

# Surface-Initiated Anionic Polymerization of Styrene by Means of Self-Assembled Monolayers

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**Abstract:** A synthetic concept of preparing dense polymer brushes on planar surfaces is described, in which a self-assembled monolayer (SAM) of biphenyllithium moieties on gold substrates is used to initiate anionic polymerization of styrene. The thickness of the resulting dry polystyrene brush, as estimated by ellipsometry and atomic force microscopy (AFM), is  $18 \pm 0.2$  nm. These techniques also reveal a smooth, homogeneous polymer surface throughout the entire substrate on the macroscopic, as well as on the microscopic, scale, with a roughness of 0.3–0.5 nm (rms). On the basis of results from in situ swelling experiments, monitored by ellipsometry, a polymerization degree of  $N = 382$  and a grafting density of approximately 7–8 chains/R<sub>g</sub><sup>2</sup>, or 3.2–3.6 nm<sup>2</sup>/chain, were calculated with use of mean-field theory. Polarized external reflection (ER) FTIR spectra of the grafted layer confirm highly stretched preferentially oriented polystyrene chains. Upon annealing, spin-coated polystyrene films dewet immediately the brush surface to give polymer droplets with a contact angle of 3°. All obtained results indicate that the described synthetic approach yields densely grafted polymer brushes whose experimental investigations were till now very limited.

## Introduction

The modification of solid surfaces by grafted polymers is a versatile and effective technique for tailoring their properties. Commonly, the choice of polymers and grafting techniques were governed by the total amount and chemical composition of the adsorbed polymer required to obtain a specific property, e.g., wetting, friction, and adsorption. However, it became clear that the *morphology* of the adsorbed polymer layer has a significant impact on the resulting properties.<sup>1</sup> One of the most intriguing structures is a polymer “brush-type” layer. The unique behavior of polymer brushes at solid interfaces results from the fact that they consists of end-grafted, strictly linear<sup>2</sup> chains of the same length<sup>3</sup> with a grafting density sufficiently high with respect to the radius of gyration ( $R_g$ ) of the grafted macromolecules. To avoid crowding, the chains are forced to stretch away from the interface, resulting in a brush height ( $h$ ) significantly larger than  $R_g$ .<sup>4</sup> Due to the confinement and the uniform polymer constitution, the brush reacts collectively to environmental stimuli such as changes of the pH or ion strength,<sup>5</sup> temperature,<sup>6</sup> solvent quality, or mechanical forces.<sup>7,8</sup> This can be used to prepare

“intelligent” materials to serve as functional devices on a nanometer scale.<sup>9,10</sup>

Traditionally, polymer brushes have been prepared by (a) selective physisorption of block-copolymers from bulk or solution onto a solid surface, where a shorter “anchor” block adsorbs strongly onto the surface, leaving the remaining “buoy” block tethered to the interface,<sup>11</sup> and (b) chemical grafting or chemisorption of polymer chains onto a reactive surface via a terminal coupling group.<sup>12</sup> However, both techniques have their limitation in terms of the maximum grafting density that can be obtained. It is easy to picture that an already adsorbed chain blocks still available grafting sites in its vicinity, because a tethered polymer chain tries to maintain its random coil conformation (Figure 1a). As the grafting density increases, the chains have to increasingly stretch to allow further grafting, which results in a decrease of the rate of grafting kinetics.<sup>13</sup> At some point, a limiting situation is reached that is dominated by the free energies of stretching, chain–chain interactions, and solvation. Hence, the grafting density of a brush, formed by

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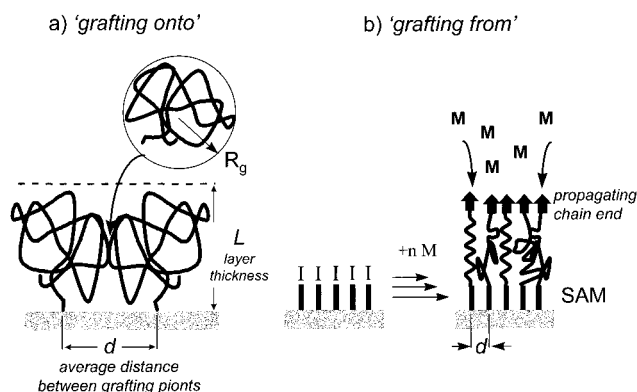
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**Figure 1.** Schematic depiction of the formation of polymer brushes via the “grafting onto” and the “grafting from” technique with  $R_g$  as the radius of gyration of a random coiled polymer in a good solvent,  $L$  as the layer thickness,  $d$  the average lateral distance between grafting points,  $M$  an arbitrary monomer, and  $I$  an initiation site able to induce a surface initiated polymerization.

the traditional “transplanting” methods, is self-limiting. Indeed, although brushes have been successfully modeled theoretically, using scaling arguments,<sup>14,15</sup> polymer brushes on solid surfaces, where the average distance between grafting points  $d$  is much smaller than  $R_g$ , have not been observed experimentally, and their technological potential<sup>16,17</sup> could not be fully exploited. This limitation can be overcome by a promising technique, the so-called “grafting from” method (Figure 1b).

In this method a reactive group is created on the surface that is able to initiate the polymerization, and the propagating polymer chain is growing from the surface. It can be employed with all polymerization types, and a number of papers have reported high amounts of immobilized polymer by using radical polymerization with various initiators.<sup>18</sup>

Because of the intrinsic difficulty of investigating the polymer layers on small particles, the characterization of the obtained materials was mainly restricted to accounts of the total grafted amount of polymer and to estimations of the grafting density based on the remaining initiation sites. Hence, no information on morphology and brush characteristics could be provided. Here the work of Voronov et al. has to be mentioned. In a series of papers they address further details on the in situ grafting with free radical polymerization, which also includes SPM studies on the morphology of the resulting polymer layers.<sup>19</sup>

Recently Rühle et al. reported a detailed study of a similar system using azo initiators on silica to polymerize styrene via free radical polymerization. The initiators were modified and could be detached from the surface to allow quantification of polymer characteristics of the grafted chains and therefore

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addressing similarities and differences of the process of radical polymerization in solution and in a confined system.<sup>20</sup>

However, cross-linking, competitive side, and termination reactions are augmented in surface-initiated polymerizations due to the extremely small total number of reactive chain ends, as well as their high concentration, confined in a thin layer.<sup>21</sup>

Recalling the characteristics of a brush, as a layer of linear chains of uniform length, living polymerization reactions should be the preferred routes for their formation. Spange and co-workers successfully employed surface-initiated living cationic polymerization,<sup>22</sup> and recently we reported on the first successful living cationic ring-opening polymerization of 2-ethyl-2-oxazoline on planar surfaces.<sup>23</sup>

The living anionic polymerization of vinyl monomers is known to result in strictly linear polymers with the lowest polydispersities, due to the highly living nature of the propagating species and total absence of side reactions.<sup>24</sup> However, it is also extremely sensitive to impurities, and therefore only a few examples of surface-initiated anionic polymerization reactions can be found in the literature. Taking advantage of the higher surface area, all were conducted on small particles such as carbon black,<sup>25</sup> carbon fiber,<sup>26</sup> graphite,<sup>27</sup> and silica,<sup>28</sup> mainly under the premise of improving their colloidal stability.

The only cited work on surface-initiated anionic polymerization of styrene and isoprene, carried out on planar silica surfaces, is by Schouten and co-workers.<sup>29</sup> They immobilized a layer of 4-trichlorosilylstyrene on the silica surface, and using *sec*-butyllithium (*s*-BuLi) have created a layer of initiators. However, low conversions (in terms of layer thickness) and reproducibility problems, probably due to contamination and competitive side reactions at the silica surface, were reported when planar substrates were used.

The ideal systems for creating suitable initiation sites on surfaces are self-assembled monolayers (SAMs), especially those of  $\omega$ -functionalized organic thiols on gold.<sup>30</sup> First, gold surfaces are chemically homogeneous, easy to clean, and virtually free of contaminations. Second, they allow a broad variety of analytical techniques, frequently used for the characterization of thin films. Third, SAMs of different types of functionalized thiols, for example, aryl or *n*-alkyl derivatives, enable the control of the reactivity of the initiator, crucial to obtain a suitable ratio of the initiation and propagation step of consecutive polymerization reactions. Finally, mixed SAMs allow the control of the lateral concentration, and hence grafting density of polymer chains. This approach was found very effective in our recent account on the preparation of amphiphilic polyoxazoline brushes, initiated by SAM of  $\omega$ -functionalized *n*-alkanethiols.<sup>23</sup>

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## Experimental Section

**Materials: (a) Chemicals.** All solvents used were of HPLC grade and used as obtained from Aldrich or EM Science. Solvents used for the anionic polymerization were additionally dried, degassed, and purified following standard procedures.<sup>31</sup> Styrene, *s*-BuLi and 2-propanol were purchased from Aldrich, purified, and transferred into ampules with use of a high-vacuum, all-glass setup as described elsewhere.<sup>31</sup> Monodisperse polystyrene ( $M_w = 66K$ ;  $M_w/M_n = 1.06$ ) and block copolymers of poly(4-vinylpyridine-*block*-styrene) with different compositions (P4VP(3,600)-PS(35,300), P4VP(13,200)-PS(31,900)), and P4VP<sub>20</sub>-*d*-PS<sub>220</sub> used for the comparative studies were obtained as a gift from Exxon.

The synthesis and purification of 4'-bromo-4-mercaptobiphenyl and 4'-hydroxy-4-mercaptobiphenyl will be reported elsewhere.<sup>32</sup>

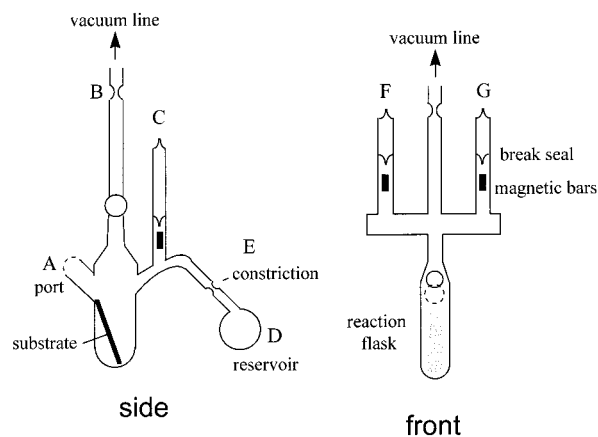
**(b) Substrates.** Gold Substrates were prepared by thermal evaporation of titanium (10 nm) as an adhesive layer and gold (150 nm) onto planar microscope glass slides (2.5 × 5 cm, Fischer Scientific). The glass slides were cleaned with ethanol in an ultrasonic bath for 15 min, dried with a jet of nitrogen, and further cleaned for 15 min by argon plasma treatment (PLASMOD, March Instruments Inc.). Substrates were immediately transferred into a UHV evaporation setup (Key Vacuum, Inc.). At a base pressure of no more than 10<sup>-6</sup> Torr, titanium and gold were consecutively deposited.

**Synthesis and Sample Preparation: (a) SAMs.** Self-assembled monolayers (SAMs) of 4'-bromo-4-mercaptobiphenyl and 4'-hydroxy-4-mercaptobiphenyl were prepared by exposing a freshly prepared and cleaned planar gold substrate to a solution of the thiol (10 μM) in ethanol for 16 h. Monolayer quality was monitored by using ER FTIR spectroscopy and ellipsometry on simultaneously prepared substrates. The monolayer thickness estimated by ellipsometry was 1.4 ± 0.2 nm (with  $n = 1.462$ ), in agreement with a complete formation of a monomolecular layer with molecules oriented normal to the surface.<sup>31</sup> FTIR spectra were in agreement with previously obtained results.

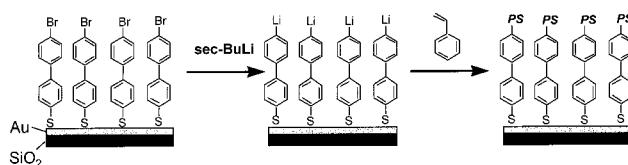
**(b) PVP-PS Brush Formation on SAMs and SiO<sub>2</sub>/Si Wafers.** For the preparation of comparative polystyrene brushes, a SAM of 4'-hydroxy-4-mercaptobiphenyl was exposed to dilute solutions of PVP-PS copolymers in toluene. Brush formation was monitored by ellipsometry and ER FTIR spectroscopy (*ex situ*). Brush formation was considered to be complete (approximately after 5 days) until no further increase in thickness values or change in the IR spectra could be detected. PS brushes prepared in this manner were reproducible and are comparable to samples previously obtained in a similar manner on silicon dioxide/silicon wafers.<sup>33</sup> PVP<sub>20</sub>-*d*-PS<sub>220</sub> brushes on silicon wafers (standard wafers with naturally oxidized surface,  $d_{SiO_2} \sim 1.5$  nm) were prepared as previously described.<sup>34</sup>

**(c) Anionic Polymerization.** Figure 2 presents the experimental setup used to carry out the anionic polymerization under high vacuum conditions.<sup>35</sup>

After placing SAM-coated gold surfaces (0.25/0.8 in.) into the reaction flask, the port (A) was sealed off, and the reactor was evacuated. 350 mL of dry and degassed solvent (cyclohexane:benzene



**Figure 2.** Illustration of the used all-glass reactor for the surface-induced anionic polymerization of styrene. The substrates were transferred into a modified all-glass reactor commonly used for the preparation of block-copolymers by means of anionic polymerization. Under high vacuum conditions the SAM was metallized by adding BuLi and the polymerization of styrene was carried out by using a standard procedure described elsewhere.



**Figure 3.** Reaction scheme for the surface-induced living anionic polymerization by using the self-assembled monolayer of 4'-lithio-4-mercaptobiphenyl.

60:40 (*v:v*)) was distilled into the reaction flask, and the reactor was sealed off (B). With use of a break seal, *s*-BuLi ( $4.9 \times 10^{-4}$  mol in 5 mL cyclohexane) was added (C) and allowed to react with the SAM overnight to form a monolayer of biphenyllithium. The solution was poured into the reservoir and the solvent was distilled back into the reaction flask. This was repeated 6 times to ensure an almost complete removal of excess of *s*-BuLi and impurities. The reservoir (E) was detached from the reactor, and, using a break seal, styrene monomer (22.6 mL) was added (F). Polymerization was allowed to complete within 3 days at room temperature, before it was terminated with 2 mL of 2-propanol (G) for 1 day. The samples were taken out of the reactor and immediately washed 5 times with benzene. As measured by GPC, the molecular weight of the "bulk" polymer formed in the solution was  $1.6 \times 10^6$  g/mol.<sup>36</sup>

**Characterization: (a) Ellipsometry.** Ellipsometric data were obtained on an AutoEL Rudolf Research ellipsometer with a He-Ne laser ( $\lambda = 632.8$  nm) and a fixed angle of incidence of 70°. For the calculation of the layer thickness, a refractive index of  $n = 1.462$  for the SAM and  $n = 1.520$  for the polymer layer was used.

The *in situ* ellipsometry measurement (swelling experiment) was performed as follows: The sample substrate was placed on the ellipsometer stage, and two stripes of filter paper were placed ~1 mm apart to allow the laser beam to reflect from the surface. The filter papers were covered with glass slides to minimize the evaporation rate of the solvent as well as temperature fluctuations during the experiment and then soaked with the solvent. During this soaking procedure the first data points were collected. We observed stable readings when a thin solvent film was formed between the filter papers as seen through the optics of the ellipsometer (maintaining a constant solvent coverage of the surface by constantly adding additional solvent from both sides). It is noteworthy to mention that by this fairly simple technique the swelling behavior of a polymer film in a bulk *liquid* and not only in a vapor phase can be monitored. The time resolution of collected data points was typically 40 s. Given values are averaged from consecutive

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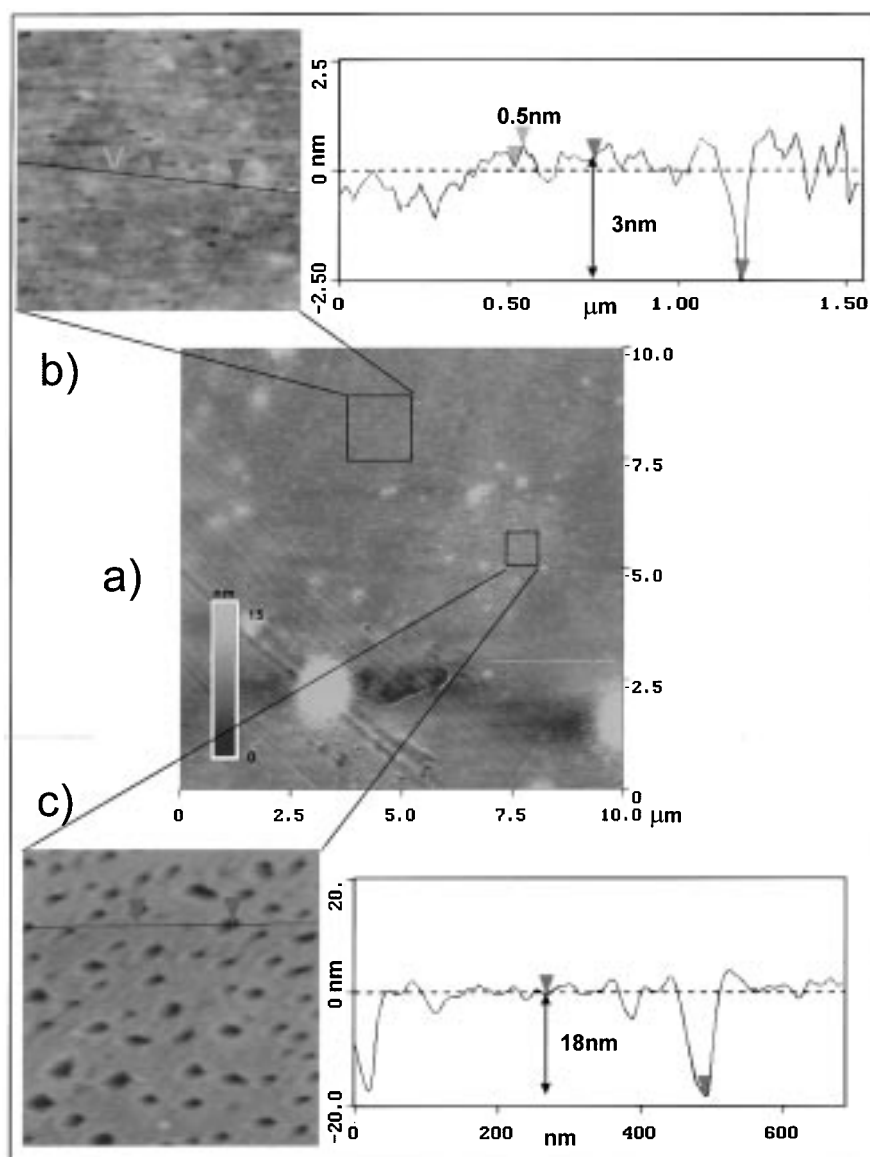
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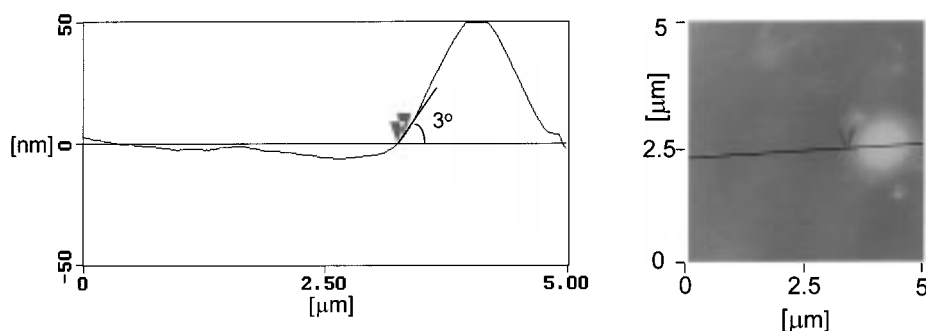
(34) Since a direct measurement of the molecular weight as well as the polydispersity index of the obtained polymer is not trivial, if not impossible due to the very small total amount of grafted chains, no experimentally accessible values can be given at this point. However, experiments are currently ongoing to address this question. An alternative way would be the preparation of PS brushes on small particles to increase the surface area and therefore the total amount of polymer. Following the idea of Rühle et al. after detachment of the entire layer, the polymer could be characterized by using mass spectrometry or chromatographic techniques. This would not be a legitimate solution to the problem because growing polymers on a curved surface present sterically an entire different system, affecting the kinetics of the starting and propagation reaction as well as brush conformation of the final material. Thus, one cannot directly compare such a system with the one presented in this paper.

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(36) Polymerization in the solution has to be expected due to the relatively high excess of added *sec*-BuLi.



**Figure 4.** Surface topography of the grafted polystyrene layer after Soxhlet extraction as probed by contact atomic force microscopy. (a) Typical scan ( $10 \times 10 \mu\text{m}^2$ ) with detailed scans as marked in the overview along with the dept profile analysis along the indicated lines (digital instruments, Nanoscope III).

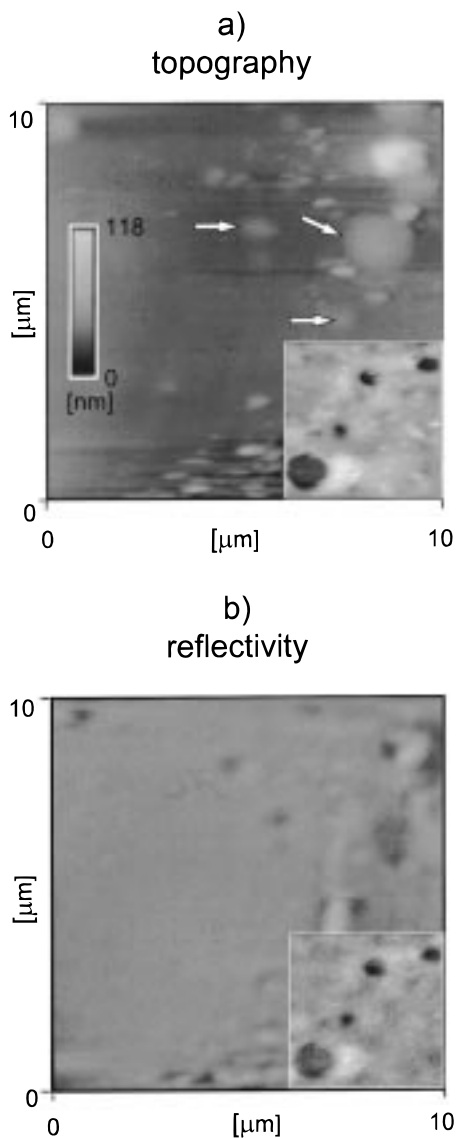


**Figure 5.** AFM scan of a single droplet of polystyrene on top of the polystyrene brush along with its dept profile and contact angle.

measurements showing a stable reading for a minimum time interval of 15–20 min at three individual spots. The scattering of all measured thickness values was smaller than 0.5 nm. Although a “swelling kinetic” can be recorded in this manner, repeated experiments showed that the time dependency of the swelling step was not reproducible due to a strong influence of the homemade setup (solvent diffusion rates through the filter paper) as well as the rather poor time resolution. To verify the reliability of this technique, a control sample of a deuterated poly-

(styrene-*block*-4-vinylpyridine) ( $N = 220$ ), anchored to a silicon substrate by the poly(4-vinylpyridine) block ( $N = 20$ ), was tested with this method. The swelling of the layer from 10.4 nm in air as a poor solvent to 25.4 nm is in excellent agreement with the height measured by AFM and neutron reflection in toluene liquid.<sup>37</sup> The accuracy of all thickness values is typically within  $\pm 0.2$  nm.

(b) **External Reflection (ER) FTIR Spectroscopy.** ER FTIR spectra were recorded with a Magna 760 IR spectrometer (Nicolet) equipped



**Figure 6.** (a) Surface force micrograph showing the topography of a dewetted polystyrene film (same sample as in Figure 5) on top of the polymer brush. (b) Near-field scanning optical micrograph (NSOM) of the same surface section. The inserts in the lower right corners are corresponding scans ( $8 \mu\text{m}^2$ ) showing the topological as well as optical contrast between the bare gold and the polystyrene brush.

with a grazing angle setup (fixed angle of  $80^\circ$ , FT-80, SpectraTech), a polarizer (p-polarization), and a MCT-A detector cooled with liquid nitrogen. The sample compartment was purged with dry and  $\text{CO}_2$ -free air. 2000 scans were accumulated for each spectrum with a spectral resolution of  $2 \text{ cm}^{-1}$ . Data manipulation was restricted to a manual baseline correction for display purposes. Evaluations of positions band maxima and integral band areas were performed on raw data only.

**(c) Scanning Probe Microscopy Techniques.** Atomic force microscopy (AFM) of the polymer brush surface and measurement of contact angles of the polystyrene droplets were performed with a Nanoscope III (digital instruments) in contact mode, minimizing tip-surface interaction to reduce sample deformation.

Near-field scanning optical microscopy (NSOM) was performed by Bernd Müller-Zülw with the AURORA system (Topometrics).

**(d) Wetting Experiments.** Water contact angles were determined with a Ramé-Hart goniometer equipped with a CAD camera and computer aided image analysis. For static contact angles, the angle at

both sides of the free-standing droplet was measured at 4 different spots of the same substrate. Given results are average values of all measurements. Advancing and receding angle measurements were found to be most accurate and reproducible if the tilting plate method was used.

To test the wetting behavior of the polystyrene brush by bulk polystyrene, a 20 nm thick layer of monodisperse polystyrene ( $M_w = 66\text{K}$ ,  $M_w/M_n = 1.06$ ) was spin-coated directly onto the brush surface with toluene as the solvent. The samples were annealed ( $120\text{--}130^\circ\text{C}$ ;  $T_g(\text{PS}) \sim 100^\circ\text{C}$ ; 5 min;  $10^{-4}$  Torr), cooled to room temperature, and immediately studied by AFM. The contact angles were evaluated by analyzing the line sections of detailed scans ( $2 \times 2$  to  $5 \times 5 \mu\text{m}$ ) with the software package provided with the instrument. Contact angle analysis was carried out for numerous polystyrene droplets within previously scanned areas of  $20 \times 20 \mu\text{m}$ . The obtained values did not scatter significantly from the value mentioned in the text.

## Results and Discussion

As outlined in Figure 3, a SAM of 4'-bromo-4-mercaptobiphenyl was self-assembled on a planar polycrystalline gold surface and transferred into a modified all-glass reactor commonly used for the preparation of block copolymers. The bromo-functionalized SAM was metallized by means of *s*-BuLi to obtain 4'-lithio-4-mercaptobiphenyl as the initiator for the anionic polymerization of styrene.

After the termination reaction with 2-propanol, the substrates were rinsed with benzene and subjected to Soxhlet extraction with toluene for 48 h to remove adsorbed polystyrene, polymerized in the solution.

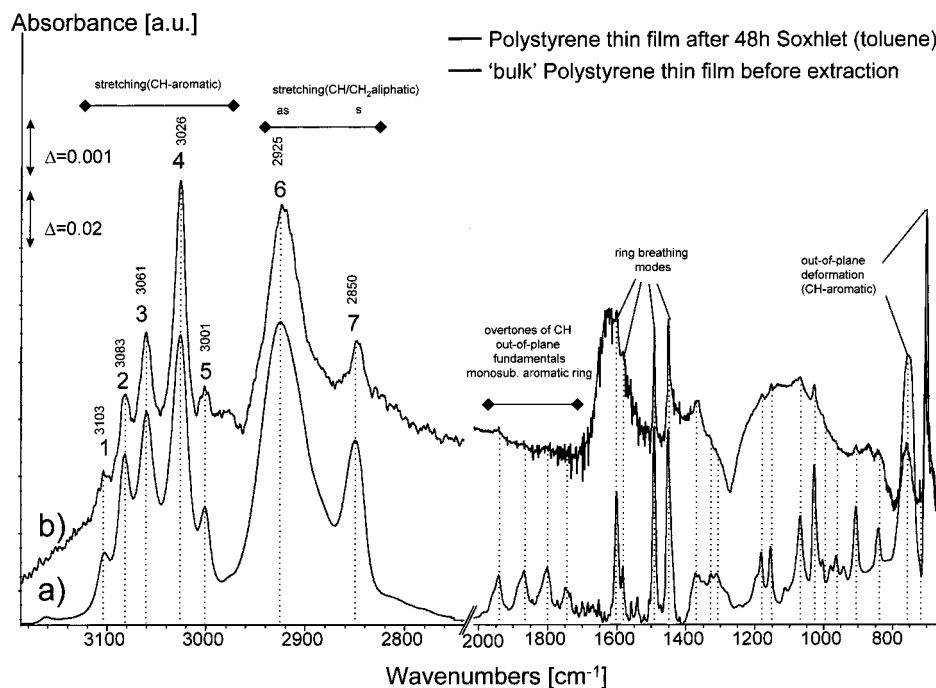
Fourier transform infrared (FTIR) spectroscopy shows that all literature-reported polystyrene peaks appear in the spectra of the immobilized layer, confirming a successful grafting reaction (see Figure 7 below). Thickness measurements with ellipsometry revealed a uniform film with an average layer thickness of  $18 \pm 0.2 \text{ nm}$ . The small scattering of the thickness values of only 0.5 nm indicates a homogeneous polymerization reaction across the substrate surface of  $1 \times 2 \text{ cm}$ . To address the surface topography of the polystyrene layer on a molecular scale, contact atomic force microscopy (AFM) was performed.

Figure 4a shows a typical topographic scan of the polymer layer, featuring two types of surfaces. Detailed scans of the marked areas (boxes) reveal large smooth and uniform areas with a typical surface roughness value of 0.5 nm (rms). The small variation in thickness values on the macroscopic as well as microscopic scales corroborates the assumption of a uniform reaction throughout the substrate surface and reflects a presumably small polydispersity, as expected from anionic polymerization. In addition, areas featuring several small dimples, typically 2–3 nm deep, were observed (Figure 4b). These are intersected by small areas of defects, which consist of dense arrangements of holes surrounded by rims. It is interesting to note that these holes are 18–20 nm deep, corresponding to the layer thickness as measured by ellipsometry (Figure 4c).

We have studied the wetting properties of these brushes using both water and polystyrene. The water contact angle of a sessile drop ( $10 \mu\text{L}$ ) was  $90^\circ \pm 2^\circ$  at room temperature and 30% relative humidity. Advancing water contact angle was  $92^\circ \pm 2^\circ$ , and receding contact angle was  $83^\circ \pm 2^\circ$ , respectively. These values are consistent with previous wetting experiments with water on bulk polystyrene. The small hysteresis attests to the uniformity of the layer composition as well as the low surface roughness.

Liu and co-workers have previously demonstrated<sup>33</sup> that in contrast to a simple liquid, which always spreads on a free surface of identical surface tension, a homopolymer may dewet a substrate of identical chemical composition. If the interfacial

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**Figure 7.** External reflection (ER) FTIR spectra of the polystyrene films as obtained directly after the polymerization and cold extraction by using benzene (a, gray line) and after Soxhlet extraction for 48 h. Spectra were recorded in p-polarization.<sup>42</sup> Note the different ratio between the CH<sub>2</sub> aliphatic stretching modes (6/7) in spectrum b. For details please refer to the text.

macromolecules are confined in some way, i.e., tethered at one end so that they form a dense brush, an entropic barrier is established to interpenetration.

To test the wetting behavior of the polystyrene brush by bulk polystyrene, a 20 nm thick layer of monodisperse polystyrene was spin-coated directly onto the brush surface. The samples were annealed, cooled to room temperature, and immediately studied by AFM.

Figure 5 shows that the spin-coated polystyrene layer completely dewets the surface, confirming that the grafted polystyrene chains are arranged in a stretched, dense brush configuration. The observed average contact angle of 3°, as measured by AFM, is somewhat smaller than that predicted by Leibler<sup>38</sup> in the absence of substrate deformation. In contrast to a hard surface, a brush surface can deform at the contact line in response to the vertical component of the droplet surface tension. The entropic penalty of chain stretching is balanced by minimizing the contact angle.

To ensure that the droplets depicted in Figure 5 are made of polystyrene and are not a contamination or a result of the dewetting of both layers from the gold substrate, we used near-field scanning optical microscopy (NSOM) to investigate the surface. Since polystyrene is glassy at room temperature, we found that neither scanning nor phase contrast microscopies can unambiguously distinguish between the polymer layer and a bare gold surface. The NSOM method is ideally suited for this problem, since it is sensitive to small differences in the refractive index, and hence to chemical composition, rather than mechanical properties.

Figure 6 presents a topographic image (Figure 6a) and an optical image (Figure 6b), simultaneously recorded of the same surface section. As expected, the same features that appear as blobs on the surface in the topographical mode (Figure 6a, arrows) are invisible in the optical mode, since the bulk polystyrene droplets and the polystyrene brush have the same

refractive index. The holes in the polystyrene brush seen in the topographical image (insert, Figure 6a), on the other hand, appear dark in the NSOM image (insert, Figure 6b), indicating a large refractive index difference between the polymer and the exposed gold substrate. This is the first reported use of NSOM for material identification in ultrathin films.

To estimate<sup>34</sup> grafting density and the molecular weight of the tethered chains, swelling experiments with toluene as a good solvent were carried out. The brush thickness of  $18 \pm 0.2$  nm increased to  $29 \pm 2$  nm when swollen in toluene, before decreasing back to the dry state value. The experiment was cycled a number of times with no apparent difference in thickness values. In fact, measuring different spots on the same substrate gave nearly identical results. The uniform swelling behavior as well as the mentioned AFM results reflect a uniform formation of a polystyrene brush in terms of grafting density as well as molecular weight.

By using previous results<sup>37</sup> and the thickness values of the brush in the collapsed and in the swollen states, the polymerization degree can be estimated using the self-consistent mean field theory developed by Milner and Cates.<sup>39</sup> The height  $h$  of a brush in a good solvent is given by:

$$h = (12/\pi)^{1/3} N \sigma^{1/3} (\omega/\nu)^{1/3} \quad (1)$$

where  $\omega$  is the excluded volume parameter,  $\omega$  is the excluded volume parameter, approximately  $(2 \text{ \AA})^3$ ,  $N$  is the number of monomers, and  $\nu = (a^2/3)^{-1}$ , with  $a = 6.7 \text{ \AA}$ , as the Kuhn length for a polystyrene monomer unit. Therefore, the polymerization degree can be expressed as

$$N = [1.074(h_{\text{swollen}})^{3/2}]/[(h_{\text{dry}}(\text{\AA}^2))^{1/2}] \quad (2)$$

When substituting  $h_{\text{swollen}} = 276 \text{ \AA}$  and  $h_{\text{dry}} = 166 \text{ \AA}$  (subtracting the thickness of the underlying SAM), eq 2 gives  $N = 382$ ,

(38) Leibler, A. R. *Proceedings of the OUMS—Conference on Ordering in Macromolecular Systems*, Osaka, June 1983.

(39) (a) Milner, S. T. *Europhys. Lett.* **1988**, *7*, 695. (b) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610.

and  $R_g = 50.6 \text{ \AA}$ . Similarly, the grafting density ( $\sigma = \rho_0 h_{\text{dry}}/N$ ) was obtained as approximately 7–8 chains/ $R_g^2$ , or an area of 3.2–3.6 nm<sup>2</sup>/chain. This is the highest reported value for a grafting density of a polymer brush on a planar surface so far, suggesting that the tethered chains must be highly stretched. Considering an area per molecule of 0.2 nm<sup>2</sup> in the SAM, the grafting efficiency calculates to one polymer chain for every 16–18 biphenyl thiol molecules.

To study chain conformation, the polarized infrared spectra of the polystyrene brush was compared to that of a bulk film. The polarized, reflection absorption IR spectrum is especially sensitive to chain orientation with respect to the reflecting surface, since only vibrating dipoles with components vertical to the surface are detectable.<sup>40</sup> Since in an all-trans, vertical polymethylene chain both  $\nu_s(\text{CH}_x)$  and  $\nu_{\text{as}}(\text{CH}_x)$  are parallel to the gold surface, and orthogonal to each other, their integral absorption ratio in the brush IR spectrum should provide information on the average chain orientation.

Figure 7 shows external reflection (ER) FTIR spectra of a bulk PS film (a) and the PS brush Soxhlet extraction (b).<sup>41</sup> Upon closer inspection of the  $\nu\text{CH}_x$  region (3000–2800 cm<sup>-1</sup>), the relative intensities are significantly different for both spectra. For example, while the ratio  $\nu\text{CH}_2(\text{as})/\nu\text{CH}_2(\text{s})$  (bands assigned as 6/7 in Figure 7, a and b) is  $\sim 4.5$  in the “bulk” spectrum, it is  $\geq 10$  in the brush spectrum. Differences in ratios of CH-aromatic stretching modes are also noticeable. This indicates an apparent difference in the average orientation of the polymer backbone between bulk and tethered polystyrene chains. Such an orientation can only be explained if the chains are considerably stretched due to the high grafting density. To verify that the relative ratio is reflecting the degree of stretching and therefore a preferred orientation of the polystyrene chains with respect to the surface normal, control experiments were performed as followed: Two block copolymers of poly(4-vinylpyridine-*block*-styrene) with different compositions (P4VP-(3,600)-PS(35,300) and P4VP(13,200)-PS(31,900)) were end-grafted via hydrogen-bond formation of the P4VP segment onto a SAM of 4'-hydroxy-4-mercaptobiphenyl. The layer thickness was 8.9 and 5.3 nm, respectively. ER-FTIR spectra were recorded before and after an annealing step (110 °C, 1 h in a vacuum). The  $\text{CH}_2(\text{as})/\text{CH}_2(\text{s})$  ratio was determined as 3.543 (3.436) and 3.365 (3.321), respectively, and did not change significantly upon annealing (values given in brackets). A comparison of the ER FTIR spectra of the PS-P4VP polymers as a bulk sample (spin coated on native Au(111)) and as a physisorbed polymer brush gave similar results with respect to the  $\nu\text{CH}_2(\text{as})/\nu\text{CH}_2(\text{s})$  ratio, confirming our assumption of the impact of the relative surface/chain orientation upon the ratio of the  $\text{CH}_2$ -adsorptions. However, the effect was not as significant as reported for the SAM-PS sample, which can be

(40) Blanke, J. F.; Vibcent, S. E.; Overend J. *Spectrochim. Acta, Part A* **1976**, 32, 163.

(41) The ER FTIR spectrum of the substrate before extraction can be considered as a bulk spectrum due to the high amount of adsorbed but not grafted polystyrene on top of the grafted layer.

explained due to the lower grafting density of the PS-P4VP brush, as well as to the presence of  $\text{CH}_2$  groups in the P4VP foot adsorbed on the solid surface.<sup>42</sup>

It is noteworthy that even drastic treatments such as repetitive washing/rinsing or Soxhlet extraction procedures with good solvents, annealing steps at elevated temperatures, as well as prolonged storage at ambient laboratory environment (several months) do not desorb the entire polymer/SAM layer, nor were significant changes detected by ER FTIR spectroscopy, ellipsometry, or SPM. The superficial polymer brush seems to have a strong stabilizing effect because pure SAMs of organic thiols readily desorb under these conditions. The same stability was observed for polyoxazoline brushes tethered to *n*-alkyl thiols.<sup>23</sup>

## Conclusion

In conclusion, we presented the first report of surface-initiated anionic polymerization of styrene using a SAM on planar gold substrates as initiation sites. Taking the reported results together, this new synthetic approach results in homogeneous “brush-type” polystyrene layers with a very high grafting density as well as surprisingly high stability.

Experiments are underway to use mixed SAMs in an attempt to control grafting density, and to widen the synthesis to other types of monomers as well as to preparing block copolymers. The latter experiment is crucial to investigate the “livingness” of this system, since the total amount of propagating sites is extremely small and therefore very sensitive to side reactions.

While our first choice was an aromatic bromide as the initiation site, due to the advantage of the absence of elimination reactions, we are currently studying monolayers of aliphatic  $\omega$ -bromothiolate. Clearly, the nucleophilicity of alkyllithium is much higher than that of phenyllithium, thus we expect that similar reactions can be carried out using a much lower concentration of styrene.

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(42) Although all characteristic adsorption bands for PS appear in spectrum b, verifying the presence of PS, and the analysis of the CH-stretching area is meaningful due to a good signal-to-noise ratio and baseline separated bands, the spectrum is obstructed in the fingerprint region due to the appearance of  $\text{SiO}_x$  adsorption. This is due to the rather small substrate size, necessary to fit the sample though the port of the reactor (Figure 2).  $\text{SiO}_x$  adsorption bands are mainly due to beam–substrate edge interaction. Therefore no further information can be retrieved other than the simple identification of the surface layer by the characteristic PS adsorption bands.