A Robust Method for the Immobilization of Polymer Molecules on SiO$_2$ Surfaces

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ABSTRACT: In this work, we describe the use of hydridosilanes for the attachment of polymer monolayers to SiO$_2$ surfaces. In one approach, first a benzophenone group containing hydridosilane is self-assembled on the SiO$_2$ surface followed by photochemical attachment of polymer chains deposited onto the monolayer. In a second approach an ATRP initiator is self-assembled to the substrate surface, again using hydridosilane anchor groups. The surface-attached initiator groups are subsequently used for the growth of surface-attached polymer chains in a surface-initiated polymerization reaction. It is shown that, while chlorosilanes require rather stringent exclusion of moisture during self-assembly, the hydridosilanes are rather robust and functional monolayers are formed even under ambient conditions. That in turn allows for the use of silanes in standard printing processes. In contrast to printing of chlorosilanes, which must be carried out under strictly anhydrous conditions, printing of hydridosilanes thus represents a simple and versatile technique for the generation of microstructured surfaces.

Introduction

The covalent attachment of organic monolayers is one of the most powerful approaches for the surface modification of metals and metal oxides.[1] Organosilanes with the general formula R$_n$SiX$_{4-n}$ where X is the reactive leaving group have been widely used for surface modification.[2] In general, (mono-, di-, or tri-) chlorosilanes and (mono-, di-, or tri-) alkoxysilanes are most commonly used for surface modification. The obtained monomolecular layers are usually referred to as self-assembled monolayers (SAMs). The SAMs may be viewed as 2-D siloxane networks that are supported by the surface.[3] While such systems are well established there is one inherent problem for practical applications in that chloro silanes and to a lesser extend also alkoxysilanes are quite sensitive to moisture and require rather specific reaction conditions. In addition, the reaction of chlorosilanes with metal oxide surfaces generates hydrochloric acid as the byproduct, which may affect the modified surfaces.

In order to overcome this difficulty, Fadeev, McCarthy, and co-workers have introduced hydridosilanes (HSiR^{1}R^{2}R^3) to modify surfaces.[4−8] In this case, if SiO$_2$ surfaces are used, a covalent bond is formed between the silicon atom of the hydridosilane and the oxygen atom of a hydroxyl group on the surface presumably with the elimination of hydrogen gas as described in Scheme 1. The distinct advantage of hydridosilanes is that they are widely stable even in moist environments and that it is possible to modify the surfaces of many different materials, such as titanium, nickel, aluminum, zirconium, etc.

As the hydridosilane moiety does not permit the presence of many functional groups in the same molecule, so far only few reports are available that describe the use of functional hydridosilanes for surface modification, i.e., of hydridosilanes that carry a second reactive group aside from the Si−H moiety.[5] Such groups would either be used to induce specific interactions

Scheme 1
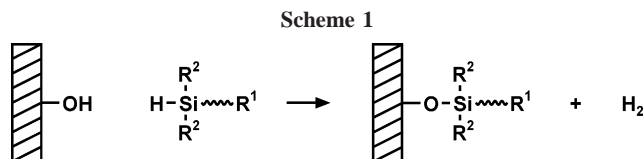
with the environment or act as reactive sites for the attachment of other, more complex groups.

On the other hand it has been shown, that polymer chains, which are covalently attached to the surface of the substrate can be successfully employed to tailor the chemical composition and accordingly the surface properties of materials. As polymer systems can be easily modified through the addition of comonomers, a precise fine-tuning of the chemical surface structure of the polymer films can be obtained. In addition, compared to simple monolayers, higher densities of functional groups can be realized. This is especially important if the latter represent probes that are used for sensor applications.

Moving from small molecules to polymer systems also allows for a much simpler way of determination of the graft density of the surface-attached molecules. Precise values for graft densities are difficult to be obtained for small molecules as the thickness differences between layers having different graft densities are quite small and are usually covered up by variations of the contamination level of the surface. If now, the small molecules are used to attach larger macromolecules, differences in the graft density of the silanization are translated into larger differences in the film thickness and thus any graft density variations are strongly amplified.

Building on experience available in our group we have decided to study two rather different systems that are described in Schemes 3 and 4. The first system makes use of SAMs from silanes that carry a photoreactive group (benzophenone). If these group are deposited, covered with (almost any kind of) polymer and irradiated, a photochemical reaction is triggered that leads to the chemical attachment of some of the polymer chains of

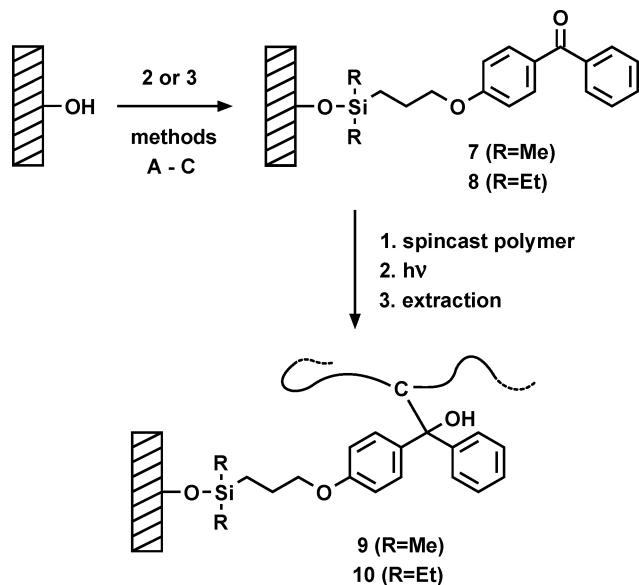* Corresponding author. E-mail: ruehe@imtek.uni-freiburg.de.
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Scheme 2
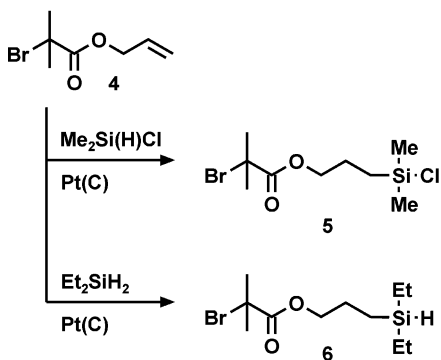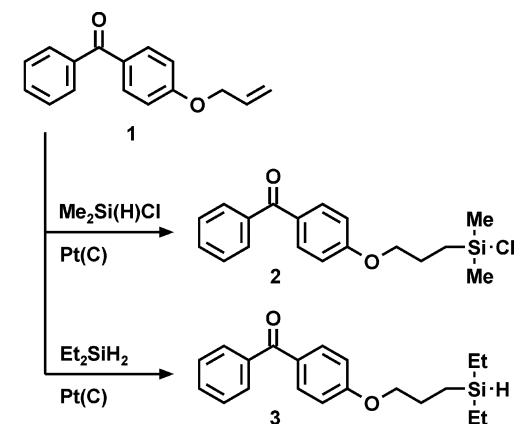
Scheme 3

the overcoat to the surface. All other chains can be washed off and a covalently bound film is left behind. The thickness of this film largely depends on the irradiation time and the molecular weight of the deposited polymers (see Scheme 3).[9,10] The second system is based on SAMs that can be used to trigger a surface-initiated polymerization based on ATRP principles.[11–17] Here ATRP initiators are attached to the surfaces and chains of the desired composition are grown directly on the surface of the substrate. Note that it is not the goal of this study to develop or explore ATRP systems as such, but solely to study the robustness of the process to bind polymer to the surface and use the polymer attachment at the same time to work out differences in the immobilization behavior of chloro- and hydridosilanes under different conditions. The polymerization

Scheme 4
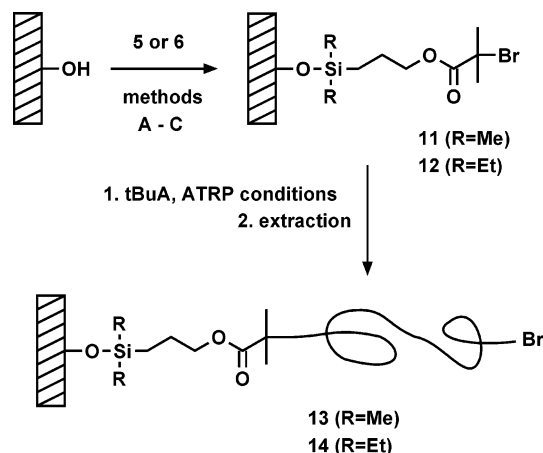
reactions were only used to amplify the graft densities of the silane monolayers obtained from deposition reactions performed under inert conditions or "in an open beaker".

Experimental Section

Materials. *tert*-Butyl acrylate (*t*-BuA), CuBr (99.999%), pentamethyldiethylenetriamine (PMDETA), methyl-2-bromopropionate, acetone, tetrahydrofuran (THF), allyl alcohol, 2-bromoisobutyryl bromide, diethylsilane, dimethylchlorosilane, triethylamine, methanol, toluene, and platinum activated on charcoal (10% Pt/C) were used as obtained (Sigma-Aldrich and Fluka, Germany). The solvents were dried according to standard drying procedures. Triethylamine (Et$_3$N) was distilled over CaH$_2$ prior to use. *t*-BuA was passed through a basic alumina column to remove any traces of acidic impurity. All other reagents were used as received. The polystyrene of known molecular weight which is used for photochemical attachment was used as received from Polymer Standard Service.

Methods. The FT-IR spectra were recorded using a Biorad spectrometer at a resolution of 4 cm^{-1}. NMR was performed using a Bruker (250 MHz) FT-NMR spectrometer using deuterated solvents. Film thicknesses were measured with a DRE−XO2 C ellipsometer operating with a 638.2 nm He/Ne laser at a 70° incident angle. Measurements were obtained on three different spots on each wafer with 3 measurements per spot. Ellipsometric images were recorded using iElli2000 from Nanofilm Technologie GmbH. Molecular weights of the free polymers were analyzed using an Agilent GPC setup. Molecular weights were calculated using software from PSS; calibration was based on low-polydispersity PMMA standards. XPS analysis was performed on a Physical Electronics 5600 spectrometer equipped with a concentric hemispherical analyzer and using an Al Kα X-ray source (15 KeV, filament current 20 mA). The samples were investigated under ultrahigh vacuum conditions (10^{-9}−10^{-8} mbar).

Synthesis of 4-(3-Hydridodiethylsilyl)propyloxybenzophenone. The synthesis of 4-allyloxybenzophenone (**1**) and the corresponding 4-(3-chlorodimethylsilyl)propyloxybenzophenone (**2**) are reported in the literature (Scheme 2).[9] For the synthesis of 4-(3-hydridodiethylsilyl)propyloxybenzophenone (**3**), 4-allyloxybenzophenone (**1**) was placed in a Schlenk tube and 20 mL of freshly distilled diethyl silane was then added along with catalytic amount of 10% Pt/C under nitrogen atmosphere. The resulting mixture was refluxed at 60 °C. The reaction progress was followed by NMR and after completion of the reaction; the excess diethyl silane was removed by vacuum distillation yielding the desired product (**3**). IR (neat): 3053, 3022, 2953, 2872, 2106, 1645, and 1597 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ in ppm): 6.8−7.9 (m, 9**H**, aromatic protons), 3.8−4.0 (t, −OC**H**$_2$−, Si−**H**), 1.7−1.85 (m, 2H, −C**H**$_2$−), 0.6 (m, 6H, −SiC**H**$_2$−), 0.9 (t, 6H, −Si(CH$_2$C**H**$_3$)$_2$−).

Synthesis of (3-(2-Bromoisobutyryl)propyl)diethylhydridosilane. The synthesis of 2-bromo 2-methyl propionic acid allylester (**4**)
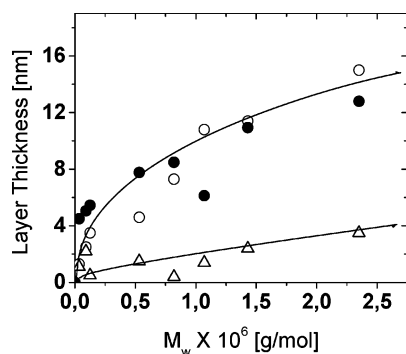
Figure 1. Influence of molecular weight of PS used for spin-casting polymer layers on layer thickness (in nm). Immobilization of the chlorosilane benzophenone layers was performed under ambient conditions (△) or inert atmosphere (●); immobilization of the hydridosilane benzophenone layers was performed in an open atmosphere (○).
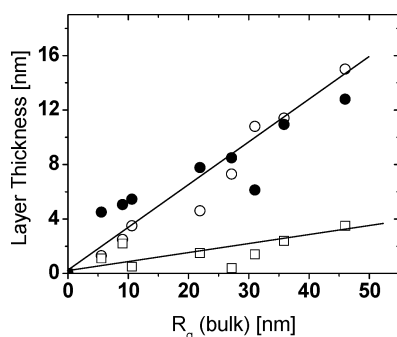

Figure 2. Dependence of polystyrene layer thickness with bulk radius of gyration, R_g, of the polymer used; immobilization of the chlorosilane benzophenone layers were performed under ambient conditions (□) or inert atmosphere (●). Immobilization of the hydridosilane benzophenone layers was performed in an open atmosphere (○).

and the corresponding (3-(2-bromoisobutyryl)propyl)dimethyl-chlorosilane (**5**) are reported in the literature (Scheme 2).[12,13] The allylic ester (**4**) was mixed with 20 mL of freshly distilled diethylsilane (Scheme 2). 20 mg of Pt/C (10% Pt) was added and the mixture was refluxed at 60 °C. The excess diethylsilane was removed under reduced pressure, yielding the silane in quantitative yields as oil. The oil was quickly filtered over anhydrous sodium sulfate to remove the residual catalyst to give the initiator hydridosilane (**6**) as pale yellow oil. IR (neat): 2978, 2993, 2105, and 1737 cm^{−1}. ^{1}H NMR (CDCl$_3$, δ in ppm): 3.8−4.1 (m, 2H, −CH$_2$O−, −Si−H) 1.9 (s, 6H, −CH$_3$−) 1.65−1.8 (m, 2H, −CH$_2$−), 0.8 (m, 6H, −SiCH$_2$−), 0.4 (s, 6H, −Si(CH$_3$)$_2$−).

General Procedures for the Modification of Surfaces with Chloro- and Hydridosilanes. We have immobilized benzophenone moieties and ATRP initiators (with chlorosilyl and hydridosilyl ends) on to the surface of silicon wafer under three different experimental conditions.

(a) Method A: Rigorous Exclusion of Moisture. The silanes were immobilized on SiO$_2$ surfaces by immersing an appropriate substrate into a dilute (typically 10^{-3} M) solution of the silanes in dry toluene under inert atmosphere. A few drops of dry Et$_3$N were added to bind the resulting HCl and to act as a catalyst.

(b) Method B: Ambient Conditions. Solution Deposition. The silanes were immobilized from toluene solutions in the open atmosphere at 80 °C for 18 h. The substrates were then rinsed with toluene, methanol, and acetone and dried in a stream of nitrogen.

(c) Method C. Ambient Conditions. Spin-Casting. The silanes were deposited by spin-casting of a solution of the silane in toluene. The samples were then baked in an oven at 80 °C for 18 h. The wafers were then rinsed with toluene, methanol and acetone to remove any unreacted materials.

Immobilization of Benzophenone Moieties on Silicon Wafers. Precleaned substrates were taken in a Schlenk tube and dried in

vacuum followed by filling with a stream of dry nitrogen (Scheme 3). Dry toluene was added until the substrates were completely covered. 5 mL of benzophenone chlorosilane (**2**) in toluene (0.1 mol/L) was added along with few drops of triethylamine (as an acid scavenger) under inert atmosphere (method A). We have also immobilized benzophenone chlorosilane using method C. After the reaction, the samples (**7**) were rinsed with toluene, methanol and acetone to remove excess of initiator and the byproducts. For benzophenone hydridosilane (**3**), immobilization was performed by spin-casting solution of (**3**) in toluene (0.1 mol/L) at a typical spin speed of 2000 rpm for 1 min (method C). The substrates were then placed in an oven at 80 °C for 18 h for monolayer immobilization. The samples (**8**) were then rinsed with toluene, methanol, and acetone.

Immobilization of ATRP Initiators on Silicon Wafer Surfaces. Precleaned substrates were taken in a Schlenk tube and dried in a vacuum (Scheme 4). After this the Schlenk tube was backfilled with dry nitrogen. Dry toluene was added until the substrates were completely covered and then 5 mL of initiator hydridosilane (**6**) in toluene (0.1 mol/L) was added. The Schlenk tube was covered with aluminum foil and was immersed in an oil bath maintained at 80 °C for 18 h (method B). After the reaction, the samples (**12**) were rinsed with toluene, methanol and acetone to remove the excess initiator and byproducts. For initiator chlorosilane (**5**), immobilization was performed in an inert atmosphere with triethylamine as an acid scavenger (method A) and also immobilized using method B. The samples (**11**) were then rinsed with toluene, methanol, and acetone.

Preparation of Polymer Layers Using the BP Route. Thick overcoats (>100 nm) of polystyrene were prepared by spin-casting a solution of PS in toluene (concentrations of 10 mg mL^{-1}) at a typical spin speed of 2000 rpm for 1 min (Scheme 3; samples **7** and **8**). The samples were dried in air and used directly for illumination experiments. These experiments were performed at room temperature using a high-pressure mercury UV lamp (500 W, Oriel). A water filter (8 cm) was used to remove IR light from the beam, and a dichroitic mirror eliminated short wavelengths with λ < 340 nm. The integral light intensity at the sample location was 100 mW cm^{-2}. After illumination the samples were extracted in a Soxhlet apparatus with toluene for 18 h to remove the nonbonded polymer. The thicknesses of the resulting polystyrene layers (Scheme 3; samples **9** and **10**) were determined again by ellipsometry.

Procedure for Surface-Initiated Atom Transfer Radical Polymerization. To a reaction tube containing the surface functionalized silicon substrate (Scheme 4; samples **11** or **12**) a mixture of *t*-BuA (8 mL, 0.0819 mol), methyl 2-bromopropionate (0.273 mmol), CuBr (0.273 mmol), PMDETA (0.273 mmol), and acetone (2 mL) were added.[18] We have not used any Cu[II]Br as reported in the literature. Instead we use methyl-2-bromopropionate as sacrificial initiator, which will provide necessary concentration of the Cu(II) complex to control the surface-initiated polymerization.[19,20] The polymerization mixture was carefully degassed through several freeze−thaw cycles to remove dissolved oxygen and the polymerization was carried out at 60 °C in an oil bath maintained at this temperature. The silicon substrates (Scheme 4; samples **13** or **14**) were removed from the polymerization mixture after the desired time period rinsed with acetone and dried. Subsequently they were then placed in a Soxhlet apparatus, continuously extracted with THF for 18 h, and dried. The polymer generated in solution by the added sacrificial initiator was recovered by precipitating the reaction mixture into methanol:water (1:1) mixture, filtering and drying in vacuum. For GPC analysis solutions of the polymers were briefly filtered over alumina to remove residual copper complex.

Results and Discussion

The synthesis of the hydridosilanes used in this study was derived from standard procedures of silane synthesis as they are also used for chloro silanes or alkoxysilanes. In all cases olefinic precursors, appropriate silanes and standard hydrosi-
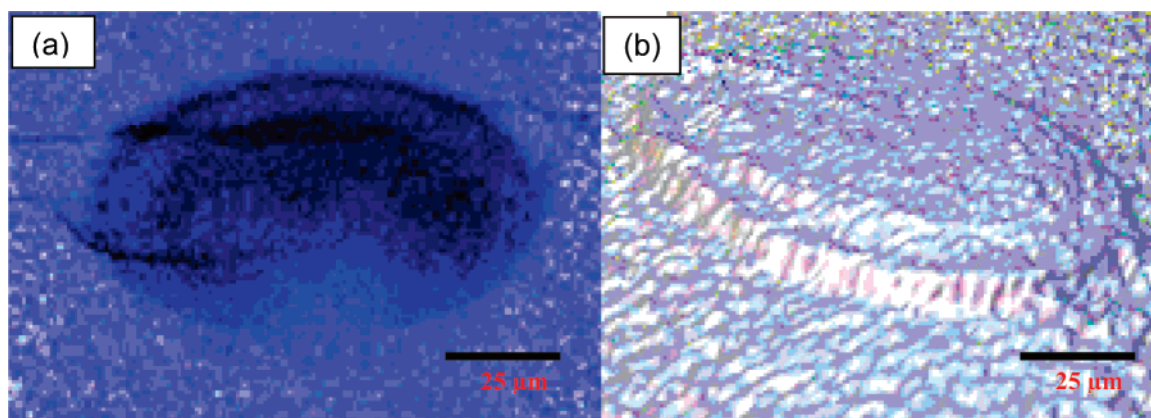
Figure 3. Images of a microstructured silicon wafer using an imaging ellipsometer: (a) 2D-image of the spot of PS layer with thickness of 14 nm; (b) 3D-image of the same spot.

lylation protocols[21] lead to the desired compounds in quantitative yields. However, compared to chlorosilanes, the reaction is much slower for hydridosilanes and a vast excess of silane must be used during the reaction as the silane serves both as reactant and as the solvent. The spectra show that during the hydrosilylation reaction, due to the large excess of the dihydridosilane, the symmetric side product is only formed in negligible amount. This byproduct cannot react during the immobilization reactions and is thus washed away during work up. Besides the somewhat long reaction times for bishydridosilanes (days rather than hours as for chlorosilanes), no general problem was evidenced in the synthesis of functional hydridosilanes. One can very well imagine that in some cases catalysts other than Pt(C) could largely reduce reaction times. However, this was not the focus of our study.

As mentioned in the introduction section, it was our goal to compare the performance of hydridosilanes and chlorosilanes during the self-assembly on a SiO_2 surface. The study mainly aimed at differences in the graft density at layers obtained from hydrido- and chlorosilanes deposited under different reaction conditions. Special emphasis was put on the question as to how rigorously moisture needs to be excluded during the reaction of the silanes with the silanol groups of a SiO_2 surface. After immobilization all samples were used for the attachment of polymers either by photochemical treatment of predeposited layers (benzophenone silanes) or by surface-initiated ATRP (silanes with respective initiator groups). The conditions for these reactions were kept constant for all samples to allow for a comparison of the results of these reactions as a function of the silane and deposition method used during generation of the self-assembled monolayers.

Photochemical Attachment of Polymer Layers. The general procedure for the photochemical attachment of polymers to benzophenone monolayers is described in the literature.[9,10] In brief, a thick polystyrene layer was deposited on the substrates carrying benzophenone monolayers (Scheme 3; **7** and **8**) by spin-casting. Upon irradiation with UV light, the benzophenone moieties absorb light at around 350 nm due to a n,Π* transition. Further radical reactions lead to a covalent attachment of the polymer to the BP-moiety, which in turn is attached to the surface.[9,10] Any nonbonded polymer was removed by Soxhlet extraction with toluene.

In Figure 1, a plot of the thickness of the bound polystyrenes as a function of the molecular weight of the polystyrene used for the film formation is shown. It is observed that benzophenone hydridosilane layers, which were immobilized to the surface by spin-casting (method C) and benzophenone chloro-

rosilane layers, which were immobilized to the surface in an inert atmosphere (method A) with triethylamine as an acid scavenger give comparable results. In contrast to this, the corresponding chlorosilane benzophenone layer which is immobilized under ambient, i.e., not waterfree, conditions (method C as in the case of hydridosilane) shows little to no attachment of polymers. This clearly demonstrates that immobilization of chlorosilane benzophenone by spin-casting without triethylamine leads to poor monolayers which subsequently affects photochemical attachment of polystyrene layers. This is further confirmed by the relationship between the bulk radius of gyration of polystyrene (R_g) and the layer thickness, shown in Figure 2, which shows a linear relation. The bulk radius of gyration is calculated from the average molecular weight of the polymer (M_w) using the equation,[22,23]

$$R_g = 0.03 \sqrt{M_w} \text{ [nm]} \tag{1}$$

While this linear relationship can be observed in case of the chloro silane deposited via method A and the hydridosilane deposited via method C, no such correlation is obvious for the chlorosilane which was simply spin-casted (method C).

The moisture sensitivity of the monolayer formation is especially important when it is attempted to print the silanes in needle-printer or ink-jet print processes as such printing processes cannot be easily performed under inert conditions. In the experiments described here the silane was deposited on a precleaned silicon wafer using a microarray printer which was typically used for the preparation of DNA chips and protein chips. After printing, the silicon wafer was heated in an oven at 80 °C for 18 h for monolayer attachment. The silicon wafers were then rinsed with toluene, methanol and acetone and dried in a stream of nitrogen. Subsequently, these substrates were coated with polystyrene (M_w = 2 350 000) and irradiated with UV light as mentioned above. The substrates were then subjected to Soxhlet extraction to remove the nonbonded polymer and characterized using an imaging ellipsometer. Figure 3 shows the images of one particular spot in the microarray. Clearly the polymer is only bound in the areas at which the hydridosilanes were deposited using the needle printer and no polymer is found in all other areas. Image analysis revealed a thickness of 14 nm which is consistent with the values obtained from the above-mentioned investigations on SAMs covering the entire substrate. In contrast to this result obtained from printed arrays of hydridosilane benzophenone we did not succeed in generating similar polymeric arrays by printing the chlorosilane analog in the same way followed by polymer attachment
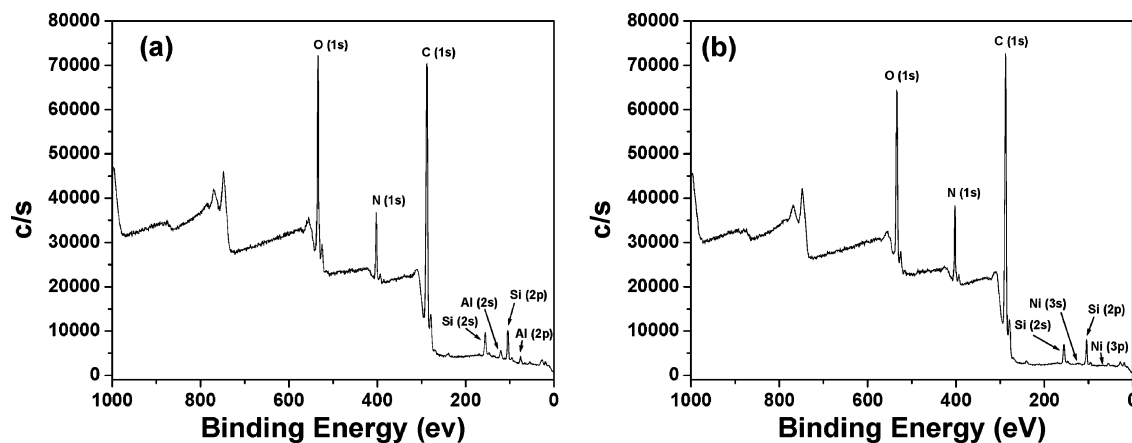
Figure 4. X-ray photoelectron spectra of poly(*N,N'*-dimethylacrylamide) (PDMAAm) layer on (a) an aluminum surface and (b) a nickel surface

reaction. These results directly visualize the advantage of the superior robustness of the hydridosilane based process compared to that based on chlorosilane derivatives.

It is also possible to immobilize hydridosilanes to a wide variety of surfaces. As an example, we have immobilized hydridosilane benzophenone to aluminum and nickel surfaces. Then we have photochemically attached poly(*N,N'*-dimethylacrylamide). Figure 4 shows X-ray photoelectron spectra of poly(*N,N'*-dimethylacrylamide) attached aluminum and nickel surfaces, which prove the presence of the polymer.

Surface-Initiated ATRP. In a second set of experiments we have also studied as to how appropriate functional hydridosilanes can be used to grow polymer brushes using ATRP protocols. In order to be able to compare results also to data known from the literature we have chosen a system that is well established for *t*-BuA polymerization in solution.[18] Again the ATRP initiator silanes were deposited following the methods A and B as outlined above. The ATRP initiator modified silicon wafer (Scheme 4; **11** and **12**) were thoroughly rinsed with toluene, methanol and acetone and dried in vacuum.

Growth of Poly(*t*-BuA) Brushes. The ATRP reactions of *t*-butyl acrylate were carried out from the modified silicon wafers (**11** and **12**) as described in the experimental section. Methyl-2-bromopropionate was added as the free initiator to control the polymerization. The addition of the free initiator creates the necessary concentration of the Cu(II) complex, which in turn controls the polymerization from the substrate as well as in solution.[19,20] The substrates (**13** and **14**) were removed from the polymerization tube at desired time intervals, rinsed with acetone, and then extracted in THF for at least 18 h in a Soxhlet apparatus to remove any nonbound polymer. Control experiments carried out under exactly the same polymerization conditions but with blank wafers proved, that the entire free polymer (formed by the free initiator) could be removed from the surface during the subsequent extraction procedures.

The layer thicknesses of the polymer brushes are plotted as a function of polymerization time in Figure 5. An increase in the film thickness with time is observed in the case of ATRP initiator chlorosilane (immobilized under inert conditions) and ATRP initiator hydridosilane (immobilized under ambient conditions). No such correlation is observed for chlorosilane ATRP initiator which is immobilized under ambient conditions.

As in other ATRP reactions, we observed control over the thickness, molecular weight, and polydispersity values, which is evident from Figure 6 and Figure 7. The molecular weight and polydispersity index of the free polymer formed in the solution was plotted against polymerization time as shown in Figure 6. This shows a linear relationship with respect to time
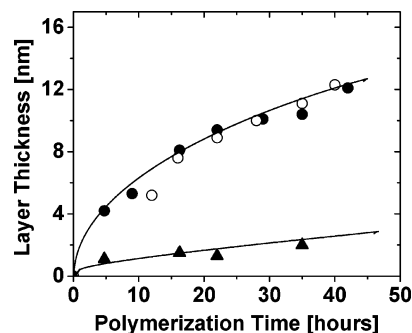

Figure 5. Thickness of P(*t*-BuA) brushes obtained by surface-initiated polymerization as a function of reaction time; polymer brushes from chlorosilane ATRP initiator immobilized in an inert atmosphere (○) and hydridosilane ATRP initiator in an open atmosphere (●). (▲) polymer brushes from chlorosilane immobilized in an open atmosphere. Conditions: CuBr/PMDETA/methyl-2-bromopropionate/tBuA = 1/1/1/300.

indicating that the concentration of the propagating species is constant during the course of polymerization. The polydispersity values (M_w/M_n) are fairly low and constant throughout the polymerization reaction indicating that the polymerization is well controlled for both cases in which brushes could be obtained.

If now the film thicknesses of the obtained monolayer are plotted as a function of the molecular weight of the free polymer, a linear relationship is observed as shown in Figure 7. As the film thickness increases linearly with M_n of the free polymer it suggests that the M_n of the grafted polymer is very similar to or at least proportional to that of the free polymer. This linear relationship between molecular weight, film thickness and time also demonstrates that under the reaction conditions described here, good control of the polymerization process is achieved. The average graft density of P(*t*-BuA) brush grafted using hydrido silane ATRP initiator was found to be 0.39 μmol/m^2 [0.23 chains/nm^2] and the corresponding graft density of P(*t*-BuA) brush from chlorosilane ATRP initiator was found to be 0.42 μmol/m^2 [0.26 chains/nm^2]. All these details confirm that using an hydridosilane-based ATRP initiator, which has been immobilized under ambient conditions, it is possible to grow polymer brushes in a controlled fashion just as with the ATRP initiator chlorosilane (immobilized under inert conditions). Again, only very thin polymer layers were obtained if the ATRP initiator chlorosilane was immobilized under ambient conditions. This clearly reveals the higher stability of hydrido silanes as compared to the chloro silane derivatives under ambient conditions.
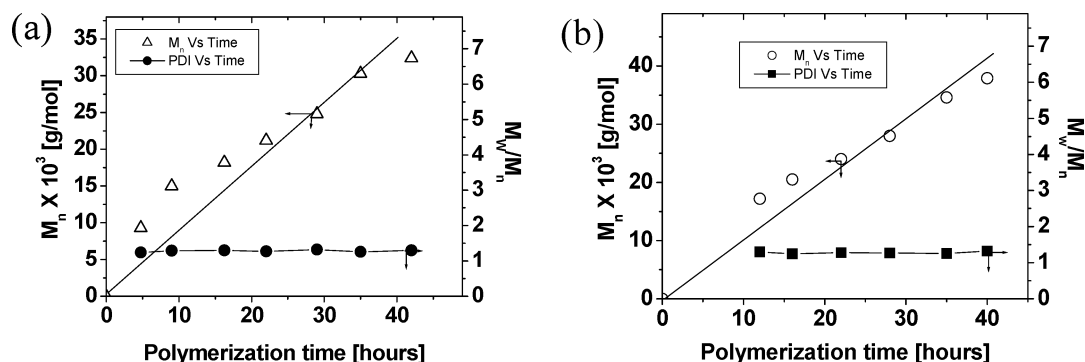
Figure 6. Molecular weight (M_n) and polydispersity (M_w/M_n) of the free polymer as a function of polymerization time. Brushes were grown on an SiO$_2$ surface using a selfassembled monolayer of an ATRP initiator (a) with a chlorosilane group and (b) with a hydridosilane group.
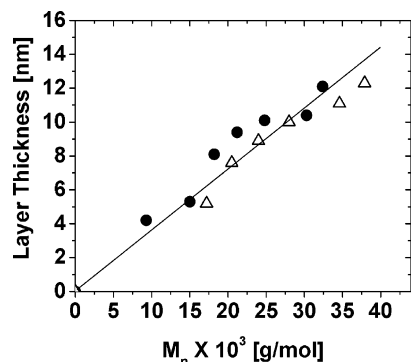

Figure 7. Correlation of the monolayer film thickness with the molecular weight (M_n) of free P(*t*-BuA) produced by the sacrificial initiator in solution; polymer brushes from chlorosilane ATRP initiator immobilized in an inert atmosphere (●) and hydridosilane ATRP initiator in an open atmosphere (△).

Conclusions

We have used hydridosilane chemistry to generate polymer monolayers covalently attached to oxidic surfaces. To this we have successfully introduced benzophenone groups via the hydridosilane route for the photochemical attachment of polymers and ATRP initiators to grow polymers from the surface. Hydridosilanes give almost identical results as the corresponding chlorosilane derivatives as far as the immobilization process and the subsequent transformation reactions are concerned. However, in contrast to conventionally used chlorosilanes the immobilization reaction for the hydridosilanes can be carried out in the presence of moisture while chlorosilanes are highly sensitive to the presence of water and need to be reacted under more or less strictly inert conditions. The robustness of the hydridosilane process allows for the deposition of silane monolayers using rather simple printing protocols under ambient conditions, which in turn allows for a very simple generation of microstructured surfaces and the deposition of (functionalized) polymers with high spatial resolution.

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