

Amphiphilic Polysilane with Poly(ethylene oxide) Side Chains

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ABSTRACT: The synthesis of an amphiphilic polysilane with poly(ethylene oxide) grafted segments (PS-g-PEO) through the addition of an allyl-terminated poly(ethylene oxide) (AT-PEO) to poly[diphenylsilane-co-methyl(H) silane] (PSH) in a homogeneous system and using catalyst platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane is reported. The process involves the activation of the polymer by microwave irradiation as a preliminary stage with the view to perform the subsequent addition stage at room temperature, when side reactions are prevented. The PS-g-PEO structure was characterized by NMR, FT-IR

spectral analysis and GPC methods. The amphiphilic properties were estimated by comparison of the water sorption isotherms of the PS-g-PEO copolymer with those of the component segments. The core-shell micellization in water and the morphological aspects of the self-assembled structures were investigated by DLS and SEM. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1284–1291, 2012

Key words: synthesis; graft copolymers; polysilanes; amphiphiles; hydrosilylation; microwave synthesis

INTRODUCTION

Nowadays, nanostructured materials have become a major field of research, especially for systems that are obtained by self-assembly processes. Prominent examples for such nano-objects are the micellar systems, which can be formed from amphiphilic copolymers. The self-assembly of amphiphilic copolymers in selective solvents with respect to their micellar behavior, as well as their applications in biotechnology and pharmaceuticals, have been widely investigated.^{1–13}

Because of their unique properties, the use of polysilanes for the manufacture of ordered materials at nanometer scale is a very interesting topic both scientifically and technologically. Polysilanes are linear silicon-containing polymers with potential applications as electroluminescent, nonlinear optical, lithographic, and semiconductor materials owing to their particular electronic properties.^{14–17} In the past years, an increasing number of papers described various methods to obtain polysilanes with interesting properties and complex architectures.^{18–22} A simple approach toward the synthesis of structurally diverse polysilanes uses polyhydrosilanes as starting materials. The incorporation of methylhydrosilyl

segments within the main polysilane chain provides interesting properties, such as high solubility, intense fluorescence, and the potential for chemorestructuring in mild conditions with formation of silicon nanoparticles.^{23–26} The electro-optical properties of polysilanes are correlated with the extent of the σ -electrons delocalization, which, in turn, depends on linearity and conformation of the macromolecular chain. Therefore, assembling of polysilanes in nano-aggregates with increased conformational order will unlock the potential for the development of new generations of nanostructured materials with improved optical and/or electronic properties.

Previously published works showed that hydrophobic polysilanes could be modified to be amphiphilic by incorporating the hydrophilic or amphiphilic chains in a block-copolymer.^{27–29} The present work investigates the possibility of altering the dispersive/polar interactivity properties of the polysilanes by attaching pendant hydrophilic segments, with the view to generate new grafted polymeric architecture capable to aggregate in micellar nanostructures.

EXPERIMENTAL

Materials and equipment

Diphenyldichlorosilane, $(C_6H_5)_2SiCl_2$ (puriss, >98%) and methylchlorosilane, $CH_3(H)SiCl_2$ (puriss, >98%) were purchased from Fluka and were distilled prior to use. Poly(ethylene oxide) 1000,

Additional Supporting Information may be found in the online version of this article.

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m.p. = 37–40°C, pH (5% water, 20°C) = 5.5–7 was purchased from Fluka and used as received.

Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, [Pt(dvs)], as a solution in xylene with a content of ~ 2% Pt, was purchased from Sigma–Aldrich and was used as received.

Toluene and tetrahydrofuran (THF) were purchased from a commercial source and were distilled over sodium wire prior to use.

Allyl-terminated poly(ethylene oxide) (AT-PEO, $M_w = 1000$ g/mol, $M_n/M_w = 1.02$) was synthesized starting from poly(ethylene oxide).³⁰ The unsaturated groups were introduced at one end of the poly(ethylene oxide) chains by reacting poly(ethylene oxide) with allyl bromide, in melt, in the presence of NaOH pellets (NaOH/OH ratio: 1/0.5), at 70°C, for 24 h. The content in unsaturated allyl groups was determined by reacting AT-PEO with mercury acetate in methanol, followed by titration of the resulting acetic acid with 1N KOH.^{31,32}

The ¹H- and ¹³C-NMR spectra were recorded in CDCl₃ at room temperature using a DRX Bruker instrument at 400 MHz. FT-IR spectra were recorded with an FTS 40A Bio-Rad spectrometer at room temperature on KBr pellets. GPC experiments were carried out in THF solution at 25°C, at a flow rate of 1 cm³/min using a Spectra Physics 8800 gel permeation chromatograph with two PL-gel packed columns (103 and 500 Å). Polystyrene standards with low polydispersity (PLLab.) were used to generate a calibration curve. The differential refractive index increment for polysilanes in THF at 25°C was measured with a Rayleigh interferometer, LIR-Russia (dn/dc = 0.21 cm³/g).

PSH was activated using a single-mode cavity microwave reactor Discover LabMate CEM with IntelliVent Pressure Control System. The irradiation power, temperature, and irradiation time are automatically controlled by the Windows-based Synergy software. Water vapors' sorption capacity of the samples was measured with a fully automated gravimetric analyzer IGAsorp supplied by Hiden Analytical (Warrington, UK). An ultrasensitive microbalance measured the weight change as the humidity is modified in the sample chamber maintained at constant temperature. The pressure of the water vapors was increased incrementally with 10%, with a preestablished equilibrium time between 30 and 40 min (minimum time and time out, respectively). At each step, the weight gained by the sample is measured by electromagnetic compensation between tare and sample when equilibrium is reached. An anticondensation system is available for vapor pressure very close to saturation. The cycle was ended by decreasing the vapor pressure in steps to also obtain the desorption isotherms. The drying of the samples before sorption measurements was

carried out at 25°C in nitrogen flow (250 mL/min) until the weight of the sample was in equilibrium at RH < 1%.

Synthesis of poly[(diphenylsilane-co-methyl(H)silane] oligomer (PSH)

A sodium dispersion was prepared from sodium (10 g, 0.4 mmol) in refluxing dry toluene (120 mL) by vigorously stirring the melted sodium with a mechanical stirrer under dry argon atmosphere for 2 h. A mixture of dichlorodiphenylsilane (25.3 g, 0.1 mol) and dichloromethylsilane (11.5 g, 0.1 mol) in dry toluene (30 mL) was prepared separately. Approximately three-fourths of the mixture of monomers was added to the sodium dispersion in one portion at 60°C, and then the reaction mixture was stirred at the same temperature for 2.5 h. The temperature of the reaction mixture was gradually raised to 100°C with a rate of 2–3°C/s, and then the remaining mixture of monomers was added dropwise at a rate that keeps the solvent under gentle reflux. When the addition was complete, the mixture was heated at reflux temperature for 2 h, and then it was cooled to room temperature, quenched with a water–ethanol mixture (100 mL, 1 : 1 v/v), and washed with distilled water (500 mL). The organic layer and the solid insoluble polymer were separated by ultracentrifugation, and the solvent (toluene) was stripped-off. The colorless residue was dissolved in THF (20 mL). The polymer that resulted by adding the THF solution to 2-propanol (800 mL) was filtered and extracted with boiling diethyl ether (30 mL). The solvent was removed and the polymer was precipitated by the addition of methanol. The resulted white solid was filtered and vacuum-dried at 50°C to obtain PSH (10 g, 27.5% yield) having a low molecular weight.

FT-IR (ν_{\max} , cm⁻¹): 3070–3000 (C–Har), 2980 and 2860 (C–Halkyl), 2090 (Si–H), 1455 and 1100 (Si–C₆H₅), 1250 and 880 (Si–CH₃), 750 and 705 (Si–C), 460 (Si–Si) [Fig. 2(a)]. GPC (1% in THF, 1 cm³/min⁻¹, 25°C): 5200 g/mol ($M_w/M_n = 1.20$). ¹H-NMR (CDCl₃, δ ppm): 0.15–0.65 (3H, br, SiCH₃), 3.80 (1H, SiH), 7.3–7.6 (10H, SiC₆H₅). ¹³C-NMR (CDCl₃, δ ppm): –8.2, –0.8 (SiCH₃), 126.5–135.7 (SiC₆H₅). UV (CHCl₃, λ_{\max} nm) : 280 ($\epsilon = 6500$ dm³ mol⁻¹ cm⁻¹) and 350 ($\epsilon = 14800$ dm³ mol⁻¹ cm⁻¹).

Synthesis of polysilane–poly(ethylene oxide) graft copolymer (PS-g-PEO)

A solution of PSH (0.5 g) in dry toluene (2 mL) was irradiated ($P = 250$ W, $T_{\max} = 60^\circ\text{C}$) in a sealed 10-mL microwave vial under good stirring for 1 min, and then it was cooled to room temperature. AT-PEO (0.7 g, 0.7 mmol, calculated for 7

methylhydrosilyl units) and the catalyst (20 μL) were then added to the stirred reaction mixture. The reaction was completed in 1.5 h (as estimated by monitoring the intensity of the —Si—H band at 2090 cm^{-1} by FT-IR). Then, the solvent was removed under reduced pressure (10 mm Hg) at 70°C to give a solid that was dissolved in THF (4 mL). The polymer solution was added dropwise to a stirred mixture of methanol and hexane (100 mL, 1 : 1 v/v) to afford the grafted copolymer that was filtered and vacuum-dried to a yellowish solid (58%).

GPC (1% in THF, $1\text{ cm}^3/\text{min}$, 25°C): 11300 g/mol ($M_w/M_n = 1.2$). FT-IR (KBr, cm^{-1}): 3086 (C—Har), 2850–2960 (C—Halkyl), 2090 (Si—H), 1600 and 1513 and 1458 (Car—Car), 1265 (Si—CH₃), 1150 (C—O—C), 470 (Si—Si) [Fig. 2(b)]. $^1\text{H-NMR}$ (CDCl_3 , δ ppm): 0.08 (br, —SiCH_3), 1.13 ($\text{—CH}_2\text{—}$), 3.37 ($\text{—CH}_2\text{O—}$), 3.54 ($\text{—CH}_2\text{—}$), 3.72 (—SiH), 6.5–7.34 ($\text{—SiC}_6\text{H}_5$) (Fig. 3). $^{13}\text{C-NMR}$ (CDCl_3 , δ ppm): -6.2 (—SiCH_3), 8.5 ($\text{—SiCH}_2\text{—}$), 10.4 (—CH_3), 24.2 ($\text{—CH}_2\text{—}$), 72.3 (OCH_2CH_2), 126.9–136.1 (br, $\text{—Si C}_6\text{H}_5$).

Micellar structures preparation

Stable micellar aggregates of PS-*g*-PEO in aqueous solution have been obtained by the co-solvent approach method. For this purpose, the copolymer was dissolved in THF (0.1 g/10 mL THF) and twice distilled water (4 mL) was added dropwise to the stirred solution. Subsequently, the mixture was subjected to continuous concentration and dilution with water ($3 \times 10\text{ mL}$) to obtain a homogenous white opaque dispersion. Through the same approach, samples with PS-*g*-PEO concentrations within 10^{-2} – 10^{-1} g/L have been prepared using balanced amounts of copolymer, solvent, and water.

Scanning electron microscopy (SEM) studies were performed in aqueous dispersions with a Quanta FEI 250 instrument operating in extended vacuum mode (ESEM) at 30 kV with secondary electrons. For imaging, samples were placed into a the Peltier cooled holder of the detector, which was kept at the temperature of 1°C , and the holder was inserted into a sample chamber with the water vapor pressure of 650 Pa. At these conditions, the relative humidity in the chamber was 99% and evaporation of water from the sample was very slow.

Both the critical micelle concentration (CMC) and size distribution of the micellar structures have been determined by dynamic light scattering (DLS) using a Malvern Zetasizer NS (Malvern Instruments; UK). Each sample was measured after an equilibration time of 3 min. The Zetasizer NS was operating at a fixed angle 90° with a 4 mW He—Ne laser at 633 nm and non-invasive back-scatter technique (NIBS) at a constant temperature of 25°C . The measurements were conducted in the manual mode using 20 sub-

runs of 10 s. The size distribution by intensity and number was calculated from the correlation function using the multiple narrow mode of the Dispersion Technology Software version 4.00 (Malvern, Herrenberg, Germany).

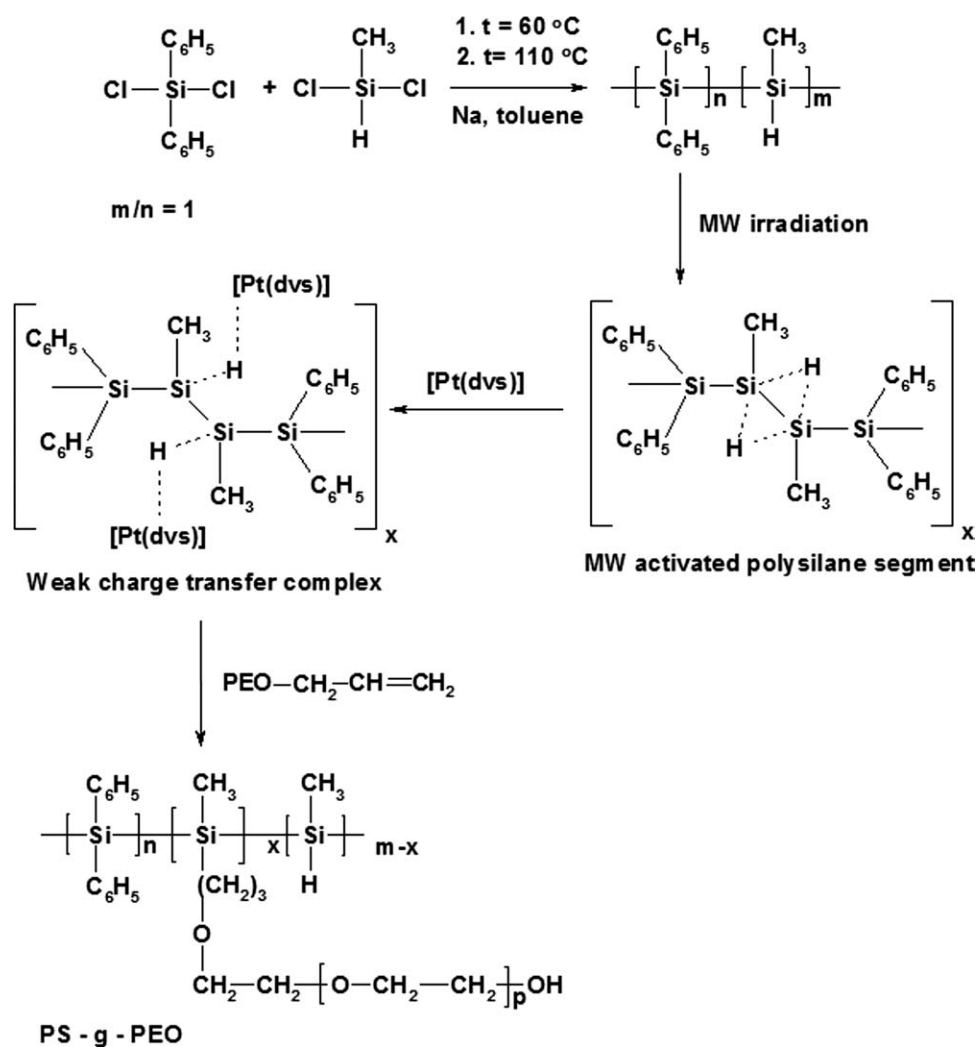
RESULTS AND DISCUSSION

PS-*g*-PEO was synthesized by the homogeneous addition reaction of AT-PEO in the presence of [Pt(dvs)] (Scheme 1).

The first step of the process is the synthesis of the reactive polyhydrosilane oligomer PSH through a heterogeneous Würtz coupling.³³ It is known that owing to the specific σ -electrons delocalization, the optical and electronic properties of polysilanes depend on the number of silicon atoms in the chain. However, a strong variation of these properties could be observed only for oligomers with less than 10 silicon atoms in the main chain. Also, detailed structural investigations revealed that larger polysilane macromolecules are in fact collections of shorter segments formed by random changes of conformation.³⁴ Therefore, we could assume that, in general, linear polysilanes with both low and high molecular weight should have comparable optical and electronic. Inclusion of even oligosilanes segments within various polymeric architectures is a way to impart their valuable opto-electronic properties to the new structures.

The best results in polysilane synthesis were provided by the Würtz-like coupling in heterogeneous reaction systems with molten sodium dispersion. A slightly modified reported procedure was employed in the present study with the view to afford a high yield of polyhydrosilanes with low molecular weight. This was accomplished by lowering the reaction temperature in the first stage of the synthesis. According to earlier work,³³ a low reaction temperature prevents the side reactions caused by the free electrons in excess in the initiation phase, while it also slows down considerably the chain-growth ratio. The GPC chromatogram of the polymer before fractionation shows the specific bimodal distribution in the high molecular weights region corresponding to the linear polyhydrosilanes. A much smaller peak is situated in the low molecular weight region of the chromatogram and corresponds to the (Si)₅ and (Si)₆ cyclo-silanes (Supporting Information Fig. 1S). After fractionation, the GPC analysis shows a single peak corresponding to a molecular weight of 5200 g/mol ($M_w/M_n = 1.20$) (Fig. 1a and Supporting Information Fig. 2S).

FT-IR spectrum confirmed the presence of the Si—H band in the starting PSH at approximately 2090 cm^{-1} [Fig. 2(a)]. Also, the NMR analysis of the initial polyhydrosilane confirmed the chemical



Scheme 1 Synthesis of PS-g-PEO.

structure of the copolymer (Supporting Information Fig. 4S). The molecular ratio of the co-monomeric units $\text{Si}(\text{C}_6\text{H}_5)/\text{Si}(\text{H})\text{CH}_3$, was calculated from $^1\text{H-NMR}$ spectrum by dividing the corresponding signal integrals ($M_r = 1$).

The second stage of the process is the synthesis of PS-g-PEO. The amphiphilic properties of such a copolymeric structure depend on the content in hydrophobic moieties versus the hydrophilic ones. From this point of view, a good starting point is to use in synthesis of PS-g-PEO equivalent molecular weights of the two components. This means that in a polysilane chain with $M_w \sim 5000$ g/mol about five PEO segments with $M_w \sim 1000$ g/mol should be enclosed. Therefore, taking into account also the reaction yield it was decided to use in synthesis a PSH/AT-PEO molecular weight ratio of 1/7. The classical approach requires long reaction times and relatively high temperatures, and an exposure to temperatures over 80°C for more than 60 h is detri-

mental for both the chemical structure of the reagents and/or the reaction course. In the present work, the synthesis of PS-g-PEO is based on the so-called microwave pre-activation technique. Basically, the polyhydrosilane solution in a non-polar solvent such as toluene is subjected first to microwave irradiation. It was observed experimentally that when this activated system is brought in contact with the allyl derivative in the presence of the $[\text{Pt}(\text{dvs})]$ catalyst, the addition is initiated instantly and proceeds with a high rate to produce the copolymer in high yields. The mechanism involved in microwaves assisted synthesis is still under debate. It is known that microwaves produce an almost instant energy transfer owing to the oscillation of molecular dipoles in the electric field. In a nonpolar solvent, the energy of microwaves is entirely transferred to the polysilane backbone, thus activating σ -electrons donor centers.^{35,36} The small size of the substituents in the methylhydrosilyl groups

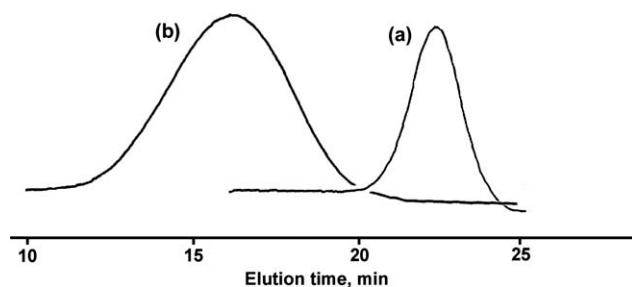


Figure 1 GPC traces of PSH (a) and PS-g-PEO (b).

allows the participation of these electron donor centers in close range charge transfer processes with the [Pt(dvs)] catalyst. This process produces the reactive weak charge transfer complex intermediate that is crucial for the addition of allyl derivative (Scheme 1).

The GPC traces of the graft copolymer showed a broad peak with short retention volume which was assigned to the corresponding graft copolymer [Fig. 1(b) and Supporting Information Fig. 3S). Notably, no traces of unreacted macromonomers were detected. A molecular weight of 11,300 g/mol ($M_w/M_n = 1.2$) was recorded for the graft copolymer, which represents a significant increase from the molecular weight of PSH.

The chemical structure of the obtained graft copolymer was confirmed by NMR and FT-IR analysis.

The FT-IR spectrum of the grafted copolymer reveals characteristic absorption bands of both AT-PEO and PSH structures [Figs. 2(b,c)]. Therefore, one should notice the strong $1000\text{--}1150\text{ cm}^{-1}$ signal due to the C—O—C symmetric and asymmetric stretching of ether bonds in PEO side-chain.^{37,38} Also, the strong C—H(alkyl) bonds stretch absorption bands at $2850\text{--}2960\text{ cm}^{-1}$ and the broad O—H band at 3435 cm^{-1} can be easily observed [Fig. 2(c)]. In addition, the FT-IR spectrum of PS-g-PEO shows clearly the remnant of the polysilane Si—H group absorption at 2090 cm^{-1} . The much lower intensity of this signal compared with the parent PSH proves that the addition reaction took place in high yields. This is confirmed also by the absence of the —CH=CH₂ absorption band at around 1644 cm^{-1} and the strongly modified profile in the $838\text{--}687\text{ cm}^{-1}$ region due to the newly formed C—H aliphatic groups. The —Si—C₆H₅ bonds which should be observed at 1125 cm^{-1} are overlapped by the strong —C—O—C— absorption. However, the C—H aromatic groups could be identified by the characteristic absorption bands around 3100 cm^{-1} . The IR absorption bands of the polysilane Si—Si backbone could be also observed in the grafted copolymer spectrum within the $400\text{--}500\text{ cm}^{-1}$ region.

The ¹H-NMR spectrum of the graft copolymer shows the strong characteristic peak of the

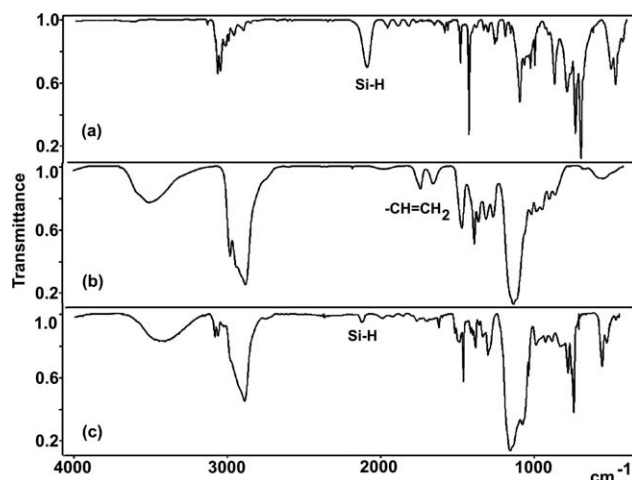


Figure 2 FT-IR spectra of (a) PSH pristine structure; (b) AT-PEO; (c) PS-g-PEO.

—O(CH₂)₂O— from the PEO side-chain at 3.54 ppm (Fig. 3). Additionally, the —SiCH₂— and —CH₂O— protons of the propylene bridge at 1.13 and 3.37 ppm, respectively, are indicative of the successful chemical incorporation of the macromonomer into the graft copolymer. The ¹³C-NMR analysis also supports the structure of the graft copolymer through the specific peaks of the propylene bridge at 8.5 ppm (—SiCH₂—), 24.2 ppm (—CH₂—), and 72.3 ppm (—OCH₂CH₂—). The assignment of the signal corresponding to the unreacted —SiH groups by ¹H-NMR was difficult owing to its overlapping with the peaks of the protons in the propylene bridge. Even so, we hypothesize that the weak peak at 3.72 ppm should be assigned to the —SiH proton.

The capacity of the grafted copolymer for water sorption was investigated for a relative humidity range (RH) of 0–90% at 25°C.

The percentage of water gain, defined as the amount of water adsorbed in the PSH, AT-PEO, and PS-g-PEO films at time *t* are plotted in Figure 4. The percentage of water loss under the same conditions is also plotted. For the PSH film, the amount of adsorbed water is very small. The amount of water adsorbed by the hydrophilic AT-PEO is larger, as expected. The percentage of water loss in AT-PEO is

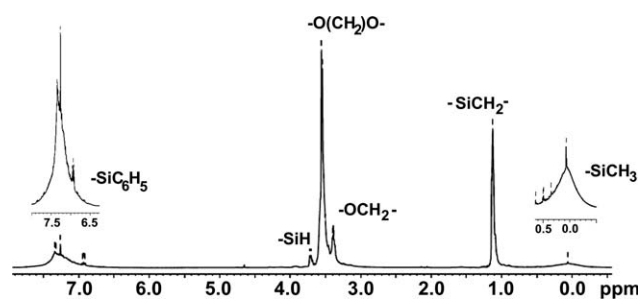


Figure 3 ¹H-NMR spectrum of PS-g-PEO.

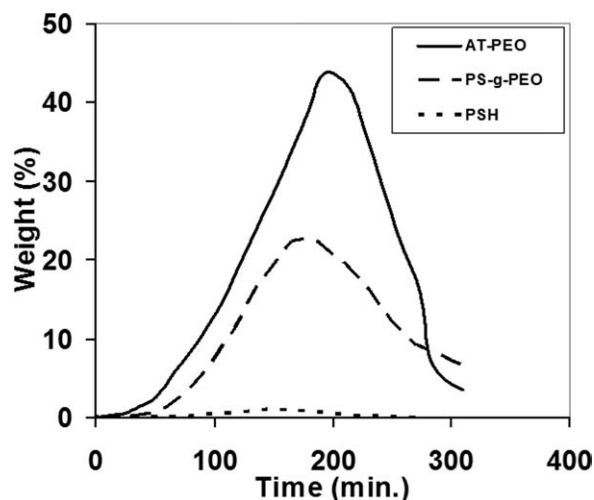


Figure 4 Percentage of water gain/loss in PSH, AT-PEO, and PS-g-PEO films.

larger than that of water gain after the same amount of time, which means that water desorption is faster than water sorption for this polymer. The percentage of water loss is initially linear, indicating that water desorption is an evaporation-limited process.³⁹ In the case of water desorption, the initial water content is 45 wt %. The sluggishness of water sorption process is a result of both the much lower water content and lower water diffusion coefficient in the polymer film. The amount of water adsorbed by PS-g-PEO graft copolymer is situated, as expected, in between the amounts of water adsorbed by PSH and AT-PEO.

Due to its amphiphilic properties, PS-g-PEO should be able to participate to self-assembling processes in water with formation of micellar-like structures. Environmental scanning electron microscopy (ESEM) was used to verify if this assumption was also right for PS-g-PEO. Images taken from samples of PS-g-PEO in water taken at low magnification shows undoubtedly that large micellar aggregates are present [Fig. 5(a)]. A closer look at a higher magnification reveals the spherical morphology of the micelle with the polysilane hydrophobic core and the hydrophilic poly(ethylene oxide) coronas [Fig. 5(b)].

Further investigations were done to study the self-assembling of PS-g-PEO with formation of the micellar structures. Such processes start only after the system reaches the so-called critical micelle concentration (CMC). Usually the most sensitive method to determine CMC is based on a fluorescent probe which have one or more specific emission bands that could be easily analyzed by fluorescence measurements. It is difficult to apply this method to polysilanes because they are themselves materials with fluorescence properties and their emission varies within a large interval of values. A different

approach to determine the CMC of PS-g-PEO is based on the dynamic light scattering (DLS) analysis. For this purpose, measurements have been made on samples containing different concentrations of PS-g-PEO in water. Below the CMC, the intensity of scattered light detected from each concentration was similar to that of water. Once the CMC was reached, the intensity increases significantly due to the presence of micelles. Therefore, a plot of the intensity of scattered light as a function of the PS-g-PEO concentration in water shows an abrupt change of slope due to micelles formation and was used to determine the CMC value at 0.053 g/L (Fig. 6).

The size of the micellar structures was determined by DLS. DLS trace of the PS-g-PEO aqueous dispersion shows an average particle diameter of 298 nm and relatively low polydispersity (0.243) as inferred from the relevant histogram (Fig. 7).

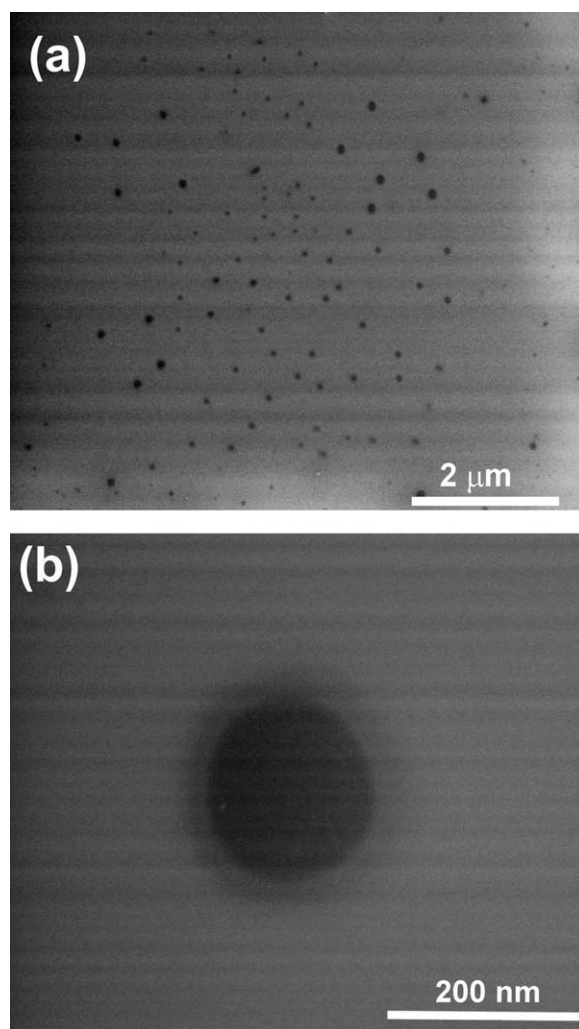


Figure 5 SEM analysis of the PS-g-PEO aqueous dispersion: (a) low magnification image showing the presence of the micellar aggregates; (b) high magnification image of a micellar structure showing the hydrophobic core and hydrophilic corona.

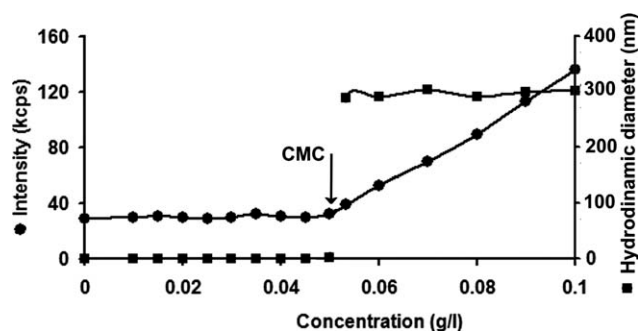


Figure 6 Plot of the intensity of scattered light (kcps) and hydrodynamic diameter (nm) obtained for various concentrations of PS-g-PEO in water. The inflection point at 0.053 g/L in the intensity data corresponds to the CMC value.

The effect of the polymer concentration on the particle size was studied by DLS analysis of samples containing PS-g-PEO in concentrations higher than CMC (Table I). The results showed that there is no particular correlation between the copolymer concentration and the size of the micellar structure which remains close to the average value.

CONCLUSIONS

This work presents a synthetic approach for a novel polyhydrosilane-graft-poly(ethylene oxide). First, the synthesis of the starting polyhydrosilane was achieved by a modified Würtz coupling technique in two stages of temperature, which leads to a high content in linear low molecular weight structures. Then, the graft copolymer was prepared by a microwave pre-activated catalytic addition of allyl-terminated poly(ethylene oxide) to poly[diphenyl-*co*-methyl(H)]silane. The reaction was performed using a

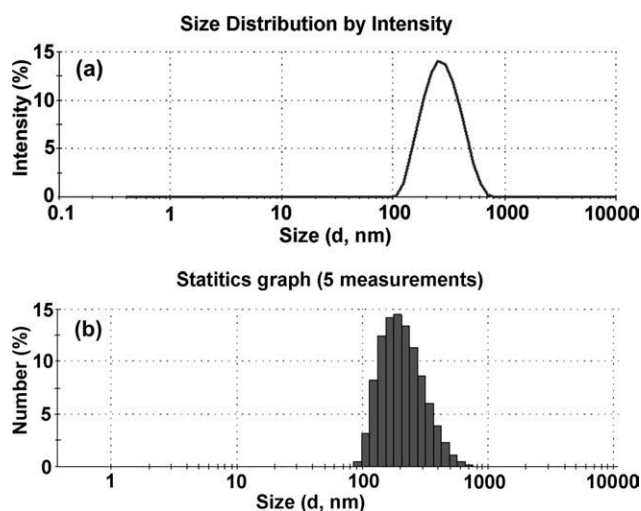


Figure 7 Dynamic light scattering (DLS) measured size distribution of PS-g-PEO micellar structures in water: (a) size distribution by intensity; (b) size distribution by number.

TABLE I
Properties of the PS-g-PEO Micellar Structures

Concentration (mg/mL)	Particle size (nm)	Polydispersity
2.5	298	0.243
0.2	283	0.256
0.5	301	0.233
0.9	296	0.249

non-stoichiometric molecular ratio, which ensures that a part of the SiH groups remains available for further developments such as the creation of cross-linked networks of both hydrophilic and hydrophobic domains. Knowing that polysilanes are highly photosensitive, the synthesized grafted copolymers have an interesting potential use in biomedical application such as light-controlled drug delivery.

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