

Polystyrene Brush Evolution by Grafting to Reaction on Deglazed and Not-Deglazed Silicon Substrates

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Two model substrates for the grafting to reaction are considered: not-deglazed silicon, whose surface is coated by a thin oxide layer with reactive silanol groups on its surface; and deglazed silicon, where the oxide layer is removed by treatment with hydrofluoric acid. The reactive polymers are hydroxy-terminated polystyrenes with molecular weights ranging from 3.9 to 13.9 kg mol⁻¹. The grafting to reaction is carried out at different temperatures and for different periods of time on the two different substrates. The thickness and the thermal stability of the resulting brushes are evaluated. Furthermore, the grafting of a highly dispersed system is simulated by blending two polymers with different molecular weights. Although the brush thickness growth is found to be faster on deglazed silicon, the preferential grafting of short chains occurs with equal chain selection propensity on both substrates.

decades across various application fields, ranging from microelectronics^[3–6] to biomedical sciences.^[7–10] In this respect, the prominent role of the grafting to reaction derives from the precise control that such an approach guarantees over the two crucial parameters that determine the polymer brush properties, namely the brush thickness (H) and the number of anchored chains per unit of area, referred to as grafting density (Σ). Indeed, the grafting to reaction is generally considered to be a self-limiting process, meaning that both H and Σ increase with the grafting time until they reach a limiting value.^[11] In particular, when the reaction is carried out in the melt, the limiting H value is approximately equal to two times the radius of gyration (Rg)

of the grafted polymer.^[11] In addition, for dry brushes, Σ is commonly estimated by Equation 1,^[12]

$$\Sigma = \frac{H d N_A}{M_n} \quad (1)$$

in which d is the polymer density, N_A is the Avogadro's number and M_n is the number average molecular weight of the grafted polymer. Consequently, the limit value of H, approximately equal to 2Rg, corresponds to a limit value of $\Sigma \sim N^{-0.5}$, since Rg scales with $N^{0.5}$, where N represents the degree of polymerization of the grafted polymer. This simple relationship between Σ and N was recently exploited in applications involving precision doping of silicon.^[13–15] The grafting to process was adopted with a procedure consisting in the synthesis of telechelic polymers containing a phosphorus dopant atom in the terminal moiety followed by the thermally induced grafting reaction of these polymers onto the silicon surface. The self-limiting nature of the grafting reaction resulted in a limit value of Σ and, consequently, of the phosphorus dose accumulated on the semiconductor surface that can be simply tuned by changing the molecular weight of the polymer. The most employed polymers for these applications are conventional polystyrene and polymethyl methacrylate,^[13,16] although bioinspired polypeptides^[17] have been also integrated in this technology.

Although the grafting to reactions can be carried out on almost any type of surface, the most investigated substrate is undoubtedly silicon oxide (SiO₂), which exposes reactive silanols at the surface.^[11,13,18–22] E.g., a dedicated experiment was performed

1. Introduction

The grafting to reaction, the chemical reaction of end-functional polymers with a substrate, is nowadays an extremely convenient and versatile approach for the synthesis of polymer brushes, which consist of thin films of polymers anchored by one end to a substrate.^[1] Thanks to their potential as surface modifiers,^[2] polymer brushes have attracted considerable attention in recent

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by using a silicon substrate covered with native oxide and hydroxy-terminated polymers to elucidate the physical-chemical origin of the self-limiting behavior of the grafting to process for that particular reaction.^[23] In such experiment, a polymer brush obtained by grafting partially deuterated poly(styrene-st-methyl methacrylate) statistical copolymers [P(S-st-MMA)-OH] at the limit value of H was covered by a layer of identical fully hydrogenated P(S-st-MMA)-OH and subsequently annealed at 250 °C. After removal of unreacted chains and determination of the brush composition by TGA-GC-MS (thermogravimetry-gas chromatography-mass spectrometry), a substantial substitution of deuterated chains with the hydrogenated counterparts was observed. This clearly indicates the occurrence of degrafting reactions, probably promoted by water molecules adsorbed onto the SiO₂ surface or coming from the grafting reaction. The above result suggests a dynamic behavior of the limit state which is typical of chemical reactions approaching their thermodynamic equilibrium. Interestingly, such a dynamic behavior was recently exploited^[24] to produce patterned brushes by spinning thin films of diblock copolymers containing functional homopolymers, with each homopolymer being compatible with only one block of the block copolymer, onto previously formed brushes. After self-assembly of the diblock copolymers, the dynamic grafting to process promoted the placement of the distinct homopolymers in regular registry controlled by the block copolymer morphology.

The SiO₂ substrate was also used as a suitable platform to evaluate the effect of polymer dispersity in grafting to reactions.^[11,25,26] To model the grafting to reaction of polymers featuring a wide molecular weight distribution, equimolar blends of partially deuterated and fully hydrogenated P(S-st-MMA)-OH copolymers, characterized by different molecular weights but narrow distribution, were grafted in the melt state onto a silicon substrate covered by native oxide.^[27,28] Preferential grafting of the shortest chains was observed, regardless of the grafting temperature and time. The enrichment of shorter chains in the brush becomes more pronounced as the difference between the molecular weight of the two polymers in the original blend increases. Interestingly, a similar behavior was also described for grafting to reactions carried out in solution onto similar substrates.^[29,30] The enrichment of shorter chains was related to their higher reaction rate due to the lower entropy loss that occurs in the confinement of the end-group near the surface.^[11,31] Due to the enrichment of short chains, the average molecular weight of the polymer in the brush is significantly lower than that of the starting sample. Consequently, Equation 1 becomes unable to predict the grafting density of brushes, especially when widely dispersed polymers are employed.

Despite the relevance of the grafting reaction, few information is available for substrates other than SiO₂. An interesting alternative substrate for investigating the grafting to reaction is deglazed silicon, obtained by selectively etching the native SiO₂ that is present on the silicon substrate by treatment with hydrofluoric acid solution. The removal of the SiO₂ layer leads to a surface that exposes Si-H functionalities which are able to react with both hydroxy^[32–36] and phosphate^[37] functional groups, thus allowing the formation of polymer brushes.^[38] Moreover, the use of this substrate is particularly relevant for precision doping applications, as the diffusion of the dopant atoms in the silicon substrate does not encounter any kind of diffusion barrier during

Table 1. Number average molecular weight (M_n), dispersity index (\mathcal{D}), degree of polymerization (N), and radius of gyration (R_g) of PS_{3,9}OH, PS_{13,9}OH, and PSD_{4,8}OH.

Sample	M_n [kg/mol]	\mathcal{D}	N	R_g [nm] ^{a)}
PS _{3,9} OH	3.9	1.09	37	1.70
PS _{13,9} OH	13.9	1.07	134	3.21
PSD _{4,8} OH	4.8	1.17	43	1.82

^{a)} The radius of gyration was calculated by considering $R_g = (N/6)^{0.5}b$, where b is the statistical segment length which in case of polystyrene samples is assumed equal to 0.68 nm.^[39]

drive-in by high-temperature thermal treatment, as in the case of the not-deglazed silicon substrate, where a low diffusivity SiO₂ layer is present.^[38]

In this work, hydroxy-terminated polystyrenes were used as model polymers to compare the grafting to reaction performed in melt onto not-deglazed and deglazed silicon substrates. In addition, fully deuterated and hydrogenated polymers with different molecular weights were used to evaluate the effect of the molecular weight dispersity on the final characteristics of the brushes.

2. Results and Discussion

Two fully hydrogenated and one fully deuterated polystyrene samples were synthesized by Activators ReGenerated by Electron Transfer-Atom Transfer Radical Polymerization (ARGET-ATRP) using 2-hydroxyethyl-2-bromoisobutyrate as the initiator to obtain hydroxy-terminated polymers.^[13] Such samples were characterized by size exclusion chromatography (SEC) analysis (chromatograms are included in the Supporting Information) and the number average molecular weights (M_n) were found to be 3.9 and 13.9 kg mol⁻¹ for the hydrogenated samples, indicated as PS_{3,9}OH and PS_{13,9}OH respectively, and 4.8 kg mol⁻¹ for the deuterated one, which is referred to as PSD_{4,8}OH. The M_n and the dispersity index (\mathcal{D}) of the samples are collected in **Table 1**, together with the corresponding degree of polymerization (N) and radius of gyration (R_g).

The workflow for grafting to reactions in melt has been extensively described in literature.^[13,26,28] All samples were deposited by spin-coating onto both not-deglazed and deglazed silicon wafers to produce ≈30 nm thick films and the grafting to reaction was then promoted by annealing the samples at 190 and 250 °C in inert atmosphere. A schematic picture representing the grafting reaction onto the two substrates is provided in **Figure 1**. At the end, the unreacted chains were removed by sonication in toluene.

The brush homogeneity was confirmed by AFM analysis as demonstrated by sample images included in Figures S2 and S3 (Supporting Information). The brush thickness was evaluated by spectroscopic ellipsometry and the H values at different grafting times are reported in **Figure 2**. Irrespective of the grafting temperature and the substrate employed, a rapid initial increase in H was observed, followed by a slower rate of layer thickness growth over longer periods of time. Ultimately, H approached a limit value which is slightly higher than two times the radius of gyration of the polymer. Likewise, H results linearly proportional to the logarithm of the reaction time ($H \sim \log t$), as evident

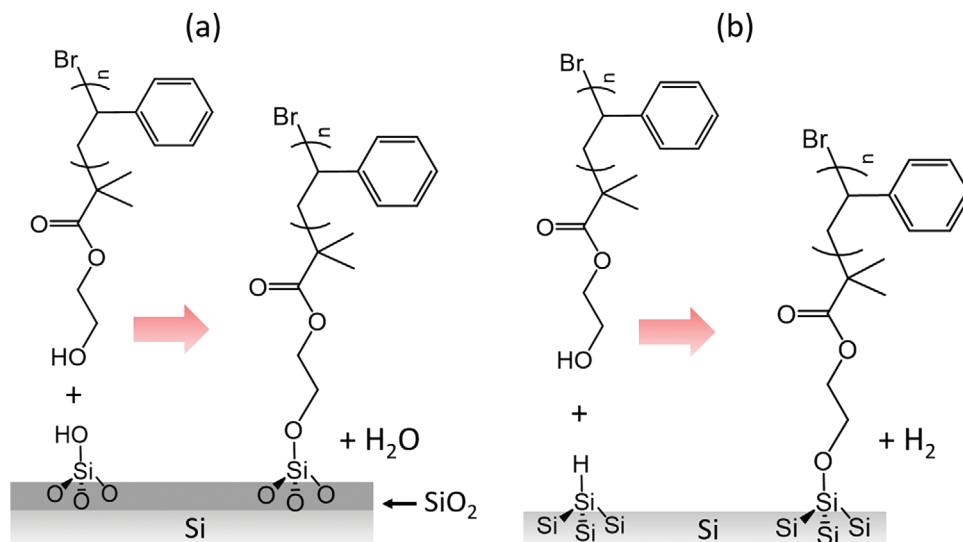


Figure 1. Schematic representation of the grafting to reaction of hydroxy-terminated polystyrene onto not-deglazed (a) and deglazed (b) silicon substrates.

from Figure S4 (Supporting Information). Furthermore, the reaction rate constant increases with increasing temperature and is higher on the silicon deglazed substrate. The $H \sim \text{Log } t$ relationship deserves some additional considerations. This behavior is commonly encountered in grafting to reactions.^[11] As the brush thickness increases, the penetration of further chains toward the substrate is limited for entropic reasons related to the chain stretching, thus ultimately resulting in the above H versus t relationship.^[39] For the reactions involving hydroxy-terminated polymers and the not-deglazed silicon substrate, it has been shown that H tends to converge to an equilibrium value, where the degrafting rate, promoted by water adsorbed on the substrate or generated by the grafting to reaction, becomes similar to the grafting rate.^[11,23] A similar reasoning does not seem to apply when the deglazed silicon substrate is used. In this case, the grafting to reaction produces hydrogen as a by-product,^[33] which cannot contribute to the reverse reaction. Furthermore, the deglazed silicon surface is completely non-polar, disfavoring the presence of adsorbed water molecules. In this perspective,

the decrease in the thickness growth rate is solely due to diffusion reasons. It therefore appears that the grafting to reaction of hydroxy-terminated polymers on a deglazed silicon substrate is kinetically self-limited,^[40–42] unlike the grafting to reaction on a silicon substrate with a SiO_2 layer. Unfortunately, it is not possible to obtain a definitive indication of the reaction mechanism from the evaluation of the H versus t curves, as their profiles are similar in the case of equilibrium-driven reactions and kinetically limited processes, at least in the experimentally accessible time frames.^[11]

A dedicated experiment was also carried out in order to exclude any chemical adsorption phenomena that could occur between the monomer units of the polymer and the substrate, thus contributing to the formation of the observed brushes.^[43] In detail, a polystyrene sample with $M_n = 10 \text{ kg mol}^{-1}$ and without reactive end groups was deposited onto deglazed silicon and annealed at 250°C for 900 s. After the sonication in toluene, no organic layer was detected on the silicon surface, thus excluding adsorption phenomena. In the case of not-deglazed substrates, the need

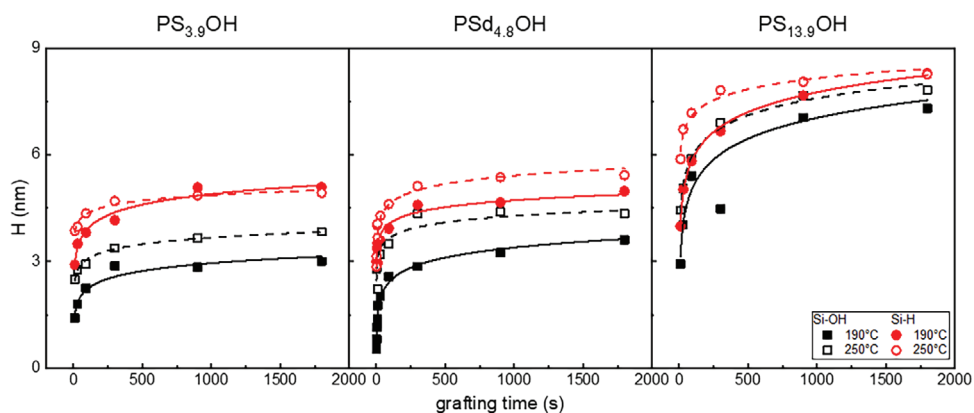


Figure 2. Brush thickness (H) as a function of the grafting time, temperature, and substrate for the $\text{PS}_{3.9}\text{OH}$, $\text{PS}_{d4.8}\text{OH}$, and $\text{PS}_{13.9}\text{OH}$ samples.

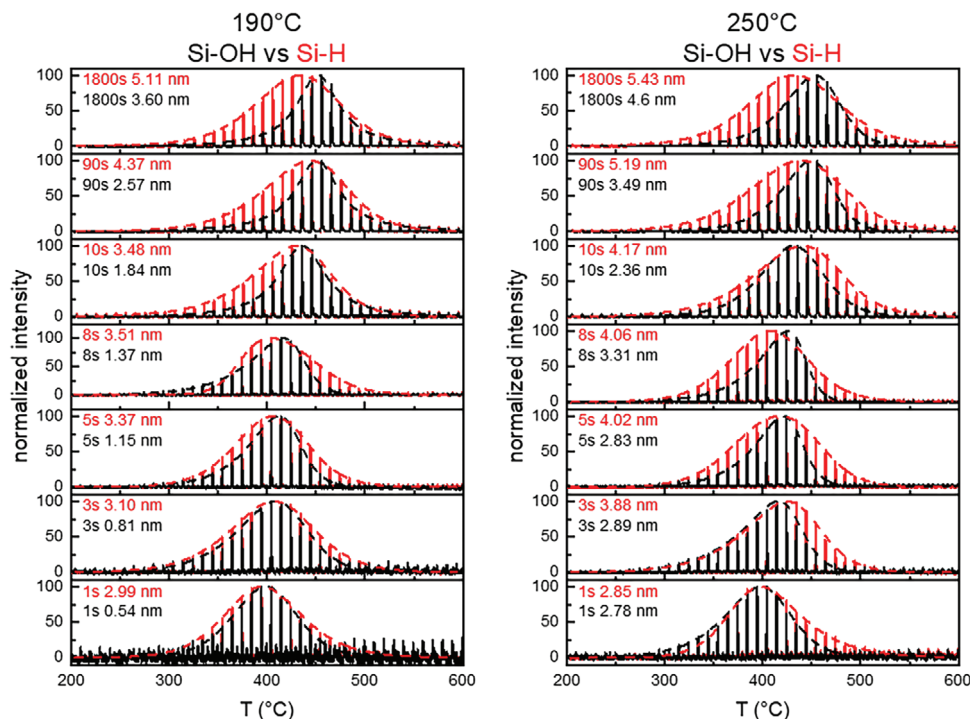


Figure 3. TGA-GC-MS chromatograms of the polymer brushes obtained by grafting the $\text{PS}_{d_{4,8}}\text{OH}$ sample onto both not-deglazed (black curves) and deglazed (red curves) silicon substrates at 190 and 250 °C for different times.

for reactive end-groups for the brush formation has already been confirmed, at least in the experimental conditions discussed in this work.^[40]

The thermal stability of the polymer brushes was then evaluated by TGA-GC-MS analysis. Since the thermal degradation of polystyrene occurs mainly via a depolymerization reaction leading to the corresponding monomers, all polymer brushes were subjected to a heating ramp in a thermogravimetric analyzer (TGA) and the evolved monomers, styrene from $\text{PS}_{3,9}\text{OH}$ and $\text{PS}_{13,9}\text{OH}$ or deuterated styrene from $\text{PS}_{d_{4,8}}\text{OH}$ were separated in a gas chromatograph (GC), and quantified by mass spectrometry (MS).^[44] As a typical example, **Figure 3** reports the chromatograms of deuterated styrene from brushes of $\text{PS}_{d_{4,8}}\text{OH}$ on both deglazed and non-deglazed substrates prepared at different grafting temperatures and therefore characterized by different H values. The brushes grafted onto the not-deglazed substrate result slightly more stable than those on the deglazed substrate and the thermal degradation occurs in a narrower temperature range. Both effects become more pronounced as the grafting time increases, thus suggesting that some kind of inhomogeneity in the polymer chain distribution at the substrate surface may occur during the formation of the brush on the deglazed substrate. This effect may be related to the irreversible nature of the grafting to reaction on this substrate. In contrast, the grafting reaction carried out on a non-deglazed substrate is reversible. Therefore, any inhomogeneity in the polymer chain distribution at the substrate surface can be corrected through a series of grafting and degrafting reactions to ultimately achieve the most stable polymer chain arrangement at the substrate surface.^[45]

The second aspect evaluated in this work is the effect of polymer dispersity in the composition of the brushes obtained by the grafting to reaction of hydroxy-terminated polystyrenes onto not-deglazed and deglazed silicon substrates. An equimolar polymer blend containing the deuterated $\text{PS}_{d_{4,8}}\text{OH}$ (short component) and the hydrogenated $\text{PS}_{13,9}\text{OH}$ (long component) was used as a model of a highly dispersed system. The blend was spin-coated onto both the not-deglazed and deglazed substrates and the grafting to reaction was promoted by thermal annealing at 190 and 250 °C. As usual, the unreacted chains were removed by toluene washes. An equiv. procedure was recently reported for the grafting of $\text{P}(\text{S-st-MMA})\text{-OH}$ blends onto the not-deglazed silicon substrate.^[27,28] The thicknesses of the as-obtained brushes are reported in **Figure 4a** (the same data are presented in **Figure S5**, Supporting Information using the Log_t scale). As in the case of individual polymers, the thickness increases over time approaching a limit value. In addition, higher thicknesses are observed by increasing the temperature from 190 to 250 °C, especially when deglazed silicon is employed as the substrate. Detailed information on the brush composition can be obtained by analyzing the samples via TGA-GC-MS. The relative amount of the two monomers, collected separately in the mass spectrometer, can be used in combination with H to estimate the composition of the brush. In detail, following the procedure described in the Supporting Information and using Equations S2 and S3 (Supporting Information), the grafting density of both the deuterated $\text{PS}_{d_{4,8}}\text{OH}$ ($\Sigma_{\text{PS}_{d_{4,8}}\text{OH}}$) and the hydrogenated $\text{PS}_{13,9}\text{OH}$ ($\Sigma_{\text{PS}_{13,9}\text{OH}}$) and the total grafting density (Σ_{tot}) were evaluated. The obtained values are reported in **Figure**

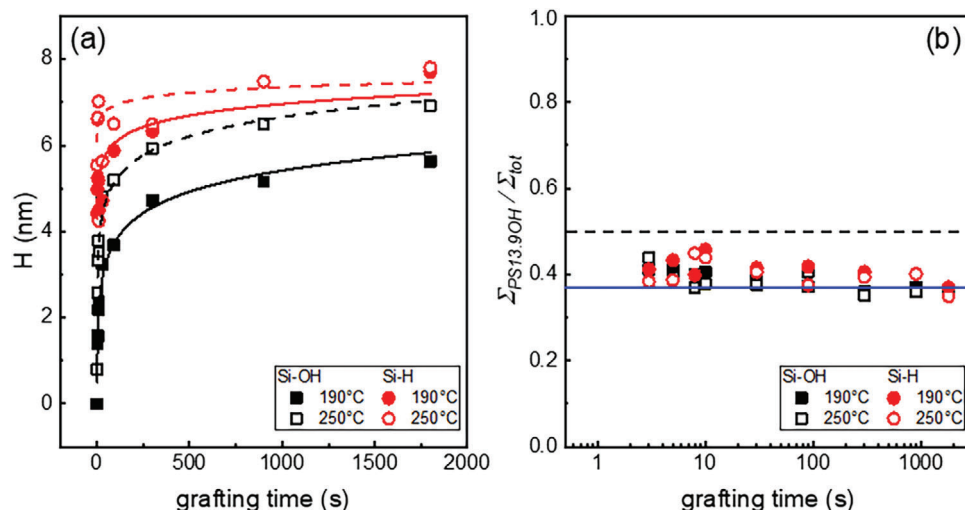


Figure 4. a) Brush thickness (H) as a function of the grafting time, temperature, and substrate for the blend containing the $\text{PS}_{d_{4,8}}\text{OH}$ and $\text{PS}_{13,9}\text{OH}$ samples. b) Molar fraction of $\text{PS}_{13,9}\text{OH}$ ($\Sigma_{\text{PS}_{13,9}\text{OH}}/\Sigma_{\text{tot}}$) as a function of the grafting time, temperature, and substrate for the brushes obtained by grafting the blend containing the $\text{PS}_{d_{4,8}}\text{OH}$ and $\text{PS}_{13,9}\text{OH}$ samples. The composition of the initial blend and the one predicted by Equation 2 are also represented as a black dashed line and a blue solid line, respectively.

S6 (Supporting Information), included in the Supporting Information, and exhibit a similar trend to that observed for the brush thicknesses. A more comprehensive understanding of the brush composition can be obtained by reporting the molar fraction of $\text{PS}_{13,9}\text{OH}$ ($\Sigma_{\text{PS}_{13,9}\text{OH}}/\Sigma_{\text{tot}}$) of each sample, as shown in Figure 4b. It appears that, starting from an equimolar blend in which the molar fraction of the functional terminal groups for each polymer is 0.5, the resulting brushes are systematically depleted of the $\text{PS}_{13,9}\text{OH}$ sample, resulting in an average molar fraction of less than 0.4. Therefore, $\text{PS}_{d_{4,8}}\text{OH}$ reacts preferentially, regardless of the grafting time, temperature, and substrate. This fact is completely compatible with what was already observed for P(S-st-MMA)-OH polymers grafted onto the not-deglazed silicon substrate.^[27,28] Furthermore, in the case of an equimolar blend containing two generic P(S-st-MMA)-OH polymers, simply defined polymer 1 and 2, the composition of the brush obtained by the grafting to reaction results predictable by Equation 2,

$$\frac{\Sigma_1}{\Sigma_2} = \left(\frac{M_{n,1}}{M_{n,2}} \right)^{-0.5} \quad (2)$$

in which Σ is the grafting density of the generic polymer in the grafted brush and M_n is number of average molecular weight. When Equation 2 is used with the $\text{PS}_{d_{4,8}}\text{OH}$ and $\text{PS}_{13,9}\text{OH}$ polymers to predict $\Sigma_{\text{PS}_{13,9}\text{OH}}/\Sigma_{\text{tot}}$, the result obtained is 0.36, in good agreement with the experimental data reported in Figure 4b.

The systematic enrichment of the shortest chains and the validity of Equation 2 were theoretically justified by observing that the entropy loss resulting from the confinement of the end-group near the surface depends on the polymer size. This fact leads to a reaction rate constant of the grafting to process that depends on the molecular weight of the grafted polymers as $k \sim M_n^{-0.5}$.^[11,31] Therefore, since the increased reactivity of the short chains due to entropic reasons satisfactorily explains the experimental data, it can be inferred that specific interactions of the polymer functional groups with the substrate do not play any significant role.

Finally, it is noteworthy that, despite the grafting to reaction of hydroxy-terminated polystyrenes is chemically different when deglazed or not-deglazed silicon substrates are used, the resulting brushes display remarkably similar characteristics. In fact, for sufficiently long grafting times, the thicknesses of the brushes exceed $2R_g$ in both cases and the preferential grafting of short chains occurs with identical chain selection propensity.

3. Conclusion

The grafting to reaction of three hydroxy-terminated polystyrenes with different molecular weights was performed in melt onto both deglazed and not-deglazed silicon substrates. The thickness growth rate of the brush is faster on deglazed silicon, thus resulting in slightly but systematic higher thicknesses of the brushes. Furthermore, it was observed on both substrates that the short chains react preferentially, thus resulting in a lower molecular weight of the polymer in the brush compared to polymer before the grafting process. As the preferential grafting of the short chains takes place with the same chain selection propensity, it appears that the driving force of this process is fully entropic in nature without contributions coming from interactions of the polymer chain or the functional groups with the substrates. These results clearly indicate that further work is necessary to fully elucidate the chemico-physical mechanism governing the grafting to process and develop a predictive model that accounts for all different phenomena taking place during this process.

4. Experimental Section

Materials: 2-hydroxyethyl-2-bromoisobutyrate (HEBIB), copper(II) bromide (CuBr_2), tin(II) 2-ethylhexanoate [$\text{Sn}(\text{EH})_2$] and anisole were purchased from Sigma-Aldrich and used as received. Tris [2-(di-methylamino) ethyl] amine (Me_6TREN) was purchased from Alfa Aesar and used as received Styrene and deuterated-styrene were purchased from Sigma-Aldrich and purified using an inhibitor removal column (Sigma-Aldrich) before use. All solvents, which are THF, methanol, 2-propanol,

toluene, sulfuric acid (H₂SO₄, 95.0–97.0%), hydrogen peroxide solution (H₂O₂, 34.5–36.5%) and hydrofluoric acid (HF, 48%) were purchased from Sigma-Aldrich and used without further purification.

Polystyrene Synthesis: Two fully hydrogenated (PS_{3,9}OH and PS_{13,9}OH) and one deuterated (PSd_{4,8}OH) hydroxy-terminated polystyrenes were synthesized by the ARGET-ATRP method according to the general procedure previously described.^[13] The molar ratio between the monomer and the initiator (HEBIB) was set to 100/1 for the PS_{3,9}OH and PSd_{4,8}OH samples and to 200/1 for PS_{13,9}OH. Furthermore, the molar ratios between the other reagents [HEBIB]₀/[CuBr₂]₀/[Me₆TREN]₀/[Sn(EH)₂]₀ were kept constant at values of 1/0.02/0.22/0.2. The reactions were carried out at 90 °C for 5 h when PS_{3,9}OH and PSd_{4,8}OH were synthesized and for 22 h in the PS_{13,9}OH case. The polymers were purified by precipitation in cold methanol from THF solutions. The number of average molecular weight and the polydispersity index of the samples were determined by SEC analyses.

Substrate Preparation: P-type Czochralski-grown Si (100) wafers with a nominal resistivity ranging from 1 to 5 Ω cm were acquired from Siltronic. These wafers were subsequently cleaved into 1 × 1 cm² pieces, which were used as the substrate for the grafting to processes. The deglazed substrates were obtained by washing the silicon wafers with diluted hydrofluoric acid (HF) solution with a HF to H₂O ratio of 1:10 for 2 min at room temperature. The samples were then rinsed with deionized water and dried under nitrogen flow. The not-deglazed substrates were prepared by treating the silicon wafers in a Piranha solution (H₂SO₄ and H₂O₂ in a 3:1 volume ratio) for 40 min at 80 °C. The wafers were subsequently washed with deionized water and dried under nitrogen flow. A second wash was performed in 2-propanol ultrasonic bath and dried again under nitrogen flow. Not-deglazed silicon wafers are characterized by a native SiO₂ layer of ≈2 nm thickness, measured with a spectroscopic ellipsometer (FS-1 Multi-Wavelength Ellipsometer Film Sense).

Grafting Procedure: Both the single polymers and the equimolar blend containing PSd_{4,8}OH and PS_{13,9}OH were dissolved in toluene (9 mg mL⁻¹) through sonication for 5 min. Subsequently, the solutions were deposited onto deglazed and not-deglazed silicon wafers by spin coating (3000 rpm for 30 s), resulting in polymer films with thickness of ≈30 nm. The grafting to reaction of the polymers was then promoted by annealing the samples onto a preheated hot plate (SAWATEC HP-150) placed inside a glove box (MBRAUN LABstar, inert atmosphere with H₂O/O₂ < 1 ppm). The samples were heated at 190 or 250 °C for 10, 30, 90, 300, 900, and 1800 s. The unreacted chains were finally removed by toluene washes of the samples carried out in an ultrasonic bath for 10 min.

Film Characterization: The AFM analysis was performed with a Multi-mode 8 AFM (Bruker, U.S.A.) using ScanAsystAir probes (Bruker). Images were acquired in PeakForce Tapping in ambient air using the smallest oscillation amplitude and setpoint force that granted stable imaging. Micrographs were processed with NanoScope Analysis software (ver. 1.80) by only flattening the micrographs.

The thicknesses of the polymer layers were measured with a FS-1 Multi-Wavelength Ellipsometer (Film Sense) where the brush compositions were estimated by TGA-GC-MS analysis. In detail, the TGA analyses were conducted using a Mettler Toledo TGA/DSC 3+ instrument in which the silicon wafers were directly placed on a thermo-balance plate. The TGA run was executed by heating the sample at a rate of 20 °C/min with helium (He) as the carrier gas (flow rate of 50.0 mL min⁻¹). The GC-MS analysis was performed using a Finnigan GC Trace 1300 MS ISQ LT instrument equipped with a Phenomenex DB5-5MS capillary column (30 m length, 0.25 mm inner diameter, and 0.25 μm thickness). The injector was set at 250 °C in splitless mode and helium was used as the carrier gas at a flow rate of 1.0 mL min⁻¹. The MS signal was acquired in EI⁺ mode with an ionization energy of 70.0 eV and an ion source temperature of 250 °C. The transfer line and oven temperatures were both maintained at 280 °C and 150 °C, respectively. During initial scouting experiments, data acquisition was conducted in Full-Scan mode within the 50–350 m/z range. For the final optimized method, data acquisition was switched to Selected Ion Monitoring (SIM) mode, focusing on signals at 104 m/z, which corresponds to the styrene monomer and at 112 m/z for the deuterated styrene monomer.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

deglazed silicon, grafting to reactions, interfaces, not-deglazed silicon, polymer brushes

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- [1] B. Zdyrko, I. Luzinov, *Macromol. Rapid Commun.* **2011**, *32*, 859.
- [2] A. S. Goldmann, N. R. B. Boase, L. Michalek, J. P. Blinco, A. Welle, C. Barner-Kowollik, *Adv. Mater.* **2019**, *31*, 1902665.
- [3] S. Ham, C. Shin, E. Kim, D. Y. Ryu, U. Jeong, T. P. Russell, C. J. Hawker, *Macromolecules* **2008**, *41*, 6431.
- [4] E. Han, K. O. Stuen, Y. H. La, P. F. Nealey, P. Gopalan, *Macromolecules* **2008**, *41*, 9090.
- [5] E. Han, K. O. Stuen, M. Leolukman, C. C. Liu, P. F. Nealey, P. Gopalan, *Macromolecules* **2009**, *42*, 4896.
- [6] F. Ferrarese Lupi, T. J. Giammaria, F. G. Volpe, F. Lotto, G. Seguini, B. Pivac, M. Laus, M. Perego, *ACS Appl. Mater. Interfaces* **2014**, *6*, 21389.
- [7] M. Welch, A. Rastogi, C. Ober, *Soft Matter* **2011**, *7*, 297.
- [8] L. Li, S. Chen, J. Zheng, B. D. Ratner, S. Jiang, *J. Phys. Chem. B* **2005**, *109*, 2934.
- [9] W. L. Chen, R. Cordero, H. Tran, C. K. Ober, *Macromolecules* **2017**, *50*, 4089.
- [10] M. Kim, S. K. Schmitt, J. W. Choi, J. D. Krutty, P. Gopalan, *Polymers* **2015**, *7*, 1346.
- [11] R. Chiarcos, M. Perego, M. Laus, *Macromol. Chem. Phys.* **2023**, *224*, 2200400.
- [12] L. Michalek, L. Barner, C. Barner-Kowollik, *Adv. Mater.* **2018**, *30*, 1706321.
- [13] M. Perego, G. Seguini, E. Arduca, A. Nomellini, K. Sparnacci, D. Antonioli, V. Gianotti M Laus, *ACS Nano* **2018**, *12*, 178.
- [14] A. Pulici, S. Kuschlan, G. Seguini, F. Taglietti, M. Fanciulli, R. Chiarcos, M. Laus, M. Perego, *Mater. Sci. Semicond. Process.* **2023**, *163*, 107548.
- [15] R. Chiarcos, M. Laus, M. Perego, *Eur. Polym. J.* **2024**, *208*, 112849.
- [16] R. Chiarcos, V. Gianotti, M. Cossi, A. Zoccante, D. Antonioli, K. Sparnacci, M. Laus, F. E. Caligiore, M. Perego, *ACS Appl. Electron. Mater.* **2019**, *1*, 1807.
- [17] V. M. Ospina, R. Chiarcos, D. Antonioli, V. Gianotti, M. Laus, S. Kuschlan, C. Wiemer M Perego, *ACS Appl. Electron. Mater.* **2022**, *4*, 6029.
- [18] K. Sparnacci, D. Antonioli, V. Gianotti, M. Laus, F. F. Lupi, T. J. Giammaria, G. Seguini, M. Perego, *ACS Appl. Mater. Interfaces* **2015**, *7*, 10944.

- [19] L. J. Norton, V. Smigolova, M. U. Pralle, A. Hubenko, K. H. Dai, E. J. Kramer, S. Hahn, C. Berglund, B. Dekoven, *Macromolecules* **1995**, *28*, 1999.
- [20] G. Reiter, P. Auroy, L. Auvray, *Macromolecules* **1996**, *29*, 2150.
- [21] P. Mansky, Y. Liu, E. Huang, T. P. Russell, C. Hawker, *Science* **1997**, *275*, 1458.
- [22] K. Viswanathan, T. E. Long, T. C. Ward, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 3655.
- [23] M. Laus, R. Chiarcos, V. Gianotti, D. Antonioli, K. Sparnacci, G. Munaò, G. Milano, A. De Nicola, M. Perego, *Macromolecules* **2021**, *54*, 499.
- [24] L. Wan, R. Ruiz, H. Gao, T. R. Albrecht, *ACS Nano* **2017**, *11*, 7666.
- [25] C. Brondi, A. Baldanza, R. Chiarcos, M. Laus, G. Scherillo, G. Mensitieri, G. Milano, *Polymer* **2024**, *294*, 126737.
- [26] R. Chiarcos, D. Antonioli, V. Ospina, M. Laus, M. Perego, V. Gianotti, *Analyst* **2021**, *146*, 6145.
- [27] D. Antonioli, R. Chiarcos, V. Gianotti, M. Terragno, M. Laus, G. Munaò, G. Milano, A. De Nicola, M. Perego, *Polym. Chem.* **2021**, *12*, 6538.
- [28] R. Chiarcos, D. Antonioli, V. Gianotti, M. Laus, G. Munaò, G. Milano, A. De Nicola, M. Perego, *Polym. Chem.* **2022**, *13*, 3904.
- [29] L. Michalek, K. Mundsinger, C. Barner-Kowollik, L. Barner, *Polym. Chem.* **2019**, *10*, 54.
- [30] L. Michalek, K. Mundsinger, L. Barner, C. Barner-Kowollik, *ACS Macro Lett.* **2019**, *8*, 800.
- [31] B. J. Kim, G. H. Fredrickson, E. J. Kramer, *Macromolecules* **2007**, *40*, 3686.
- [32] P. Thissen, O. Seitz, Y. J. Chabal, *Prog. Surf. Sci.* **2012**, *87*, 272.
- [33] R. Boukherroub, S. Morin, P. Sharpe, D. D. M. Wayner, *Langmuir* **2000**, *16*, 7429.
- [34] D. J. Michalak, S. R. Amy, A. Estève, Y. J. Chabal, *J. Phys. Chem. C* **2008**, *112*, 11907.
- [35] J. E. Bateman, R. D. Eagling, B. R. Horrocks, A. Houlton, *J. Phys. Chem. B* **2000**, *104*, 5557.
- [36] D. J. Michalak, S. Rivillon, Y. J. Chabal, A. Estève, N. S. Lewis, *J. Phys. Chem. B* **2006**, *110*, 20426.
- [37] R. C. Longo, K. Cho, W. G. Schmidt, Y. J. Chabal, P. Thissen, *Adv. Funct. Mater.* **2013**, *23*, 3471.
- [38] G. Barin, G. Seguini, R. Chiarcos, V. M. Ospina, M. Laus, C. Lenardi, M. Perego, *Mater. Sci. Semicond. Process.* **2023**, *165*, 107691.
- [39] E. J. Kramer, *Isr. J. Chem.* **1995**, *35*, 49.
- [40] F. Ferrarese Lupi, T. J. Giammaria, G. Seguini, M. Ceresoli, M. Perego, D. Antonioli, V. Gianotti, K. Sparnacci, M. Laus, *J. Mater. Chem. C* **2014**, *2*, 4909.
- [41] I. Luzinov, D. Julthongpiput, H. Malz, J. Pionteck, V. V. Tsukruk, *Macromolecules* **2000**, *33*, 1043.
- [42] K. S. Iyer, B. Zdyrko, H. Malz, J. Pionteck, I. Luzinov, *Macromolecules* **2003**, *36*, 6519.
- [43] Y. Fujii, Z. Yang, J. Leach, H. Atarashi, K. Tanaka, O. K. C. Tsui, *Macromolecules* **2009**, *42*, 7418.
- [44] V. Gianotti, D. Antonioli, K. Sparnacci, M. Laus, T. J. Giammaria, M. Ceresoli, F. Ferrarese Lupi, G. Seguini, M. Perego, *J. Chromatogr. A* **2014**, *1368*, 204.
- [45] M. Asai, D. Zhao, S. K. Kumar, *ACS Nano* **2017**, *11*, 7028.