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Polymer Brushes Grafted to "Passivated" Silicon Substrates Using Click Chemistry

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We present herein a versatile method for grafting polymer brushes to passivated silicon surfaces based on the Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition (click chemistry) of ω-azido polymers and alkynyl-functionalized silicon substrates. First, the "passivation" of the silicon substrates toward polymer adsorption was performed by the deposition of an alkyne functionalized self-assembled monolayer (SAM). Then, three tailormade ω-azido linear brush precursors, i.e., PEG$-$N$_3$, PMMA$-$N$_3$, and PS$-$N$_3$ ($M_n \sim$20 000 g/mol), were grafted to alkyne-functionalized SAMs via click chemistry in tetrahydrofuran. The SAM, PEG, PMMA, and PS layers were characterized by ellipsometry, scanning probe microscopy, and water contact angle measurements. Results have shown that the grafting process follows the scaling laws developed for polymer brushes, with a significant dependence over the weight fraction of polymer in the grafting solution and the grafting time. The chemical nature of the brushes has only a weak influence on the click chemistry grafting reaction and morphologies observed, yielding polymer brushes with thickness of ca. 6 nm and grafting densities of ca. 0.2 chains/nm^2. The examples developed herein have shown that this highly versatile and tunable approach can be extended to the grafting of a wide range of polymer (pseudo-) brushes to silicon substrates without changing the tethering strategy.

Introduction

The modification and the control of surface properties using tailored macromolecular architectures are essential in many industrial processes and fundamental studies.[1,2] Such architectures include covalently anchored polymer brushes which are generally prepared using mainly two strategies, i.e., "grafting-to" and "grafting-from".[3,4] Whereas the "grafting-from" approach allows for the elaboration of a wide range of polymer brushes with high grafting densities, a common mismatch between the brushes and the polymer simultaneously grown in the bulk requires a rigorous characterization of the brushes after grafting. Whereas it yields to limited thickness/grafting density, the "grafting-to" approach takes advantage of the well-known structure of the linear brush precursors. Several tethering methods have been reported in the literature in order to graft polymer brushes to silicon substrates. They generally involve two steps in order to first introduce the required functionalities on the substrate and the brush precursors, with the grafting procedure being performed in a second step. Most examples involve the reaction between silanols from the silicon wafer surface and ω-(tri)chlorosilane, ω-(tri)hydroxy-, or ω-(tri)alkoxysiloxane polystyrene, and monomethoxy-poly-

(ethylene glycol) linear precursors.[5−11] Other classical grafting pathways include esterification, condensation, or amidation reactions between of ω-functionalized polymers and silanols covering silicon wafers or functionalized SAMs.[1,12−15] The grafting is generally performed in solution or in melt, with the latter requiring long annealing times but yielding higher grafting densities. The main limitation of these systems consists of the limited range of brush variety synthetically accessible. Also, even if easily processable these grafting methods do not prevent the adsorption of the brush and linear precursors, which reduces the grafting density of the resulting brushes. Such "passivation" toward polymer adsorption has been successfully performed using a vinyl-functionalized SAM and taking advantage of the grafting of SiH-terminated polymers by Pt-catalyzed hydrosylation.[16,17] Such a system has been extensively applied to poly(dimethyl siloxane) brushes by Leger et al.,[18−20] in order to study the

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molecular dynamics and the friction at interfaces. Yang et al.[21] developed a similar approach to tether poly(methylhydrosiloxane) and derivatives to silicon substrates. Also, Maas et al.[22] tethered vinyl-terminated polystyrene brushes to hydrogen-functionalized silicon substrates in melt. Another efficient method consists of using a pseudo-brush layer made of functional polymers able to react covalently with the substrate and subsequently with the brush linear precursor chain ends. For example, Luzinov et al.[23–25] tethered monomethoxy-poly(ethylene glycol) and ω-hydroxy polystyrene in the melt to a primary layer of poly(glycidyl methacrylate) and epoxydized polybutadiene, respectively.

This brief overview on linear polymer brushes grafted to silicon substrates clearly points out that grafting strategies are generally only applicable to a narrow range of brush variety. Moreover, the functionalities eventually carried by the polymer backbone can alter the efficiency of the grafting reactions. The main limitation of these methods resides on their specificity and the need to re-adapt constantly the grafting strategies according to the brush chemical nature. New "grafting-to" procedures are therefore needed in order to perform the grafting of a wide range of (functionalized) polymer brushes in different reaction media without changing the tethering strategy. These new methods should be efficient, tunable, and easy to process. Also, the "passivation" of the substrate toward the adsorption of brush precursors might be required when studying polymer brushes able to adsorb to the substrate, e.g., PMMA, PDMS, or PEG.[19,20]

With respect to these requirements, we present herein a versatile and tunable "grafting-to" approach based on click chemistry, an advanced synthetic pathway originally developped by Sharpless et al.[26,27] The most studied and reliable click reaction to date is based on the Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition of an azide ($R-N_3$) and an alkyne ($R-C\equiv CH$). The facility to introduce these functional groups and the high-yielding click coupling recently produced increased attention from several research groups focusing on materials design.[28–35] Indeed, this reaction proceeds with high yields under mild conditions, shows tolerance to water, oxygen, and surrounding functionalities, and can be performed in a wide range of media including protic and aprotic solvents. Moreover, the resulting 1,4-disubstituted 1,2,3-triazole ring is thermally stable and relatively inert to hydrolysis, oxidation, and reduction. The numerous advantages of click chemistry and its previous applications to surface modification represent important assets to develop an efficient and versatile strategy for the grafting of a wide range of polymer brushes with

Scheme 1. Click Chemistry Grafting of Polymer Brushes to "Passivated" Silicon Substrates
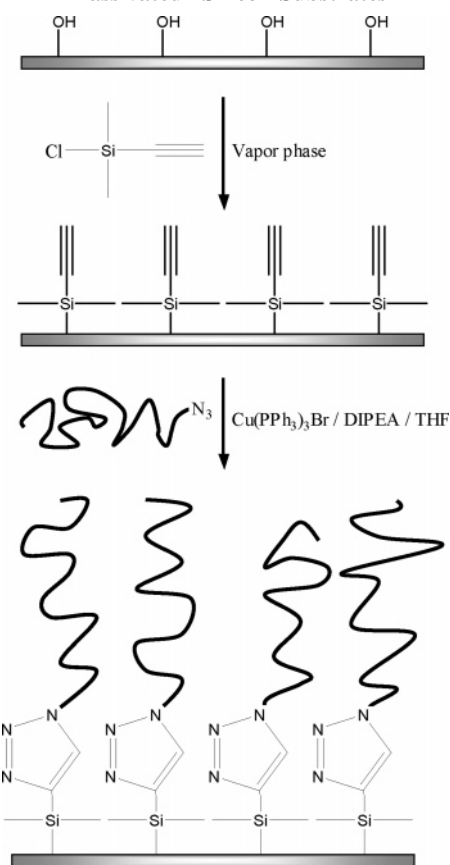
tunable properties using a single synthetic strategy.[36–42] The click chemistry "grafting-to" approach presented herein requires two steps (Scheme 1). First, silicon wafers are "passivated" by the deposition of a self-assembled monolayer (SAM) of a monochlorosilane bearing an alkyne functionality. Then, the click chemistry grafting process relies on the Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition between ω-azido linear polymers and alkynes from the silicon substrates. To illustrate the versatility of this general "grafting-to" approach, the grafting of three tailormade polymer brushes was studied, i.e., ~20 000 g/mol polystyrene (PS), poly(ethylene oxide) (PEO), and poly(methyl methacrylate) (PMMA), with the latter two being known to interact strongly with crude silicon substrates.

Experimental Section

Materials. Ethynyldimethylchlorosilane (EDMS, **1**) and 2,2,5-trimethyl-3-(1-(4′-chloromethyl)phenylethoxy)-4-phenyl-3-azahexane (**2**) were synthesized as describe previously.[43,44] Monomethoxy-

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poly(ethylene glycol) (**6**) (M_n = 20 000 g/mol, PDI = 1.05) was purchased from Polymer Source and used as received. Methyl methacrylate (Aldrich, 99%) and styrene (Acros, 99%) were distilled over calcium hydride. All other reagents and solvents were purchased from Aldrich and used as received. Silicon wafers (orientation 100, 525 μm thick with a SiO_2 layer of thickness 1.7 nm) were purchased from Freiberger Elektronikwerkstoffe GmbH (Germany).

Characterization Methods. Monomer conversions were determined by ^1H NMR (Bruker 300 MHz) in $CDCl_3$. SEC experiments were performed in tetrahydrofuran at 22 °C and a flow rate of 0.5 mL/min using a system equipped with a Waters 410 differential refractometer, PLGel mixed C column (internal diameter 7.8 mm, length 30 cm). Number average molecular weights (M_n) and polydispersity indices (PDI) were calculated using calibration curves obtained from polystyrene, poly(methyl methacrylate), and poly-(ethylene glycol) standards. FTIR spectra were taken on a Perkin-Elmer FT-IR Spectrometer. Film thickness was measured with a UVISEL spectroscopic ellipsometer (Horiba Jobin Yvon) at a fixed angle of incidence of 70°, on at least five different places on the sample. A three-layer model ($Si + SiO_2$ + brushes) was used to simulate experimental data. Brush thickness values were obtained from the best Cauchy fits using the refractive index of bulk polymers (n = 1.45, 1.49, and 1.59 for PEG, PMMA, and PS, respectively). For the calculation of the grafting densities, the densities of the anchored polymers were assumed to be identical to the bulk values (ρ = 1.05, 1.19, and 1.13 g/cm^3 for PS, PMMA, and PEG, respectively). Advancing water contact angles were measured by the sessile drop method using a GBX Digidrop Contact Angle Meter equipped with a CDD 2/3" camera. The tabulated results are averages of at least five measurements on different parts of each sample. SPM images were obtained under ambient conditions in both height and phase contrast modes using a Veeco Nanoscope IIIa in the tapping mode.

General Procedure for the Synthesis of ω-Azido Polystyrene Using NMRP, 3. A solution of alkoxyamine **2** (79 mg, 0.21 mmol) in styrene (6.0 g, 58 mmol) was degassed by three freeze−pump−thaw cycles before being sealed under vacuum. After 7 h at 123 °C, the polymerization media was diluted in dichloromethane, precipitated twice in heptanes, and dried, and ω-chloropolystyrene was recovered as a white powder (Y = 65%, M_n = 18 800 g/mol, PDI = 1.08). This powder (3.3 g, 0.17 mmol) and NaN_3 (112 mg, 1.73 mmol) were dissolved in dimethylformamide (10 mL), and the mixture was stirred in the dark for 24 h at room temperature. The reaction mixture was then filtered, concentrated, and precipitated twice from dimethyl-formamide in water. ω-Azido polystyrene, **3**, was freeze-dried from benzene and recovered as a white powder (Y = 95%, M_n = 18 700 g/mol, PDI = 1.10).

General Procedure for the Synthesis of ω-Azido Poly(methyl methacrylate) Using ATRP, 5. A solution of CuBr (15 mg, 0.11 mmol) and bipyridine (33 mg, 0.21 mmol) in methyl methacrylate (4.65 g, 46.5 mmol) and a solution of p-toluenesulfonyl chloride (39 mg, 0.21 mmol) in diphenyl ether (5 mL) were deoxygenated by argon bubbling for 90 min. The reaction flask containing the monomer, catalyst, and ligand was heated to 90 °C, and the initiator solution was transferred via cannula. After 18 h at 90 °C, the polymerization media was diluted with dichloromethane, passed through a short column of neutral alumina, and precipitated twice in heptanes. After freeze−drying from benzene, ω-chloropoly(methyl methacrylate) was recovered as a white powder (Y = 50%, M_n = 20 700 g/mol, PDI = 1.20). This powder (2.3 g, 0.11 mmol) and NaN_3 (73 mg, 1.12 mmol) were dissolved in dimethylformamide (10 mL), and the mixture was stirred in the dark for 24 h at room temperature. The reaction mixture was then filtered, concentrated, and precipitated twice in distilled water. ω-Azido poly(methyl methacrylate), **5**, was then freeze-dried from benzene and recovered as a white powder (Y = 96%, M_n = 20 900 g/mol, PDI = 1.20).

General Procedure for the Synthesis of ω-Azido Poly(ethylene glycol), 7. Methanesulfonyl chloride (35 mg, 0.31 mmol) was added dropwise to a solution of monomethoxy-poly(ethylene glycol) (**6**) (M_n = 20 000 g/mol, 2.5 g, 0.12 mmol) in dry tetrahydrofuran (30 mL). The mixture was cooled at 0 °C, and a solution of triethylamine

(32 mg, 0.31 mmol) in dry tetrahydrofuran (10 mL) was added dropwise over 30 min, forming a white precipitate. After 30 min, the ice bath was removed and the mixture was left to stir at room temperature for 18 h. Water (30 mL) was then added, tetrahydrofuran was evaporated under reduced pressure, and $NaHCO_3$ was added until pH = 8. NaN_3 (203 mg, 0.31 mmol) was added (*Caution! Explosive and toxic HN_3 forms if NaN_3 is added to an acidic solution*) and the reaction mixture was then heated to 60 °C for 24 h in the dark. The reaction was then cooled down to room temperature, and water was removed under vacuum. The polymer was dissolved in dichloromethane, filtered, and the solvent was removed under reduced pressure. ω-Azido poly(ethylene glycol), **7**, was then freeze−dried from benzene and recovered as a white powder (Y = 98%, M_n = 20 200 g/mol, PDI = 1.05).

General Procedure for the Deposition of an Alkyne Functionalized Self-Assembled Monolayer on Silicon Substrates. Silicon wafers were immersed in a piranha solution (7:3 H_2SO_4/H_2O_2) at 80 °C for 15 min and then rinsed with ultrapure water (resistivity ∼ 18 MΩ·cm) and dried with a stream of nitrogen. (*Caution! Piranha solution is a strong oxidant and should be handled with appropriate care*.) Alternatively, substrates were placed under UV/ozone etching for 30 min at room temperature. A few drops of EDMS (**1**, bp = 37−42 °C) were injected in a vial next to the etched silicon substrate placed in a flat-bottom reactor under argon. The reactor was then maintained under static vacuum (ca. 0.8 atm) in order to evaporate EDMS and to allow its condensation with the silanol groups from the surface of the silicon wafer, yielding an EDMS monolayer. The reaction was performed at the solid/vapor interface without any contact between EDMS and the silicon wafer. Reactions were carried out at room temperature for 3 h. The modified wafers were then rinsed with chloroform and dried under nitrogen stream before being involved in the grafting step.

General Procedure for the Grafting of Polymer Brushes by Click Chemistry in Tetrahydrofuran. Alkynyl-passivated silicon wafers were immersed in a solution of ω-azido polystyrene (50 mg, 0.0026 mmol of N_3, 0.6 wt %), Cu(PPh$_3$)$_3$Br (0.2 mg, 0.1 equiv of N_3), and DIPEA (1 mg, 3 equiv of N_3) in tetrahydrofuran (10 mL). After 24 h at 60 °C, the substrates were immediately rinsed by a Soxhlet extraction using chloroform to remove unreacted polymer and catalytic system before being dried under a stream of argon.

Results and Discusion

"Passivation" of Silicon Substrates with an Alkyne-Functionalized SAM. The first step to develop this general "grafting-to" approach was to introduce the dual functionalities of click chemistry, i.e., alkyne (R−C≡CH) and azide (R−N$_3$), at the silicon surface and at the chain end of the linear brush precursors. Previously reported systems involving click chemistry on silicon substrates are mainly based on azide-functionalized substrates.[39,45−48] An approach involving the grafting of bio-molecules to an alkyne-functionalized SAM anchored to 2D silicon substrates has been previously developed by Becker et al., but the morphology and the grafting kinetics were not studied.[49,50] Considering these previous studies and the poor stability of azides toward UV irradiation, alkyne functionalities were chosen to be introduced on the substrate by condensing ethynyldimethylchlorosilane (EDMS, **1**) with silanols from the surface of silicon wafers (Scheme 1).[43] Also, the use of a monochlorosilane allowed for the elaboration of a SAM having a better homogeneity than trichlorosilanes. The passivation step

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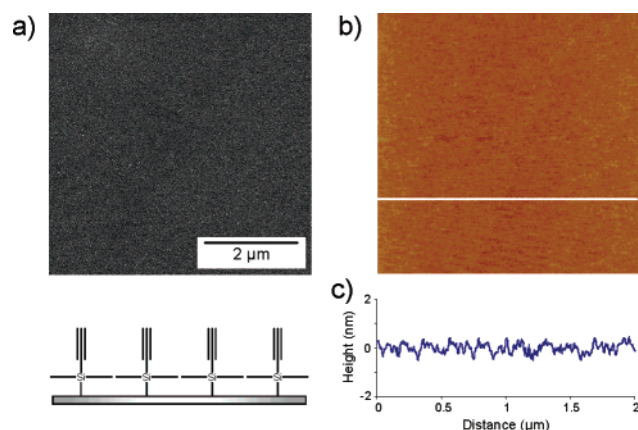
Figure 1. (a) SEM, (b) SPM height image (2×2 μm), and (c) section profile of alkyne functionalized SAM of EDMS (**1**).

was performed either in solution or in the vapor phase, with the latter being preferred as it provides substrates with an enhanced homogeneity. Before being involved in the grafting process, the SAM was characterized by ellipsometry, scanning electron microscopy (SEM), scanning probe microscopy (SPM), and water contact angle measurements.

The effectiveness of the passivation was first evidenced by the increase of the water contact angles on alkynyl functionalized SAMs ($\theta_a \sim 85°$) compared to those on silicon substrates cleaned by either piranha or UV/ozone etching ($\theta_a \sim 20°$ and $40°$, respectively). The SAM of a short silane such as EDMS is not bulky enough to allow a complete "passivation" of the underlying silicon wafer, since $\theta_a > 90°$ are not reached. The low value of hysteresis of the passivated substrate ($\Delta\theta \sim 0.5°$) reflected the macroscopic homogeneity of the SAM, whereas SEM excluded the presence of micrometer-sized aggregates (Figure 1a). At smaller length scale, SPM height image (Figure 1b) and phase image (not shown) further confirmed the good homogeneity of the SAM. Indeed, the surface roughness is in the subnanometer range resulting from the versatile vapor-phase deposition of a monofunctional chlorosilane. The modified surface exhibits texture arising from the incomplete coverage of the surface with EDMS.[51] The grafting density of the SAM ($\sigma = 1.8$ chains/nm^2) was calculated from the thickness obtained by ellipsometry ($h = 0.4 \pm 0.1$ nm). Assuming that the density of the SAM is the same as in bulk (i.e., 0.85 g/cm^3), the grafting density of alkyne functionalities is far above the highest grafting density expected by the "grafting-to" technique (ca. 0.5 chains/nm^2).[3]

Synthesis of ω-Azido Linear Brush Precursors. PEG, PMMA, and PS are among the most studied polymer brushes grafted to silicon substrates, either for practical applications or for fundamental studies.[7,20,21–25,52–58] Their different chemical and physical properties (hydrophilic, hydrophobic, semicrystalline, or amorphous) and their different manners of interacting with silicon substrates made them very attractive for this study. To establish the potential versatility of this click chemistry promoted general "grafting-to" approach, three ω-azido linear

Scheme 2. Synthesis of ω-Azido Linear Brush Precursors
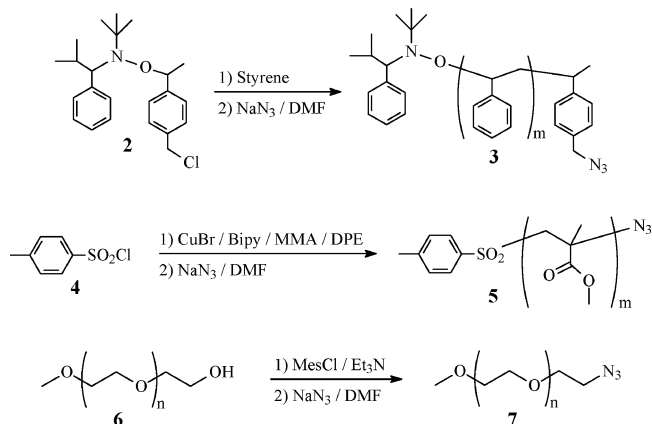
PEG, PMMA, and PS having a number average molecular weight of $\sim$20 000 g/mol were prepared by adapting synthetic procedures previously reported in the literature (Scheme 2).[44,48,59,60] Indeed, tailored ω-chloro PS and ω-bromo PMMA made, respectively, by nitroxide-mediated radical polymerization (NMRP) and atom transfer radical polymerization (ATRP) were converted to ω-azido PS (**3**) and ω-azido PMMA (**5**) by straightforward substitution of the halogen chain end by an azide group using NaN$_3$ in dimethylformamide. A similar procedure was used to convert the mesylate of monomethoxy-poly(ethylene glycol) (**6**) to the corresponding ω-azido PEG (**7**). SEC traces evidenced the absence of chain end coupling reactions during the azidation step, resulting in well-defined ω-azido polymers (Figure 2). The
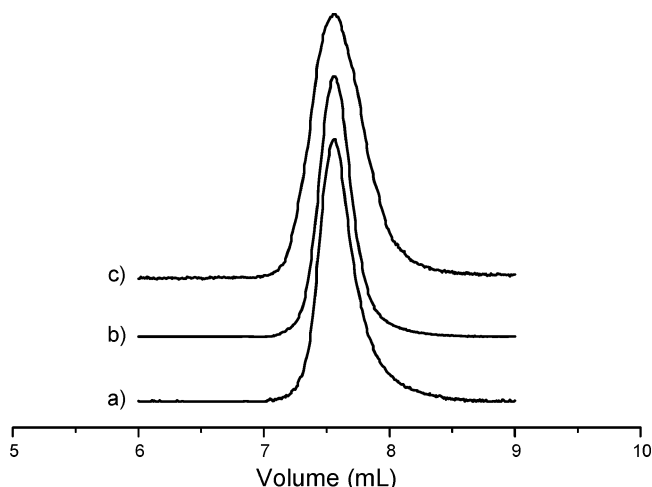

Figure 2. SEC traces of ω-azido (a) PEG, (b) PS, and (c) PMMA brush precursors.

presence of the characteristic absorption band of azides at 2100 cm^{-1} was confirmed by FTIR. ^{1}H NMR revealed the complete disappearance of the halogenated chain ends of polystyrene and poly(methyl methacrylate) linear precursors. In the case of PEG, the absence of mesylate and hydroxyl chain ends was verified by ^{13}C NMR. Whereas limited herein to $\sim$20 000 g/mol, the molecular weight of the brush precursors could be easily tuned from ca. 5000 to 100 000 g/mol using the synthetic procedures described above.

Grafting of Polymer Brushes to Alkyne-Functionalized Silicon Substrates Using Click Chemistry. Click chemistry

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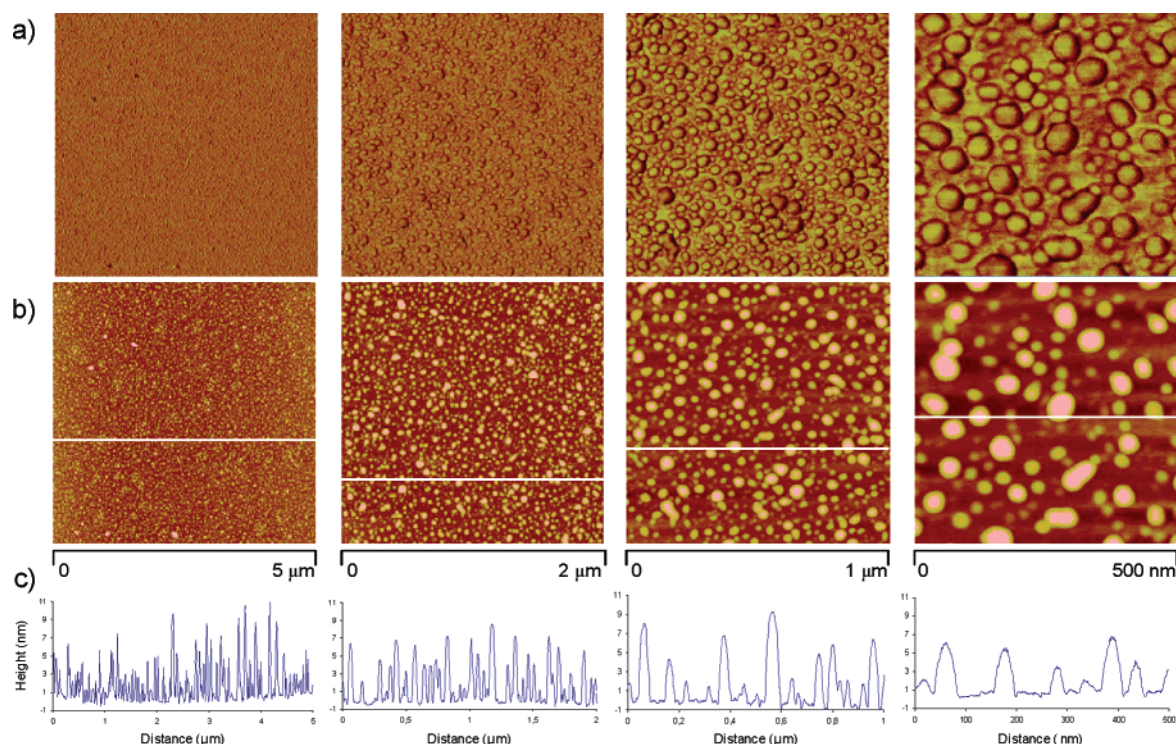
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Figure 3. SPM (a) phase image, (b) height image, and (c) cross section of PEG brushes grafted by click chemistry for 24 h at 60 °C and 2.7 wt % in tetrahydrofuran.

offers significant advantages for the grafting of polymer brushes to planar silicon substrates. One of them is the opportunity to graft a wide range of ω-azido (functional) polymers using a single versatile and tunable strategy. To demonstrate the potential of this approach, the grafting of polymer brushes by the click chemistry coupling between the ω-azido linear polymers and alkynyl-functionalized silicon wafers described in the above sections was studied (Scheme 1). Herein, the grafting was performed at 60 °C in tetrahydrofuran (THF), using $Cu(PPh_3)_3$-Br and DIPEA as a classical organo-soluble catalytic system. This media is suitable to solubilize the whole catalytic system as well as the considered polymers. The study of grafting reactions performed in water and in melt will be reported elsewhere.

Grafting of PEG Brushes. The grafting of PEG brushes on alkyne-functionalized silicon wafers was initially investigated in THF at 60 °C for 24 h using a polymer weight fraction of 2.7 wt % (25 mg/mL). After removal of any adsorbed species by Soxhlet extraction, a first evidence of the success of the grafting was the significant shift of the water contact angles which decreased from $\theta_a \sim 85°$ for alkyne-functionalized silicon wafers to $\theta_a \sim 62°$ for the tethered PEG brushes. It should be restated that the methoxy chain end of the brushes lowers the hydrophilic character of PEG, which contributes to this intermediate value. Also, the absence of adsorbed copper catalyst was confirmed by XPS experiments. The surface morphology of the brushes was then investigated by SPM (Figure 3). The grafting process led to a chemically homogeneous PEG layer fully covering the wafer surface, as evidenced by the 5×5 μm^2 SPM height and phase images. 500×500 nm^2 height and phase images particularly emphasize the presence of a globular-like morphology with spherical structures having a size distribution of ca. 6−50 nm width and ca. 1−6 nm height. The low phase contrast between the spherical structures and the background clearly points out that both features are chemically identical, consisting of PEG brushes. This type of morphology being frequently observed in the literature concerning "grafted-to" PEG and PS brushes.[23,61] The nanometer-scale morphology observed herein most probably results from the heterogeneity of the brush layer in term of grafting

density. However, identical features were obtained using either UV/ozone or "piranha" etching before the deposition of the alkynyl SAM. The thickness of the dry PEG brushes ($h = 3.9 \pm 0.5$ nm) was determined by ellipsometry, and the corresponding grafting density ($\sigma = 0.13$ chains/nm^2) was calculated using relation 1

$$\sigma = (h\rho N_a)/M_n \tag{1}$$

where N_a is Avogadro's number, M_n (g/mol) is the brush precursor number average molecular weight, and ρ is the density of the anchored polymers. The average distance between grafting points ($D = 2(\pi\sigma)^{-1/2} = 3.1$ nm) is lower than the polymer radius of gyration ($R_g \sim 4.4$ nm), confirming that the PEG grafted layer is in the brush regime, but close to the mushroom regime.[23,62−64] However, the grafting density of the PEG brushes is below the maximum grafting density (ν_{max}) achievable via a "grafting-to" approach. Indeed, as predicted by the scaling laws developed by Leger et al.,[65] the grafting density of polymer brushes is mainly governed by the brush polymerization degree (N) and the polymer weight fraction in the grafting solution (Φ), as given by relation 2

$$\nu \sim (N^{-1/2}\Phi^{7/8})/a^2 \tag{2}$$

where a represents the segmental length of the monomer ($a \sim 0.5$ nm for PEG).[66] Thus, for PEG brushes formed from the melt or for a weight fraction of 100 wt % (i.e., $\Phi = 1$), $\nu_{max} = 0.19$ chains/nm^2, and a further increase of the experimental grafting density is therefore expectable.

Influence of Chemical Nature and Polymer Weight Fraction. The thickness and the morphology of PEG, PS, and PMMA

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Table 1. Advancing Water Contact Angles for PEG, PMMA, and PS Brushes Grafted by Click Chemistry for 24 h at 60 °C and Different Weight Fractions in Tetrahydrofuran

θ_a (°)	0.06 wt %	0.6 wt %	2.7 wt %
PEG	72	60	62
PMMA	79	70	69
PS	85	95	93

brushes were studied in order to investigate the effect of brush chemical nature on the grafting process. Also, each type of brushes was grafted using different weight fraction in the grafting solution (i.e., 0.06, 0.6, and 2.7 wt % in THF at 60 °C for 24 h) in order to investigate the influence of Φ on the brush conformation and grafting kinetics. At low values of Φ (0.06 wt %), the water contact angles of the brushes (Table 1) are shifted by 0−13° compared to alkynyl passivated surfaces ($\theta_a \sim 85°$), confirming the significant grafting of polymer brushes. For polymer weight fractions higher than 0.6 wt %, the water contact angles of the brushes remain constant, indicating an effective tuning of the surface properties and an increase in the surface coverage. SPM height images of each brushes (Figure 4) show that, for a given polymer weight fraction in the grafting solution, the overall morphology remains almost identical independent of the brush chemical nature. Obviously, the click chemistry grafting process and the brush conformation are only weakly influenced by the chemical nature of the brush precursors. Conversely, the morphology of the brushes is strongly influenced by the polymer weight fraction in the grafting solution. Indeed, the number, the spacing, and the size of the spherical structures vary with Φ. For $\Phi = 0.06$ wt %, only a few globular structures are present at the surface. These zones of higher grafting density of the brushes are spaced between lower grafting density domains. However, the already significantly shifted values of θ_a compared to

"passivated" substrates as well as the low phase contrast between the top of the features and the background of SPM phase images (not shown) represents solid arguments to suggest that the surfaces are already relatively covered with polymer brushes with nanometer-sized domains varying in grafting density. Then, for $\Phi = 0.6$ wt %, a wide but reproducible distribution of globular structures is observed as a result of the increase of the overall grafting density, surface coverage, and chain extension. Finally, for $\Phi = 2.7$ wt %, a large-scale, uniform, and homogeneous distribution of nodules similar to those observed in Figure 3 for PEG were also observed for PMMA and PS, pointing out the weak influence of chemical nature on the brush morphology.

Figure 5 shows the thickness of the grafted layers as a function of the polymer weight fraction in the grafting solution. To corroborate SPM data discussed above, for all polymers (♦, ○, □) the thickness and the grafting density of the brushes increased with the weight fraction of polymer in the grafting solution. However, for 2.7 wt % a significant difference was observed for the thickness of PS brushes compared to those of PEG and PMMA ($h = 5.6, 3.8,$ and 3.6, respectively). The corresponding grafting densities calculated from thickness data and relation 2 were $\sigma = 0.19, 0.14,$ and 0.13 chains/nm², respectively. The higher values of h and σ for PS brushes can be explained by the weaker interaction of PS with silicon wafers compared to PEG and PMMA. The SAM of a short silane such as EDMS is probably not bulky enough to allow for a complete "passivation" of the underlying silicon wafer.[16,19] Thus, the interactions with PEG and PMMA are not totally screened, limiting the increase of grafting density and brush stretching. For each polymer, a further increase of the polymer weight fraction in the grafting solution should increase the thickness and the grafting density of the brushes up to ν_{max} ($\nu_{max} = 0.19, 0.16,$ and 0.17 for PEG, PMMA, and PS, respectively), yielding to a decrease of the brush
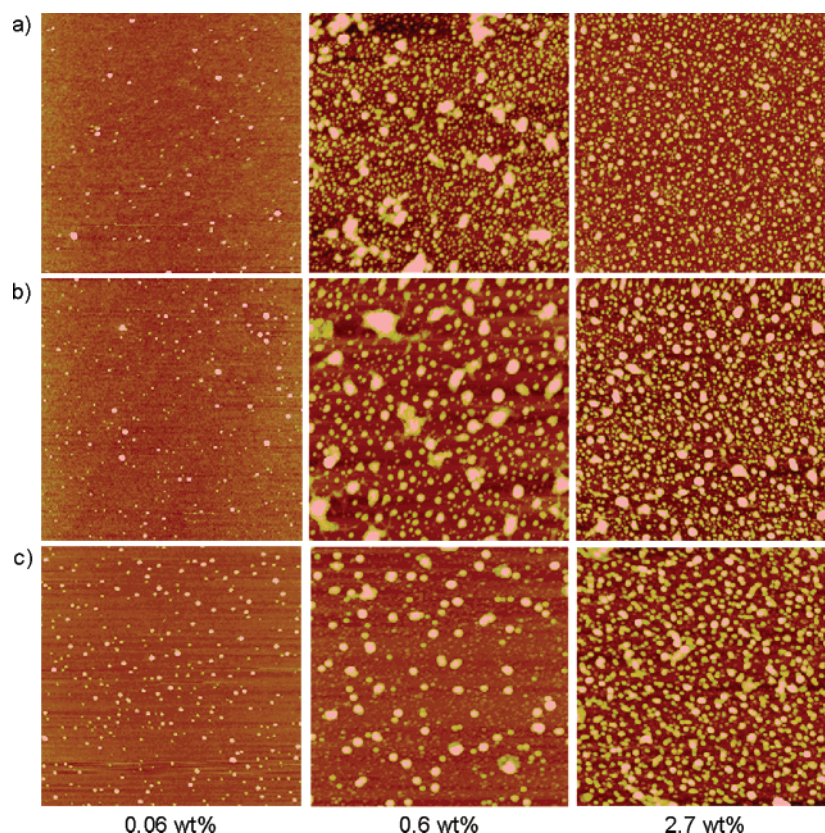
Figure 4. SPM height images for (a) PEG, (b) PMMA, and (c) PS brushes grafted by click chemistry for 24 h at 60 °C and (left) 0.06 wt %, (center) 0.6 wt %, and (right) 2.7 wt % in tetrahydrofuran. All images (2 × 2 μm).
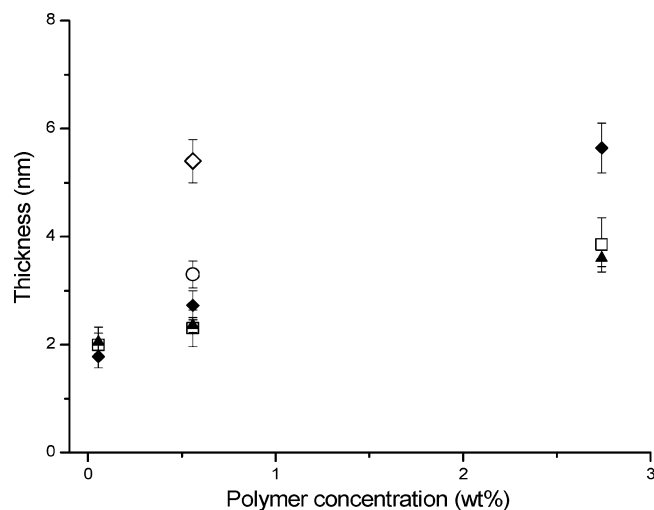
Figure 5. Thickness of (□, ○, ◇) PEG, (▲) PMMA, and (♦) PS brushes versus polymer weight fraction for brushes grafted by click chemistry for 24 h (□, ▲, ♦), 48 h (○), and 72 h (◇) at 60 °C in tetrahydrofuran.

roughness. However, the relatively large volume needed in the grafting system employed herein (ca. 4−6 mL) prohibits the detailed investigation of grafting performed at more concentrated polymer solutions. Instead, we investigated the influence of reaction time on the morphology of the brushes and their grafting density.

Influence of Reaction Time. As suggested by the results presented in the above section, this "grafting-to" approach is mainly governed by a diffusion process. We have thus investigated the influence of the reaction time, especially for longer times, to try to further increase the thickness/grafting density of the brushes and to flatten the morphology of the obtained polymer layers. Thus, PEG brushes were grafted to alkyne "passivated" silicon wafers in THF at 60 °C for 24, 48, and 72 h using a polymer weight fraction of 0.6 wt %. The resulting brushes were characterized by SPM, ellipsometry, and water contact angle

measurements (Figure 6). Water contact angles of PEG brushes decreased significantly for increasing reaction times, reflecting the improvement of the grafting density. The lowest value (θ_a ∼ 40°) was reached for 72 h of grafting, with a thickness comparable to that of PS at 24 h and 2.7 wt % (Figure 5). The grafting density ($\sigma = 0.18$ chains/nm^2) was close to ν_{max} for PEG, and therefore, an increase of time or Φ should not provide denser polymer brushes (but the latter should shorten the grafting time). SPM height and phase images illustrate the increase of the brush grafting density, yielding to a closely packed globular morphology with a sharp distribution of ca. 50−100 nm. The increase of the brush grafting density also results in a significant reduction of the surface roughness (rms = 2.8, 1.1, and 1.0 nm for 24, 48, and 72 h, respectively) in comparison with the film thickness ($h = 2.4$, 3.3 and 5.4 nm, respectively). These grafted polymer layers represent appropriate substrates to study the dynamics under confinement of supported polymer thin films of same chemical nature.

Conclusion

This work has shown the potential of this click chemistry approach for the grafting of polymer brushes to passivated silicon surfaces. The great diversity of linear ω-azido linear precursors as well as the high tolerance, selectivity, and fidelity of click chemistry represent important assets for the grafting of a wide range of polymer brushes, e.g., hydrophilic, hydrophobic, glassy, semicrystalline, amorphous, functionalized, or pseudo-brushes.

Well-defined PEG, PMMA, and PS brushes with thickness of ca. 6 nm, grafting densities of ca. 0.2 chains/nm^2, and a roughness of ca. 1 nm were prepared, showing the impact of polymer weight fraction in the grafting solution and reaction time on the morphology and the grafting density of the brushes. The click chemistry grafting reaction is not affected by the chemical nature of the brush precursor and proceeds under mild and easy
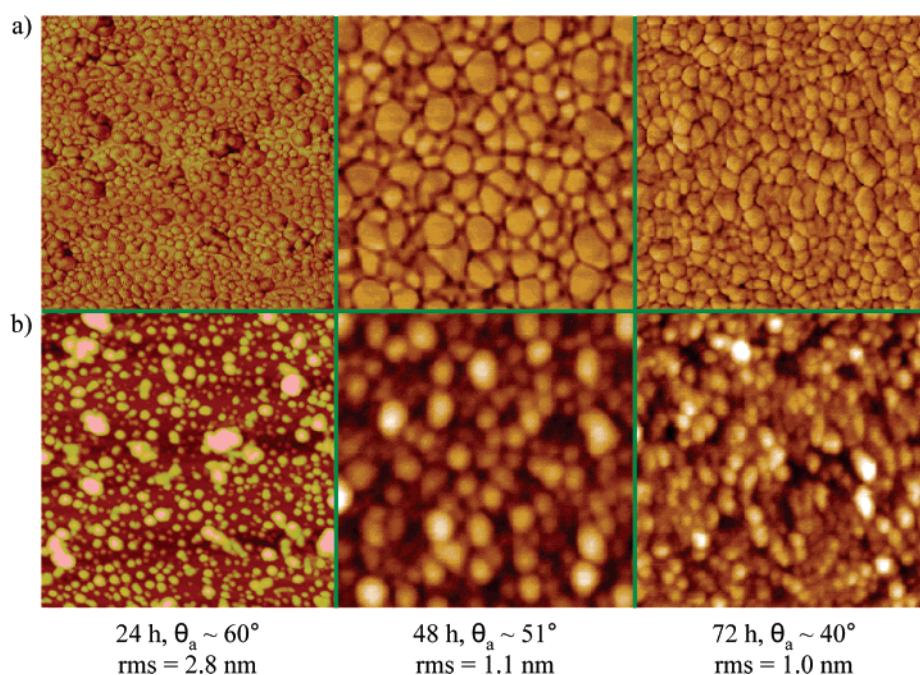

a)

b)

24 h, θ_a ∼ 60°   48 h, θ_a ∼ 51°   72 h, θ_a ∼ 40°
rms = 2.8 nm   rms = 1.1 nm   rms = 1.0 nm

Figure 6. SPM (a) phase image and (b) height image of PEG brushes grafted by click chemistry for (left) 24 h, (center) 48 h, and (right) 72 h at 60 °C and 0.6 wt % in tetrahydrofuran. All images (1 × 1 μm^2).

conditions. It offers the opportunity to graft a wide range of polymer architectures to passivated silicon substrates in a versatile fashion.

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