane in an amount equimolar to the initial amount of alkoxy groups (Scheme 8, Fig.8).



Scheme 8. Synthetic scheme of the capping reaction of hyperbranched polyethylenediaminopropylmethoxysiloxane (HBPEDAPMS) with dimethylvinylsilanol.

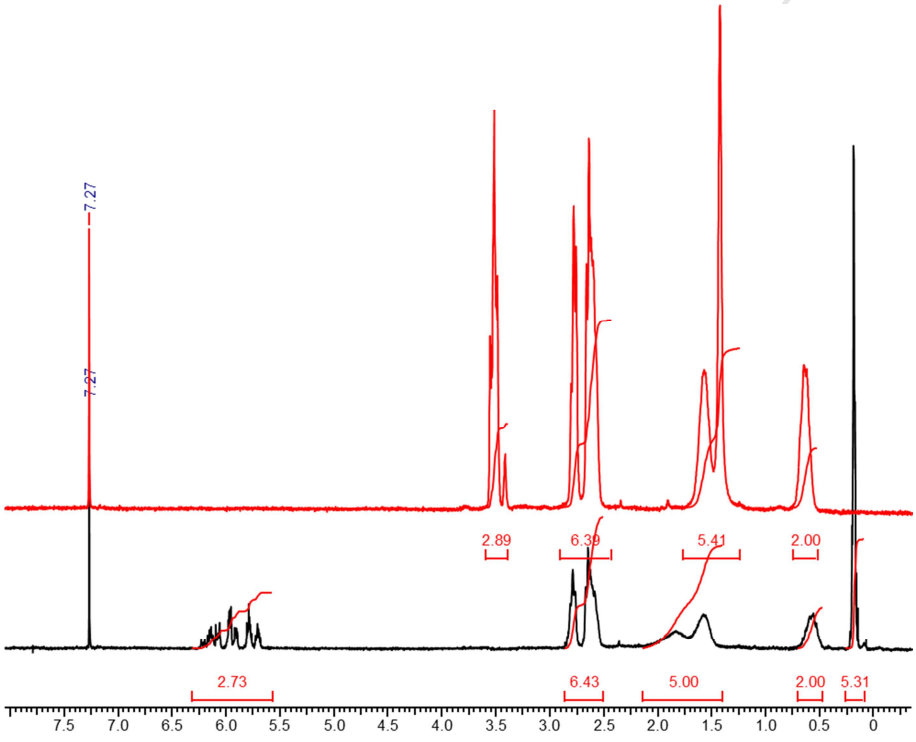
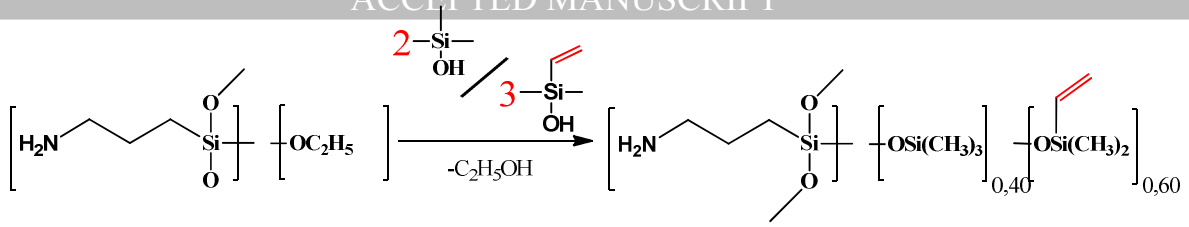


Figure 8. ^{1}H NMR spectra ($CDCl_3$) of polyethylenediaminopropylmethoxysiloxane before (—) and after (—) capping with vinyl dimethylsilanol (from bottom).

Simultaneous usage of different blocking agents makes it possible to obtain polysiloxane structures with an exactly specified ratio of different terminal units.

Thus, using trimethyl- and dimethylvinylsilanol as the blocking agents, polymeric structures with previously calculated concentrations of terminal vinyl groups were obtained (Scheme 9).

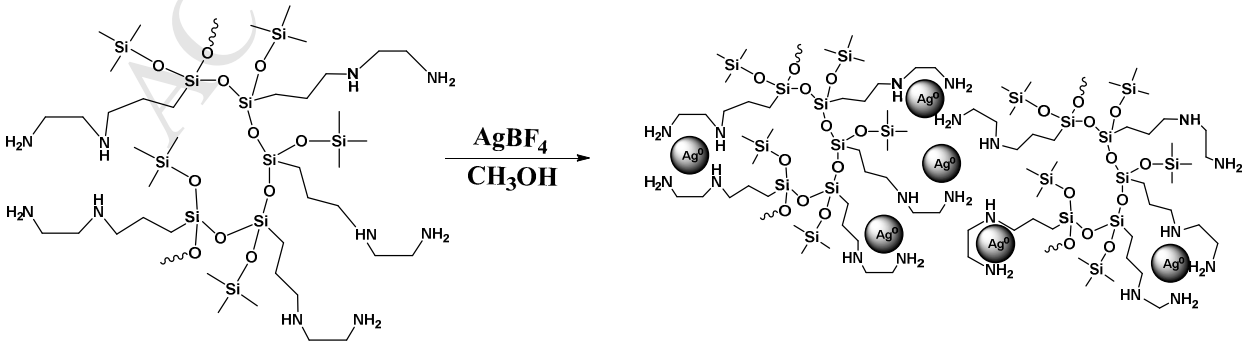


Scheme 9. Synthetic scheme of the capping reaction of hyperbranched polyaminopropylethoxysiloxane (HBPAPES) with trimethyl- and dimethylvinylsilanol; synthesis of hyperbranched polyorganosiloxane with two types of terminal groups.

3.3 Synthesis and stabilization of Ag nanoparticles with hyperbranched polyaminopropylsiloxane matrices.

The synthesized hyperbranched polyethylenediaminopropylsiloxane matrix (HBPEDAPS), terminated with trimethylsilyl groups, was used to obtain and stabilize Ag nanoparticles in methanol solution (Scheme 10). The absorption spectrum of the initial HBPEDAPS matrix in methanol, which was used both as the reaction medium and the reducing agent [27], contains very weak absorption bands in the 260-400 nm region and an intense absorption band with a maximum presumably lying in the vacuum ultraviolet region (Fig. 9, curve 1). After irradiating the mixture of the matrix and $AgBF_4$ for 30 minutes with a mercury lamp [Sylvania HSW 125W E27 Blacklight], a clear intense band of plasmon resonance with a maximum at 413 nm, typical of Ag nanoparticles [28], appears in the absorption spectrum of the mixture (Fig. 9, curve 2). The average size of the resulting nanoparticles found by DLS method was 7-16 nm (Fig. 10). However, TEM showed that the roughly spherical polydisperse Ag nanoparticles corresponded to smaller sizes of approximately 1-10 nm (Fig.11). This difference should be a consequence of the fact that the dimensions found by the DLS method correspond to the sum of the sizes of the nanoparticles forming the core and the polymeric matrix forming the shell, whereas TEM exclusively shows the dimensions of silver nanoparticles.

The resulting Ag nanoparticles successfully stabilized by the HBPEDAPS matrix undergo no aggregation or precipitation of the particles from the solution for at least 24 hours. Re-examination of the polymer composite after more than a month of storage in a dry state also showed the stability of silver nanoparticles and preservation of their initial size.



Scheme 10. Synthetic scheme of the stabilization of Ag nanoparticles with HBPEDAPS matrix in methanol.

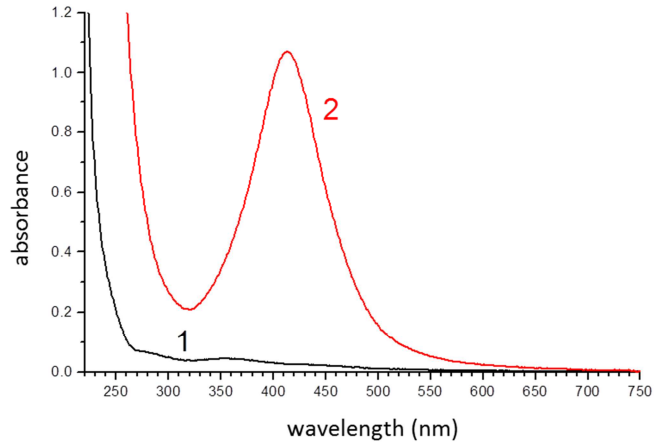


Figure 9. Absorption spectra of the HBPEDAPS matrix in methanol (5 mg/ml) (1) and a mixture of the HBPEDAPS matrix and $AgBF_4$ in methanol after irradiation (2).

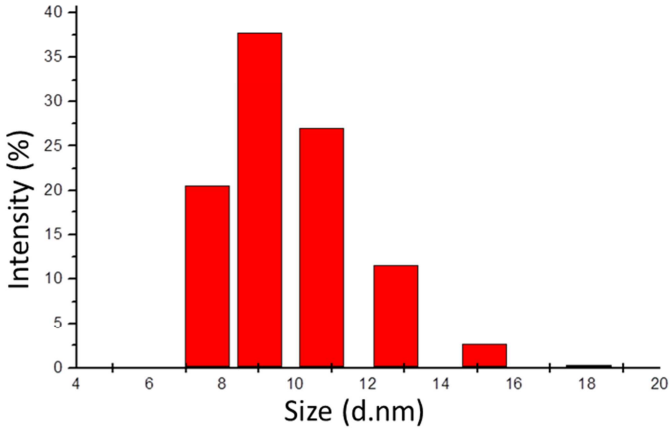


Figure 10. Distribution of Ag nanoparticles obtained after irradiation of a solution of the HBPEDAPS matrix and $AgBF_4$ in methanol, estimated by DLS method.

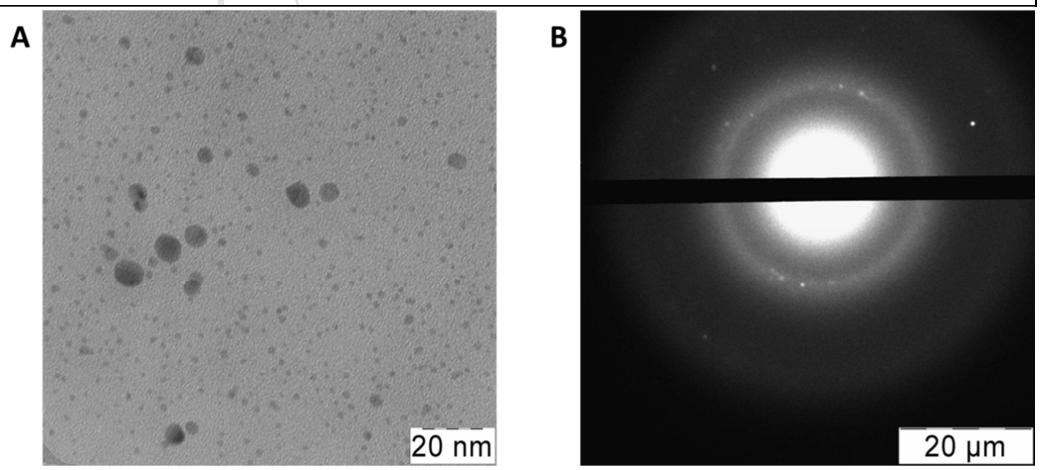


Figure 11. TEM image of Ag nanoparticles stabilized with HBPEDAPS matrix (A); electron diffraction ring pattern from a crystalline Ag specimen (B).

Unlike with the HBPEDAPS matrix, no formation of Ag nanoparticles was observed under similar conditions in the case of the hyperbranched polyaminopropylsiloxane (HBPAPS) matrix.

Under the same conditions, the use of solutions of the corresponding aminopropyltrialkoxysilane monomers instead of the hyperbranched polymers synthesized in this study leads to the formation of a black precipitate. As observed, silver is recovered from the salt, but the monomers are unable to stabilize the Ag nanoparticles produced, thus leading to their precipitation and oxidation.

4. Conclusions.

It has been shown that the reaction of NaOH with commercially available aminopropyltrialkoxysilanes is a simple and effective way to synthesize amino-containing organosilicon monomers with two types of chemically independent functional -ONa and -OAlk groups that are promising reagents for the creation of siloxane structures with controlled molecular architecture and functionality.

As an example, one of the possible uses of such AB_2-type monomers was demonstrated by the synthesis of hyperbranched structures in controlled polycondensation of monosodiumoxoaminopropyldialkoxysilanes.

The presence of a large number of residual alkoxy groups in the structure of the polymers synthesized allows further modifications of the surface of branched polymers, thus allowing their polymer-analogous transformations leading to the formation of polymer shells of various chemical nature.

The polymer matrices with ethylenediaminopropyl organic radical (HBPEDAPS) that we synthesized showed the ability to stabilize silver nanoparticles, whereas monomeric aminopropylalkoxysilanes did not possess such a stabilizing ability under the same conditions.

An important feature of the systems obtained is their water solubility, which, in combination with the high coordination ability of amino groups and the demonstrated ability of these polymer systems to stabilize metallic nanoparticles, makes the usage of these compounds potentially promising in areas related to biological or medical applications.

Acknowledgments

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Highlight

Based on the commercially available aminopropyltrialkoxysilanes new monosodium salts of organoalkoxysilanes (sodiumoxoaminopropyldialkoxysilanes) with two types of chemically independent functional -ONa and -OAlk groups at the silicon atom were synthesized and characterized. The obtained sodiumoxoaminopropyldialkoxysilanes can be regarded as AB_2-type monomers - promising reagents for providing controlled polycondensation and production of functional organosilicon polymers with controlled molecular architectures. Consequently polyaminopropylsiloxanes with hyperbranched molecular architectures were obtained by heterofunctional polycondensation of the corresponding AB_2-type monosodiumoxoorganodialkoxysilanes. Synthesized structures were characterized with methods of ^{29}Si-NMR, ^{1}H-NMR, GPC and elemental analyzes. Thus obtained hyperbranched polymer matrices, containing aminopropyl- organic radicals, showed the ability to stabilize silver nanoparticles.