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"Living" Free Radical Photopolymerization Initiated from Surface-Grafted Iniferter Monolayers

B. de Boer, H. K. Simon,[†] M. P. L. Werts, E. W. van der Vegte,[‡] and G. Hadziioannou*

Department of Polymer Chemistry, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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ABSTRACT: A method for chemically modifying a surface with grafted monolayers of initiator groups, which can be used for a "living" free radical photopolymerization, is described. By using "living" free radical polymerizations, we were able to control the length of the grafted polymer chains and therefore the layer thickness up to ~100 nm. Also, single-layer grafted block copolymers were obtained by subsequent polymerizations of styrene and methyl methacrylate monomers. The surface-grafted polymer and block copolymer layers were evidenced by direct imaging methods (transmission and scanning electron microscopy) and by indirect surface characterization methods (contact angle measurements, SFM, XPS, and IR). The ability to control the thickness of the grafted polymer as well as the synthesis of a grafted block copolymer layer in a well-defined manner affirms the "living" character of the surface-initiated free radical photopolymerization.

Introduction

Modification of surfaces of solid (in)organic materials is often utilized to change properties such as biocompatibility, wetting, adhesion, or friction. Modifications with polymer layers are recognized to play an important role, especially in printing, coating, food packaging, microelectronics, biomedical, and aerospace applications. Engineering surfaces at a molecular level gained interest during the 1990s, because this can lead to well-defined surfaces with better macroscopic properties than those obtained by coating the surface with a thin (functional) polymer film. Coating of surfaces by irreversible grafting of a stable, preformed polymer[1] or by selective adsorption of a diblock copolymer[2] leads, in general, to nonuniform thin films and poor surface coverage, due to the formation of islands and mushrooms on the surface. Other frequently used methods such as polyelectrolyte deposition,[3] plasma deposition,[4] and polymerization within a Langmuir−Blodgett (LB) film suffer from the same disadvantages. Furthermore, these techniques do not completely control the growth of stable polymer films at the nanoscale level, which is required for most of the applications.

To overcome this, direct initiation of a polymer chain from a surface can be applied, which is expected to lead to higher surface grafting densities, because monomers can more easily diffuse toward the reactive center, whereas grafting or selective adsorption of polymers is limited by steric and entropic forces.

The autoassociation process has been used for covalently attaching a monolayer with high grafting densities on a surface. Examples of this are alkanethiols, which are known to form very stable monolayers on gold,[5] and alkoxysilanes, which are used to modify solid surfaces such as glass, silicon wafers, quartz, and mica. At these surfaces, the alkoxysilane group is converted to a stable poly(siloxane) layer by coupling with the free hydroxyl groups on the surface.

To initiate a polymerization from the surface, the autoassociating molecule had to be modified with an initiator group. In most cases, conventional radical initiating species[6,7] or ionic moieties[8,9] are introduced on the surface. For the polymerization of block copolymers and for controlling the molecular weight, and thus layer thickness as well as the composition, one is restricted to using the "living" polymerization technique.

Advanced "living" free radical polymerization methods allow the synthesis of a wide variety of macromolecules with monomers that cannot be polymerized with the traditional cationic and anionic living polymerizations.[9,10] Three "living" free radical polymerization methods are often employed, namely the atom transfer radical polymerization (ATRP),[11] the nitroxide-mediated free radical polymerization (TEMPO),[12] and the polymerization method based on iniferters.[13] In this study we used the photoiniferter technique explored by Otsu et al.[14] in the early 1980s. The concept of these nonconventional initiators is based on the formation of a reactive radical and a relatively stable counter radical, where the latter does not participate in the *ini*tiation, but merely acts as a trans*fer* agent and *ter*minating species (*iniferter*). The advantages of "living" free radical polymerizations are (a) linear increase of molecular weight with time, leading to a steady growth of the uniform polymer layer on the surface, (b) possibility of the formation of block copolymers by reinitiating the polymerization in a different monomer solution, and (c) compatibility with a wide variety of monomers, e.g., acrylates, styrenes, acrylonitrile, and derivatives. Furthermore, in the particular case of surface-initiated "living" free radical polymerizations, the preparation and handling of the samples are easier,[17] which allows one to characterize the surface between two subsequent polymerizations.

[†] Present address: Hoogovens Research & Development, P.O. Box 10000, 1970 CA IJmuiden, The Netherlands.

[‡] Present address: DSM Research, P.O. Box 18, 6160 MD, The Netherlands.

* To whom correspondence should be addressed. e-mail: hadzii@chem.rug.nl.

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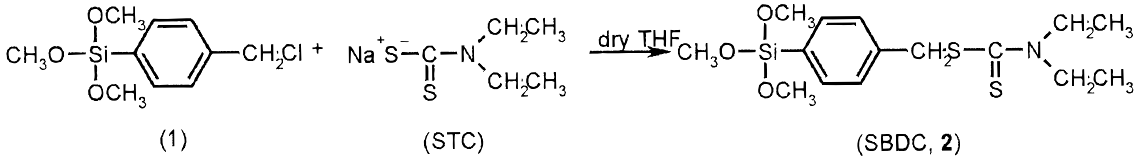
Scheme 1. Synthesis of *N*,*N*-(Diethylamino)dithiocarbamoylbenzyl(trimethoxy)silane (SBDC)



Just recently, three papers on controlled radical polymerization initiated by a surface-grafted initiator appeared.[15−17] In the first two papers, the authors used atom transfer radical polymerization (ATRP) to control the molecular weight and thereby the layer thickness. A disadvantage of this method is the presence of inorganic salts at the surface, which would require further purification steps. The third paper, by Husseman and co-workers,[17] deals with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)-functionalized chlorosilanes for the modification of the surface. The authors obtained an accurate control of molecular weight (or layer thickness) and were able to polymerize sequentially different monomers to obtain block copolymers, which is one of the ultimate goals in this field of research.

Other groups[18,19] used grafted iniferters on the surface of silica gel, which resulted in difficulties regarding the characterization of the initiator monolayer formed and of the thickness of the polymer layer on the surface. Kobayashi and co-workers[19] grafted *N*,*N*-(diethylamino)-dithiocarbamoylpropyl(trimethoxy)silane on a glass surface and initiated the photopolymerization of sodium styrenesulfonate from the surface, but a controlled radical polymerization could not be obtained, which corresponds to results found in the literature.[20] Nakayama, Matsuda, and co-workers used thin polymeric films partially derivatized with *N*,*N*-diethyldithiocarbamate groups and characterized the different grafted polymer layers with scanning force microscopy (SFM);[21] in this case the growing polymer chain is not directly bound to the (inorganic) substrate. The authors were able to obtain a patterned surface by applying a striped projection mask, which is an advantage of photopolymerizations.

In our work, initially we modified the surface with thiol-functionalized iniferters, since thiol-terminated molecules are known to form thermally stable bound monolayers on a gold surface,[22] and moreover these molecules can undergo chemical modification in such a layer similar to the reactions in solution.[23] Unfortunately, the thiol−gold bond proved to be unstable toward UV irradiation,[24] and therefore organosilane-terminated iniferters were used to graft the iniferter monolayer on silicon wafers and glass. The iniferter monolayers were used for the surface-initiated photopolymerizations of styrene (St) and methyl methacrylate (MMA) into homopolymers and block copolymers. In the case of block copolymerization of PS-*b*-PMMA, the macroinitiator efficiency is found to be less than in the photopolymerization of styrene. Furthermore, the photolysis of the dithiocarbamate end group and other side reactions in the MMA polymerization are known to play an important role in solution photopolymerizations.[25] In our case, however, due to the "confined two-dimensional" character of the photopolymerization, the efficiency may be improved and side reactions limited.

We used surfaces with chromium lines as a reference and for the facile direct visualization and measurement of the growing polymer layer with SFM. Furthermore, we used scanning electron microscopy (SEM), transmission electron microscopy (TEM), contact angles, IR, and X-ray photoelectron spectroscopy (XPS) for providing both direct and indirect evidence for the presence of the polymer layer on the substrates.

In this paper we describe the formation of densely grafted stable alkoxysilane monolayers modified with iniferter end groups and the "living" free radical photopolymerizations of styrene and methyl methacrylate into homopolymers and block copolymers initiated from these monolayers.

Experimental Section

Materials. *p*-(Chloromethyl)phenyltrimethoxysilane (ABCR), ethanol, chloroform (Labscan), and dichloromethane (Aldrich) were used as received. Prior to use, sodium *N*,*N*-diethyldithiocarbamate (Aldrich) was recrystallized from methanol, THF was distilled from potassium, and toluene was distilled from sodium/benzophenone. Water was deionized (18.2 MΩ·cm resistivity) with a Millipore Milli-Q filtration system. Styrene (Acros) and methyl methacrylate (Merck) were distilled at reduced pressure prior to use.

Synthesis of Silane-Terminated Iniferter (SBDC). *p*-(Chloromethyl)phenyltrimethoxysilane (**1**) (1.48 g, 6 mmol) and sodium *N*,*N*-diethyldithiocarbamate (STC) (1.02 g, 6 mmol) were each dissolved separately in 10 mL of dry THF (Scheme 1). The STC solution was added slowly to (**1**) via a syringe. The solution was stirred for 3 h at room temperature. A white precipitate was formed almost immediately (NaCl), and during the reaction period the solution became more yellow. The precipitate was removed by filtration through a glass filter. The THF was evaporated, and a yellow viscous liquid remained, which was vacuum-distilled in a Kugelrohr (160 °C, 0.1 mbar). The product *N*,*N*-(diethylamino)dithiocarbamoylbenzyl(trimethoxy)silane (**2**) (SBDC) was obtained as a light-yellow viscous liquid, 0.638 g (yield: 30%). By synthesizing SBDC in bulk instead of on the surface, one can purify and characterize the initiating species by ^{1}H NMR. SBDC (**2**) proved to be stable (^{1}H NMR) for months in bulk or solution when kept cool and in the dark.

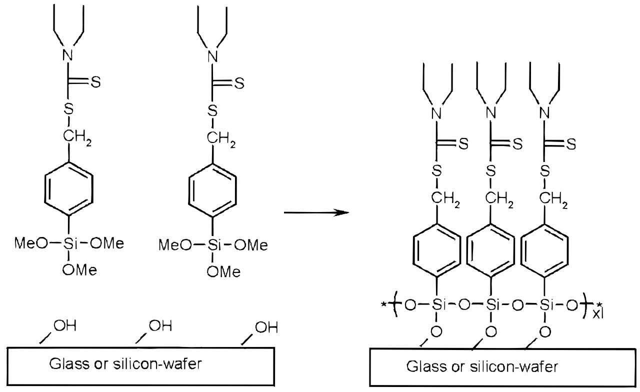
^{1}H NMR ($CDCl_3$): δ 7.65−7.38 (dd, 4H, C_6H_4, $J = 6.5$ Hz), 4.55 (s, 2H, CH_2S), 4.05 (q, 2H, NCH_2, $J = 6.7$ Hz), 3.73 (q, 2H, NCH_2, $J = 6.7$ Hz), 3.62 (s, 9H, $Si(OCH_3)_3$), 1.25 (t, 6H, CH_3, $J = 7.0$ Hz).

Grafting of Silane-Terminated Iniferter (SBDC) on Silicon. The Si wafers (or similar substrates) were rinsed with water and then sonicated for 15 min in water. This procedure was repeated with ethanol and followed by rinsing in refluxing CH_2Cl_2 for 15 min. To break the Si−O bonds on the surface, a solution of hydrogen peroxide, ammonia (25%), and water (H_2O_2:NH_3:H_2O, 1:1:5) was prepared and heated to about 70 °C, and the wafers were added to the mixture for 10 min. After thorough rinsing with water, they were immersed in a solution of hydrochloric acid (HCl:H_2O, 1:6) for 30 min at room temperature.[26] The wafers were rinsed with water, ethanol, and THF or toluene depending on the solvent used for the monolayer formation.

The freshly prepared wafers were placed directly in a 1−5 mM solution of SBDC (**2**) in THF or toluene overnight at room temperature (Scheme 2), rinsed with toluene, and dried under a dry prepurified N_2 flow.

"Living" Free Radical Photopolymerization Initiated by SBDC. A clean and oven-dry reaction tube was purged with argon. Under an argon flow, 7 mL of distilled monomer (styrene or MMA), 2.5 mL of dry toluene, and the samples,

Scheme 2. Idealized Presentation of the SBDC Monolayer on Silicon Wafers or Glass



grafted with the iniferter moiety, were added to the tube. The tube was placed at about 10 cm from a 365 nm TQ-150 UV-lamp (150 W) and irradiated for the required time at room temperature. After polymerization, the samples were submerged in 20 mL of dry toluene and sonicated for at least 10 min to remove homopolymer that may have been formed in solution and adheres to the surface. Finally, the surface was dried under a prepurified N_2 flow and kept in a sealed tube under N_2 until further use. The samples were characterized with SFM and subsequently used in blocking experiments with MMA. For the latter, the samples were submerged in 2.5 mL of dry toluene, and 7 mL of distilled MMA was added. The same procedure as described above was utilized. After the photopolymerization of the second block, the samples were submerged in 20 mL of dry toluene, sonicated for at least 10 min, and washed with toluene.

In other characterizations (IR, contact angle, SEM, and TEM) multiple samples, all prepared in one batch, were used. The samples were taken out of the solution after the required polymerization time, washed with dry toluene, submerged in dry toluene, and sonicated for at least 10 min. One sample was used for characterization, whereas the other samples were submerged in dry toluene and monomer for the consecutive photopolymerization.

Analysis. Fourier transformed ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian Gemini-200 spectrometer working at 200 MHz with chloroform as internal reference at 7.24 ppm. TEM pictures of 80 nm thick cross sections, which were deposited on a TEM grid, were taken using a JEOL EM 1200-EX microscope working at 100 kV. Scanning electron microscopy pictures were taken using a JEOL 6320F field emission microscope. Scanning force microscopy images were recorded with a Topometrix Discoverer TMX 2010, equipped with a Si_3N_4 tip. Topographic images were taken in air at a force of about 10 nN in contact mode.

Transmission IR spectra were recorded on a Mattson IR spectrometer. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Surface Science SSX-100, using Mg Kα excitation, and contact angles were measured on a home-built apparatus[27] as advancing water contact angles.

Results and Discussion

Grafting of Silane-Terminated Iniferter (SBDC) on Silicon and Subsequent Photopolymerization. The formation of the SBDC monolayer on silicon wafers and glass was investigated by measuring the contact angles of the clean and modified substrate (Table 1). Silicon wafers have typical water contact angles around 10°; when the Si surface is cleaned with organic solvents, however, slightly higher contact angles are obtained. The SBDC-modified Si surface shows a considerable hydrophobic effect as can be seen by the high contact angle of 80 ± 5° (Table 1).

Table 1. Advancing Contact Angles of Water in Air for Cleaned and Modified Si Wafers

surface	measd angle (deg)	lit. values[28] (deg)
cleaned Si wafer	16 ± 2	10–20
Si wafer modified with a monolayer of SBDC	80 ± 5	unknown
Si wafer after surface-grafted homopolymerization of St (15 h)	87 ± 3	87
Si wafer after surface-grafted block copolymerization of PS-*b*-PMMA (15 h)	66 ± 3	76

Further investigations of the SBDC-modified surfaces were done by XPS. In Figure 1 the XPS spectrum for the SBDC monolayer on a silicon wafer (Figure 1B) is given, together with a reference spectrum of cleaned silicon (Figure 1A). The strong silicon peaks of the substrate overlap with the sulfur peak of SBDC, and a small nitrogen peak (at 400 eV) is observed. Also, the carbon peak at 285 eV has increased, indicating the presence of the SBDC moiety. The ratio of the carbon and nitrogen peak areas is roughly in accordance with that expected on the basis of the molar ratio between these atoms in the SDBC monolayer.

The “living” free radical polymerization of styrene (St) and methyl methacrylate (MMA) at the SBDC modified Si surface yielded the grafted polystyrene (Si–PS) and poly(methyl methacrylate) (Si–PMMA) layers, respectively, on the Si surface.

The value for the contact angle of the polystyrene surface is in good agreement with the value found in the literature,[28] while the PMMA angle was found to be about 10° lower in most cases. The reason for this difference is not clear, but one has to consider that the literature values are determined on surfaces of PMMA bulk samples. In our case, however, we have a grafted PMMA layer with initiator end groups. Also, large differences in contact angles may originate from inhomogeneities in the very thin grafted polymer layer.

As expected, the contact angle measurements demonstrate that both polymer layers are hydrophobic. The acrylate groups of PMMA result in a significantly lower contact angle than PS (Table 1), enough to distinguish between a polystyrene layer and a poly(methyl methacrylate) layer. Thus, the contact angle measurements can be used to follow the growth of polymer bilayers upon reinitiation of the polymerization with a second monomer. The contact angle measurements, before and after the initiation of the second monomer, show qualitative changes in hydrophobicity in the same order as found upon switching from a polystyrene to a poly(methyl methacrylate) surface. The merely qualitative nature of the contact angle measurements prevents an unambiguous characterization of the surface-initiated polymer layers. Hence, transmission IR spectroscopy (TIR) was used to confirm the results of the grafted polystyrene on silicon. The wafers were about 1 × 1 cm^2 and 1 mm thick. The spectra are depicted in Figure 2. For each measurement 1000 scans were made. Water peaks were subtracted by using a reference spectrum. The first sample was measured directly after deposition of the iniferter monolayer. The other two samples were measured after photopolymerization of styrene for 4 and 10 h, respectively. The photopolymerized polystyrene samples show the typical peaks for polystyrene surfaces, as can be seen from the reference spectrum (bottom). The increasing intensity of the signals after longer

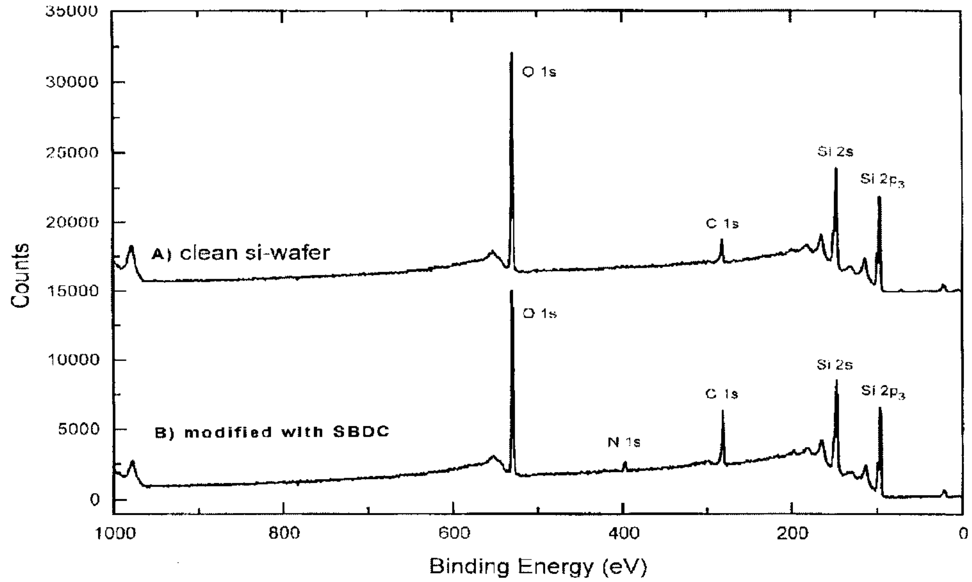


Figure 1. XPS spectra of (A) a cleaned silicon wafer and (B) a silicon wafer with the SBDC monolayer.

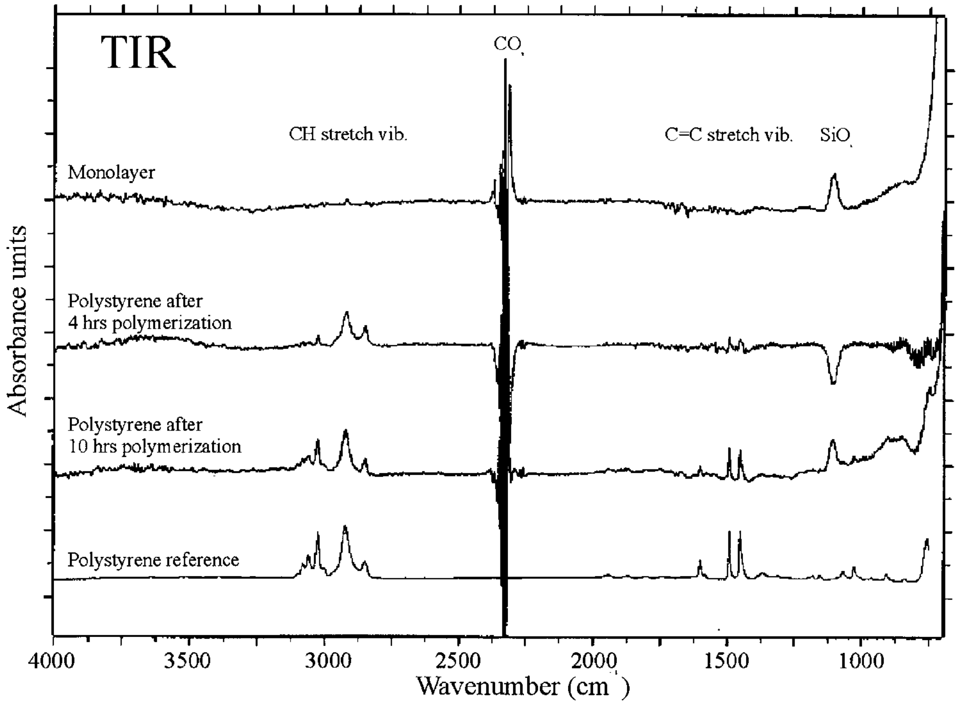


Figure 2. Transmission infrared spectra of Si wafers with SBDC monolayer (top), after photopolymerization of styrene for 4 h (second), after photopolymerization of styrene for 10 h (third), and a polystyrene reference (bottom).

polymerization time is attributed to the growth of polystyrene chains from the surface.

To directly observe these growing layers, extensive SFM studies of the polymer and copolymer layers initiated from the surface-grafted SBDC iniferter have been performed. To follow the thickness increase of the growing polymer layer, we employed a patterned glass or silicon wafer surface with chromium lines, made by photolithography. Chromium is not sensitive toward oxidation under these conditions, and the SBDC initiator monolayer is not grafting onto this metal. Only the uncovered silicon surface between the lines is coated with SBDC. This method has been used before by Fujihara et al.[29] to prepare controlled regions of fluorinated silane monolayers.

In the present study we used the height differences, measured with SFM, between the chromium and the substrate for determining directly the polymer layer thickness during photopolymerization. If the initiator SBDC monolayer, deposited between the chromium lines, initiates a “living” free radical polymerization, the layer thickness would increase with polymerization time. After each time step of photopolymerization the samples were sonicated and rinsed thoroughly to ensure that no adhesion of nongrafted polymers would occur. We like to emphasize here that homopolymer, which might be produced due to side reactions,[25] will be removed by the vigorous cleaning procedure. In Figure 3, topographic images, cross sections, and the schematic representations of typical growing homopolymer and block copolymer layers for a photopolymerization in various time steps are shown. The chromium lines are 155 ± 0.5 nm high and 0.4 μm wide. The space between the lines is 0.6 μm, ensuring an asymmetry in the

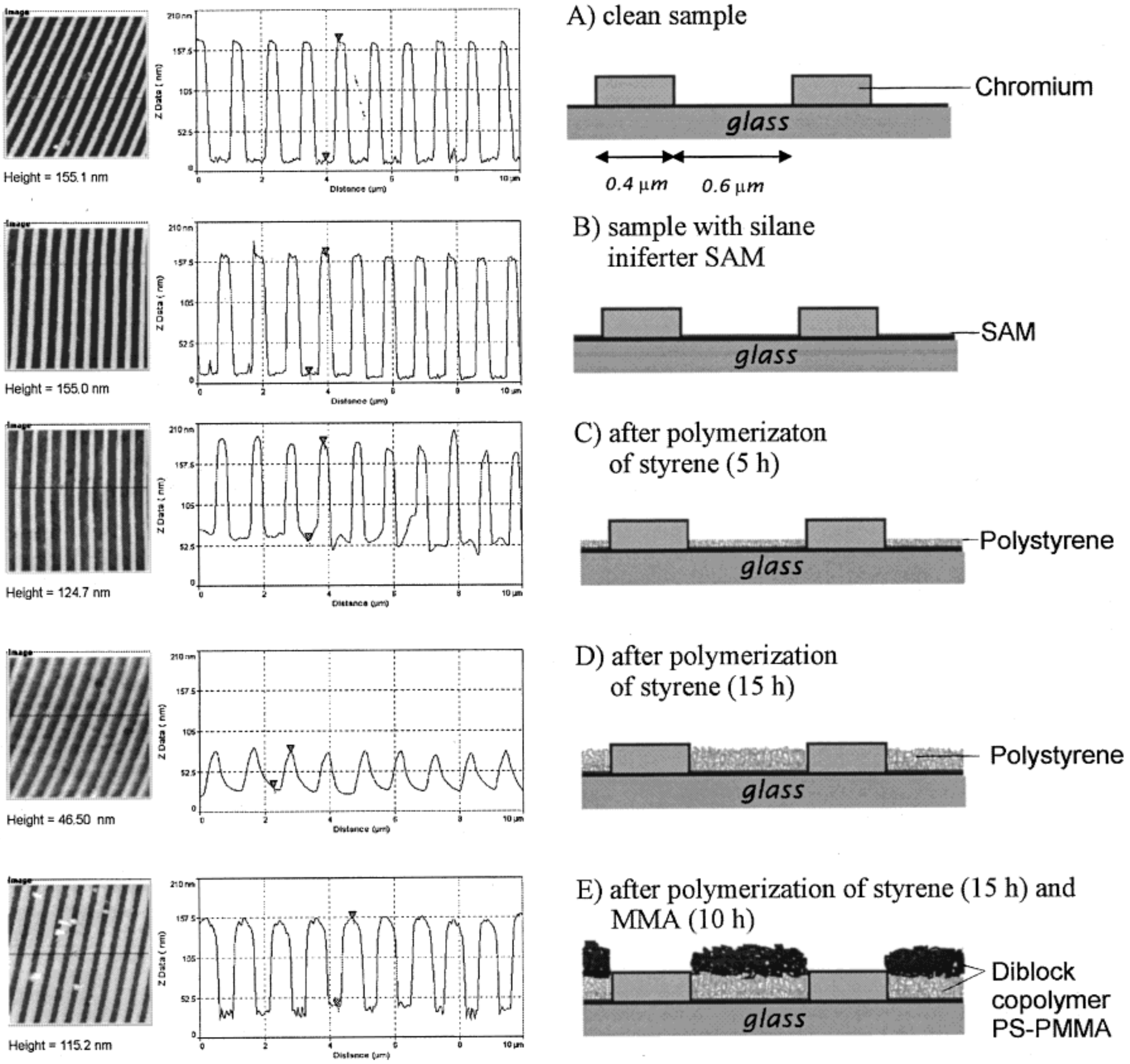


Figure 3. Topographic images, SFM scan lines, and schematic cross-sectional representation of glass slides with chromium patterns and the formation of the polymer and copolymer layer: (A) cleaned sample, (B) sample modified with SBDC, (C) after photopolymerization of styrene for 5 h, (D) after photopolymerization of styrene for 15 h, and (E) after photopolymerization of styrene for 15 h and subsequently MMA for 10 h.

pattern and facilitating the observation of the growing polymer layer. The scanned area is 10 × 10 μm. At least three scans at different places were taken for each measurements to confirm the results. The topographic images in Figure 3 depict five different stages in the polymerization process. The first image (Figure 3A) is the clean sample from which the starting height differences were determined. After deposition of the initiator SBDC monolayer (Figure 3B), no change in the height differences was observed. This was expected, since the layer thickness of a SBDC is ~1 nm, which is just beyond the resolution of the SFM in the particular experimental conditions. Moreover, larger changes in the height differences at this stage would point to polysiloxane, formed in solution from the (trimethoxy)silanes, that is adhering to the surface, or to the formation of SBDC multilayers. Obviously, such adverse effects are not present.

After exposing the sample to UV irradiation in a styrene solution for 5 h, the expected change in height difference was observed (Figure 3C). The growing chains fill the gaps between the lines to a height of 25 ± 5 nm, which is the thickness of the polymer layer that has been formed. When the same sample was used again for subsequent polymerization of styrene for 10 h, the layer thickness increased to 104 ± 5 nm (Figure 3D). Finally, the formation of a diblock copolymer was explored using MMA as the monomer for the second block. The sample, with a polystyrene layer grown for 15 h in total, was exposed to UV irradiation for another 10 h in MMA solution (Figure 3E). This yielded an inverse image: the block copolymer had exceeded the thickness of the chromium lines (155 nm), and the total thickness of the block copolymer layer had become 270 ± 5 nm. To verify that polymer did not grow or overflow on the chromium strips of the patterned surface, we used the SFM in the tapping mode configuration. Figure 4A displays a clean chromium-lined sample where the glass and chromium surfaces are comparable in hardness. The thin strips at the edges of the lines are due to topographic effects. The image on the right (Figure 4B) shows the relative hardness after monolayer deposition and 15 h of styrene photopolymerization. Here, the contrast between hard (bright) and soft (dark) areas is obvious, indicating the formation of the polystyrene layer only outside the chromium lines. Similar results have been obtained in the block copolymer case.

The continued growth of the polymer layer (Figure 3) when the sample is again irradiated by UV light after an interruption is the first proof of the “living” character

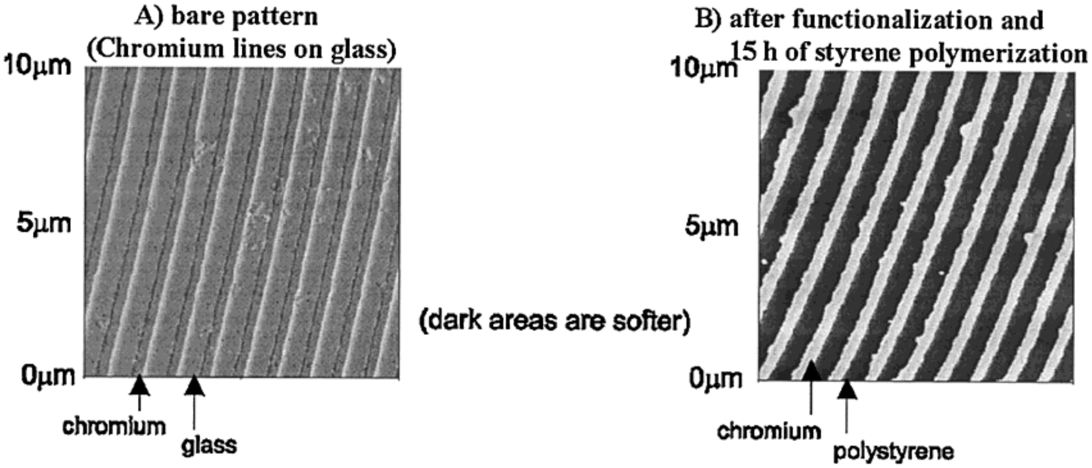


Figure 4. SFM images of the relative hardness of the surface of (A) a clean, chromium-patterned sample and (B) the same sample with grafted SBDC and subsequent photopolymerization of styrene for 15 h.

of the surface-initiated photopolymerization. Further proof of the "living" character of the photopolymerization is the fact that the consecutive use of two different monomers results in the formation of a diblock copolymer layer. According to the literature,[25] in the cross-polymerization from PS to PMMA some difficulties might occur regarding the photolysis of dithiocarbamate end groups on the PMMA growing end, resulting in a less efficient "living" character of the block copolymerization. In our experiments, however, we have a "confined two-dimensional photopolymerization" process where, due to the high grafting density, the surface-growing polymer end explores only a two-dimensional space and grows in a uniform way as well as for the first and the second block layer. It is possible that the surface-initiated "living" photopolymerization proceeds in a more efficient way and with fewer side reactions than in solution polymerizations. In fact, if during the polymerization of the first monomer, styrene, homopolymer is produced, its inclusion in the grafted polymer layer would be energetically unfavorable due to the entropy loss, and it will be washed out in the cleaning process. If during the polymerization of the second monomer, methyl methacrylate, block copolymer was not formed, then no further increase in the layer thickness would be observed. Homopolymethacrylate, if formed, would not be compatible with the grafted polystyrene layer due to unfavarable enthalpic and entropic factors. If, however, both grafted block copolymer and homopolymer are formed, the surfactant effect of the grafted block copolymer will be very inefficient. Consequently, the homopolymethacrylate is not dissolved into the grafted block copolymer layer and will be removed in the cleaning process. The observed thickness increase after the polymerization of the second monomer is therefore due to the formation of the block copolymer. Furthermore, if in all cases above homopolymers would have been produced and subsequently removed, this would have resulted in a sublinear increase of the layer thickness. On the contrary, a linear increase in the layer thickness has been observed (Figure 5).

The same methodology as above (measuring layer thicknesses with SFM) was also used to determine the growth of the polymer layer with time. Several samples corresponding to increasing photopolymerization times were measured. The results are shown in Figure 5 and demonstrate a linear relation between the increase of the layer thickness, averaged over at least 20 spots per sample, and the polymerization time. The large error bars are due to the fact that the layer thickness is not only determined by the polymer chain length but also by the grafting density of the initiator, a parameter which is difficult to control with accuracy. As a consequence, there is a large variation of the layer thicknesses from sample to sample. The continuous increase, however, in layer thickness, as displayed by the line fitted with linear regression, is the result of linear growth of the polymer chains from the surface, as expected with "living" polymerizations in general.

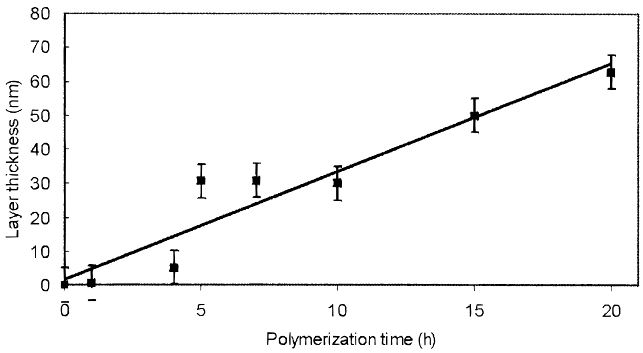


Figure 5. Layer thickness versus photopolymerization time for styrene initiated by grafted SBDC on patterned Si wafers.

Viewing a cross section of a sample with a surface-grafted polymer layer by means of electron microscopy will further complement the insights into the characteristics of our polymerization with surface-grafted iniferter initiators. For this, a scanning electron microscope (SEM) was used. The monolayer was prepared on a Si wafer, and photopolymerization of MMA for 15 h and subsequently styrene for another 15 h was performed. The wafer was then broken, and the edges of the pieces were investigated with SEM (Figure 6). Here, a polymer layer of about 100 nm thick is clearly visible as the light-gray band in the middle. The dark-gray area on the right is the silicon substrate, while the thin white line at the left edge of the polymer layer is due to scattering of the electron beam. This thickness is in agreement with the results obtained with the SFM measurements. With the use of TEM the formation of block copolymer was unambiguously confirmed. In Figure 7, a TEM image after 15 h of styrene and 15 h of MMA photopolymerization is shown. TEM samples were prepared by using small disks (diameter ca. 0.8

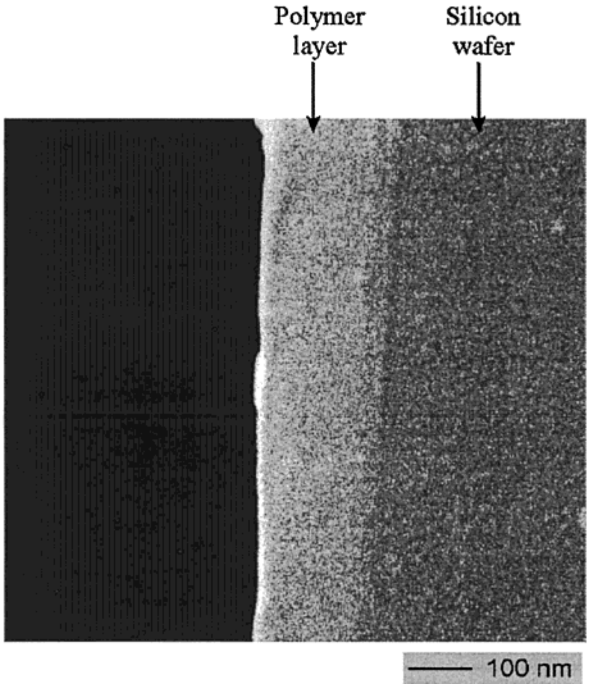


Figure 6. SEM image of PMMA–PS block copolymer grafted on the surface.

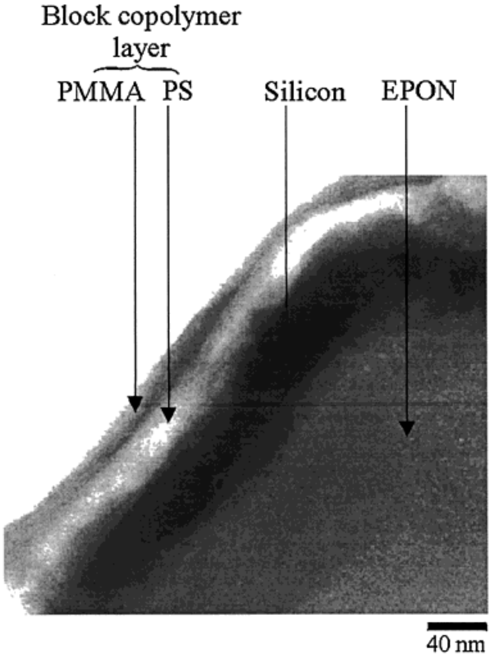


Figure 7. TEM image of block copolymer layer of PS–PMMA grafted on the surface (stained for 19 h with OsO_4).

cm) of a cross-linked epoxy resin (EPON), which were covered with 40 nm of silicon via evaporation with an electron beam. The epoxy resinous substrate used in this method, coated with a thin silicon film, could be treated in the same way as normal Si wafers. At the surface of this layer, the iniferter (SBDC) from which the copolymerization was performed was grafted. After staining with OsO_4 for 19 h, two distinct layers appeared, namely a bright layer (30 nm) covered by a very thin darker layer (15 nm). As OsO_4 stains PMMA more selectively, the upper layer is PMMA, as expected. The fact that the top layer is thin is due mainly to its depolymerization by the electron beam. Thus, direct evidence for the formation of a block copolymer layer on the surface is obtained. The confirmation of the existence of the block copolymer layer with TEM imaging demonstrates in an elegant way our initial objective of initiating a "living" free radical polymerization from a surface, producing thus, in a controlled manner, grafted thin homopolymer and block copolymer layers.

Conclusions

To modify the surface properties of (in)organic materials, we successfully covalently attached a stable monolayer, with high grafting density, of *N*,*N*-(diethylamino)dithiocarbamoylbenzyl(trimethoxy)silane on the surface of silicon wafers and glass slides, thereby creating a surface-grafted photoinitiator for "living" free radical photopolymerization. In this way, we have been able not only to change the hydrophilicity of the surface by polymerizing different monomers but also to create polymer bilayers, which are directly tethered to the surface. The increase in layer thickness after photopolymerization was directly measured by SFM using silicon wafers patterned with chromium. Furthermore, the samples were characterized by contact angle measurements, XPS, transmission IR, SEM, and TEM. The photopolymerizations of styrene and MMA monomers were used to demonstrate the surface-initiated "living" free radical photopolymerization representing a polymerization method in a "confined two-dimensional space". This is supported by (a) the linear increase of the polymer layer thickness, (b) the reinitiation of the photopolymerization after interruption of the process, (c) the occurrence of block copolymerization after switching from styrene to a methyl methacrylate monomer, and (d) the formation of a well-defined homopolymer monolayer or block copolymer bilayer.

Thus, a "living" free radical polymerization, initiated from a surface-grafted monolayer of an iniferter initiator, has been demonstrated, providing new ways to modify the properties of substrate surfaces and to create polymer monolayers and block copolymer bilayers and opening new routes toward functional surfaces.

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References and Notes

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