

Silicon Surface Modification with Silane-Functionalized Polymers

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ABSTRACT

The synthesis of trimethoxysilane end-capped linear polystyrene (PS), star-branched PS, and subsequent silicon (Si) surface modification with the linear and star polymers are described. Trimethoxysilane terminated PS was synthesized using *sec*-butyl lithium initiated anionic polymerization of styrene and subsequent end-capping with *p*-chloromethylphenyl trimethoxysilane (CMPTMS). Acid catalyzed hydrolysis and condensation of the trimethoxysilane end-groups resulted in star-branched PS. This is the first report of core-functionalized star-shaped polymers as surface modifiers and the first comparative study showing differences in surface topography between star and linear polymer modified surfaces. Comparison of polymer film properties to polymer dimensions in dilute solution revealed that the linear PS chains were in the intermediate brush regime and the star-branched PS produced a surface with covalently attached chains in the mushroom regime.

Keywords: anionic polymerization, hydrolysis and condensation, star polymers, sol-gel chemistry, surface modification, polymer mushrooms and brushes

1 INTRODUCTION

Solid surfaces are often chemically modified to improve properties such as adhesion, lubricity, wettability, biocompatibility, and environmental resistance.^[1] Self-assembled polymeric films offer significant advantages compared to other conventional modification techniques and thus are widely used as surface modifiers. While a polymeric surface modifier dictates the chemical composition of a modified surface, the chain length of the polymer also determines the film thickness. In addition, the density of polymer chains and concentration of functional groups on a modified surface may be further controlled using branched and dendritic polymer films.^[2-4] There are many approaches for modifying solid surfaces with polymers, which include physisorption, covalent attachment, and electrostatic adsorption.^[5] Physisorption is relatively easy, but suffers from thermal and solvolytic instabilities due to the absence of stable covalent bonds with the surface.^[6] Covalent grafting of polymer chains is therefore preferred. Two commonly employed approaches to covalently graft polymer chains are the “grafting to” and the “grafting from” techniques.

This paper reports the use of the “grafting to” approach to anchor core-functionalized star-shaped PS to Si. In recent years, many studies involved the use of branched polymers as surface modifiers. This is partly attributed to the high density of functional groups in branched polymers, making them attractive candidates for chemical sensors, drug delivery agents, nanoscale catalysts, and smart adhesives.^[7] Most earlier surface modification investigations with branched polymers have employed dendrimers and hyperbranched polymers. Studies on surface attached star polymers has mainly concentrated on the use of PEG-based star polymers to impart enhanced biocompatibility to silicon surfaces compared to linear polymers.^[8,9] This paper is the first report on the modification of Si surfaces with star-shaped PS, which contained surface reactive silanol functionalities in the core. Synthesis of the star-branched PS was achieved using the sol-gel process resulting from acid catalyzed condensation of trialkoxysilane-functionalized linear PS obtained using living anionic polymerization. The sol-gel condensation reported herein uniquely results in a core-functionalized star polymer. Despite the steric hindrance associated with the accessibility of the core silanols, core-functionalized polymers were attached to Si wafers and presented a significantly different surface topography compared to linear PS analogues. The differences in the surface characteristics of linear and star PS modified surfaces are discussed below.

2 EXPERIMENTAL

2.1 Materials

Styrene (99%, Aldrich) was stirred over CaH₂ for 3-4 days, distilled under reduced pressure (0.1 mm Hg, 10 °C) after repeated degassing and freeze-thaw cycles, and stored at -25 °C until further use. Styrene was distilled from dibutylmagnesium (DBM) under similar conditions immediately prior to polymerization. DBM (FMC Corporation Lithium Division, 25% solution in heptane) and *sec*-butyllithium (Aldrich, 1.4 M in cyclohexane) were used without further purification. *p*-chloromethylphenyl trimethoxysilane [CMPTMS] (95%, Gelest, Inc.) was stirred over CaH₂ for a day and vacuum-distilled (0.1 mm Hg, 50 °C) immediately prior to use. THF (EMD Chemicals), which was the polymerization solvent, was distilled from sodium in the presence of benzophenone

immediately prior to use. Methanol (EMD Chemicals) was stored over 5 Å molecular sieves.

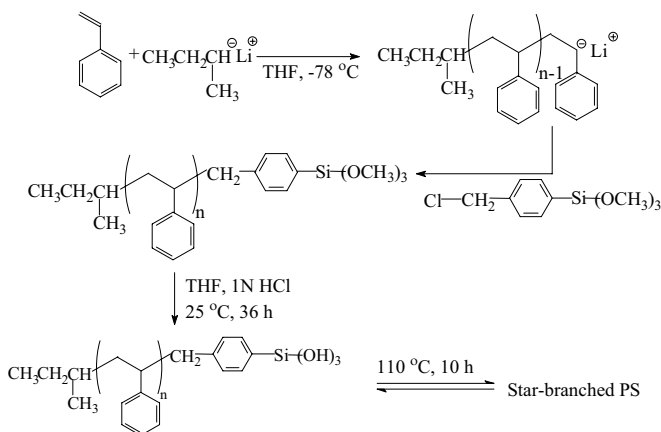
Silicon wafers used as substrates were graciously provided by Hewlett Packard Company. Conc. H₂SO₄, NH₄OH (VWR International), 30% H₂O₂, methanol, and dichloromethane (EMD Chemicals) were used as received. Milli-Q water was used for surface cleaning.

2.2 Synthesis of Trimethoxysilane End-capped Polystyrene

The synthesis of trimethoxysilane end-capped PS was achieved using anionic polymerization of styrene, which was initiated with *sec*-BuLi in THF at -78 °C and subsequently end-capped with a molar excess of CMPTMS as described by Long *et al.*^[10] The functionalized polymers were isolated by precipitation into dry methanol. The polymers were then dried at 100 °C overnight.

2.3 Hydrolysis and Condensation of Trimethoxysilane-Functionalized Polystyrene

Hydrolysis was performed in THF at 20 wt% solids and 1 N HCl solution was added as the catalyst. The reaction mixture was stirred for 24 to 36 h at 25 °C and precipitated into methanol. The polymer was then dried at 100 °C for 12 h. The synthetic scheme for the polymerization, hydrolysis, and condensation is summarized in Scheme 1.



Scheme 1: Synthesis of phenyltrimethoxysilane end-capped PS via living anionic polymerization and subsequent acid catalyzed hydrolysis and condensation to branched PS

2.4 Polymer Characterization

Triple detection size exclusion chromatography (SEC) was used to determine polymer molecular weights and molecular weight distributions using a Waters 171 SEC system with a Waters 2410 refractive index detector, a Wyatt Technology Minidawn MALLS detector, and a Viscotek 270 viscosity detector. The data from the viscosity detector was also used to calculate the branching coefficient (g') for the star-branched polymers. SEC measurements

were performed at 40 °C in THF at a flow rate of 1 mL/min. ¹H NMR and ²⁹Si NMR spectroscopy were obtained on a 400 MHz Varian UNITY using CDCl₃ as the solvent.

2.5 Substrate Treatment

Silicon wafers were cut into 1cm² pieces and sequentially sonicated for 5 min in dichloromethane and methanol. After blowing dry with nitrogen, the wafers were cleaned with NH₃:H₂O₂:H₂O (v/v/v: 1/1/5) at 60 °C for 15 minutes. After copiously rinsing with milli-Q water, the wafers were cleaned in a freshly prepared Piranha solution (conc.H₂SO₄:H₂O₂; v/v: 70/30) at 90 °C for 30 minutes. The wafers were then rinsed with milli-Q water several times, blown dry with nitrogen, and immediately spun cast with the polymer solutions. (*Caution: Piranha solution reacts violently with many organic materials and should be handled with care.*)

2.6 Polymer Brush Preparation

The trimethoxysilane terminated PS and the star PS were dissolved in toluene (1 wt% solution). These polymer solutions were filtered through a 0.2 μm PTFE syringe filter and spun cast at 2500 rpm onto silicon wafers that were cleaned as described above. The wafers were then heated at 145 °C for 24 h to enable the polymer end-groups to react with surface hydroxyls. The wafers were then exhaustively sonicated in toluene to remove any physically adsorbed polymer prior to characterization.

2.7 Surface Characterization

Topographic information on the polymer-modified silicon wafers was obtained using a Digital Instruments Nanoscope III atomic force microscope and software. TAP 300 Si₃N₄ tips with a spring constant of 40 N/m were used and set point to free amplitude ratios of 0.5 to 0.6 were used in the experiments. Static water contact angles on the surfaces were measured in the sessile drop mode on a FTA-125 contact angle goniometer with a syringe-driven droplet. Ellipsometric data were obtained on a Beaglehole ellipsometer with a He-Ne laser ($\lambda=632.8$ nm) and an angle of incidence of 70°. Refractive indices of SiO₂ and PS were determined to be approximately 1.50 in the calculation of polymer layer thickness.

3 RESULTS AND DISCUSSIONS

Living anionic polymerization leads to well-defined polymers and enables quantitative functionalization of the living chain ends with a variety of reactive groups.^[11] Thus, trimethoxysilane functionality was introduced at the polymer chain ends for subsequent silicon surface modification. ¹H NMR and ²⁹Si NMR spectroscopic analyses were used to confirm the yield of the end-capping procedure. After confirming the success of this functionalization approach, a series of molecular weights were targeted as shown in Table 1. It was necessary to add

an excess of CMPTMS in order to quantitatively end-cap the living chain ends.

Table 1: Trimethoxysilane end-capped PS of different molecular weights

[CMPTMS]: [<i>sec</i> -BuLi]	M _n (NMR)	M _n (SEC)	M _w /M _n	% end-capping
1.5:1	3,200	3,590	1.22	99
1.5:1	3,900	3,100	1.27	97
1.5:1	2,900	3,600	1.20	98
10:1	11,000	11,000	1.05	95
10:1	9,200	9,200	1.10	100

The hydrolysis and condensation of linear PS-Si(OMe)₃ resulted in star-shaped polymers. The number of arms in the star-branched polymers was determined from the MALLS SEC M_w of the precursor oligomers and the star polymers. In order to confirm a branched topology, the branching coefficient *g'* was calculated for these polymers from the intrinsic viscosity values obtained from the SEC viscosity detector. The data that were obtained for the linear and the star-branched PS are summarized in Table 2. The low *g'* values confirmed the presence of branching in these polymers, which agrees well with both theory and earlier experimental data for star-shaped polymers.^[12,13] The polymers that are described in Table 2 were synthesized from the same precursor PS (M_w=3,800) and all the polymers obtained had an average of 5-6 arms.

Table 2: Molecular weight data, degree of branching and the calculated number of arms for star branched PS synthesized by hydrolysis and condensation of PS-Si(OMe)₃ of M_w 3,800

Sample name	M _w (SEC)	<i>g'</i> =($[\eta]_{br}/[\eta]_{l}$) _M	Number of arms
PS-3k-linear	3,800	n/a	n/a
PS-24k-star	24,100	0.65	4.2
PS-21k-star	21,700	0.73	3.4
PS-19k-star	18,500	0.68	3.5
PS-18k-star	17,600	0.67	3.5

Tapping mode AFM, contact angle goniometry, and ellipsometry were used to examine surfaces modified with the linear and the star-branched PS. Many earlier studies have described the attachment of hyperbranched polymers, and dendrimers. Star PEO modified surfaces were also recently studied for their protein resistance. Many surface-sensitive techniques such as ellipsometry, contact angle goniometry, and fluorescence microscopy were used to characterize such surfaces; however, information on the surface topography after modification with the star polymers was not reported.^[8,9]

In this study, the “grafting to” approach was used to attach hydrophobic star polymers to Si wafers. The

hydrolysis and condensation of trialkoxysilane-functionalized polymers leads to star-shaped polymers with excess unreacted silanol groups in the core that are capable of reacting with silica surfaces. The synthesis of these star polymers is relatively facile and does not require additional functionalization steps to introduce surface reactive functionality. Thus it was interesting to study these silanol-containing star polymers as surface modifiers and observe differences in the star and linear PS modified surfaces in terms of the surface properties. Water contact angle on polymer modified Si wafers were greater than 90° irrespective of the PS topology, indicating the successful modification of surfaces with the polymers. However, contact angle measurements did not differentiate the linear and star polymer modified surfaces. Thus, AFM analysis was used to examine the surface topography.

AFM images of the Si surface modified with a linear PS (M_w =18,000) and a star PS (M_w =18,500) are shown in Figure 1. Although polymer topology did not influence surface roughness, star polymer modified surfaces exhibited distinct and deeper features than linear polymer modified surfaces. The well-spaced crevices in the topographic image of the star polymer modified surfaces were also observed as distinct mounds in the phase images. The tall features that were observed in the present study were attributed to inadvertent dust particles trapped in the film. The mounds observed in this case resemble mushrooms and were attributed to topology-induced reduction in chain grafting density.

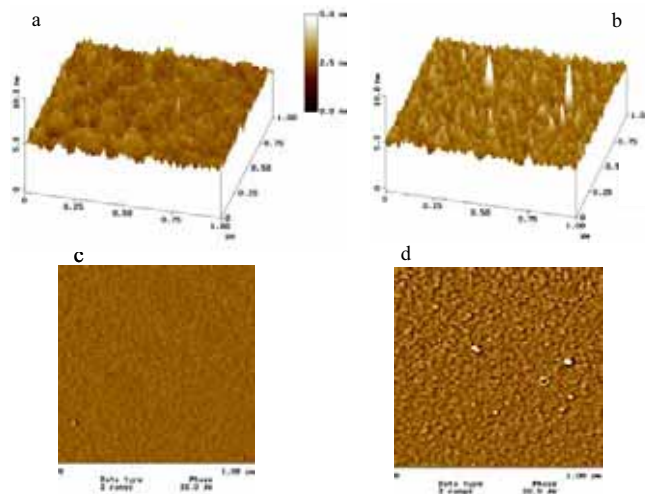


Figure 1: Tapping mode AFM topographic (a&b) and phase (c&d) images on silicon wafers modified with linear [a&c] and star [b&d] PS of M_w= 18,000. Both surfaces show an RMS roughness value of 0.28 nm

In order to prove that the observed topographic features on the star PS modified surfaces corresponded to the mushroom regime, the thickness of the linear and star PS films on Si wafers were compared to their respective radii of gyration (R_g), which was obtained in a good solvent.

Table 3: Comparison of polymer film thickness, and R_g values for linear and star PS

Sample name	R_g (nm)	Ellipsometric thickness (nm)
PS-3k-linear	2.3	4.1 ± 0.1
PS-10k-linear	3.2	7.5 ± 0.1
PS-17k-linear	5.5	10.8 ± 0.1
PS-22k-star	4.2	3.8 ± 0.1
PS-18k-star	3.8	3.2 ± 0.1

As seen in Table 3, the thicknesses of the linear polymer films were nearly double the respective polymer R_g values, which is characteristic of a polymer chain in a moderately stretched brush conformation.^[14] However, the thicknesses of the star PS films were lower than their respective R_g values. In the mushroom regime, the polymer chains have dimensions similar to their unperturbed radii of gyration. Taking into account the swollen dimensions of the polymers in THF, which is a good solvent for PS, the observed similarity in the R_g and thickness values indicated that the star polymers are in the mushroom regime. Although the comparison of polymer chain dimensions on the surface is made to the chain dimensions in a good solvent, the arguments that hold for swollen chains will also be true for unperturbed chains, as in the latter case the chain dimensions are smaller than those of the swollen chains. Any R_g value lower than those shown in Table 3 further asserts the conclusion that the linear chains were stretched and the star polymers deposited as mushrooms. It should also be noted that R_g values from intrinsic viscosity measurements for linear polymers are reliable, but the same does not hold for star polymers.^[15] In order to obtain an estimate of the R_g values for star polymers, a “g” value, where “g” is described as $[\langle R_g^2 \rangle_{br} / \langle R_g^2 \rangle_{lin}]_M$; of 0.5 was assumed, as suggested by Douglas *et al.* and R_g for the star polymers was calculated.^[14] The calculated R_g values were similar to those obtained experimentally. Therefore, it was concluded that the star PS chains were in the mushroom regime.

It is believed that this work represents the first study that shows a comparison of the surface topography of Si surfaces modified with both core-functionalized star polymers and linear polymers of nearly equivalent molar mass. From the present investigation, we conclude that use of core-functionalized star polymers as surface modifiers will lead to surfaces that are modified with polymer chains in a mushroom conformation. Such star polymers deposited as mushrooms can function as adhesion promoters in conjunction with added free chains. Also, it is possible to obtain surfaces with a large number of exposed and

accessible functional groups for further functionalization; this is achieved by controlling the number of arms in the star polymers and the use of functionalized initiators to synthesize the star polymers. Many groups have demonstrated the capability of dendrimers and hyperbranched polymers to function as sensors, nanoscale catalysts, and smart adhesives due to the presence of large number of accessible functional groups. Traditional dendrimer synthesis is relatively more tedious and hyperbranched polymer properties are less well defined. On the other hand, the synthesis of well-defined star polymers is relatively simple and can afford surfaces that have a large number of exposed endgroups.

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