Opto-Mechanical Scission of Polymer Chains in Photosensitive Diblock-Copolymer Brushes

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ABSTRACT: In this paper we report on an opto-mechanical scission of polymer chains within photosensitive diblock-copolymer brushes grafted to flat solid substrates. We employ surface-initiated polymerization of methylmethacrylate (MMA) and t-butyl methacrylate (tBMA) to grow diblock-copolymer brushes of poly(methylmethacrylate-b-t-butyl methacrylate) following the atom transfer polymerization (ATRP) scheme. After the synthesis, deprotection of the PtBMA block yields poly(methacrylic acid) (PMAA). To render PMMA-b-PMAA copolymers photosensitive, cationic azobenzene containing surfactants are attached to the negatively charged outer PMAA block. During irradiation with an ultraviolet (UV) interference pattern, the extent of photoisomerization of the azobenzene groups varies spatially and results in a topography change of the brush, i.e., formation of surface relief gratings (SRG). The SRG formation is accompanied by local rupturing of the polymer chains in areas from which the polymer material recedes. This opto-mechanically induced scission of the polymer chains takes place at the interfaces of the two blocks and depends strongly on the UV irradiation intensity. Our results indicate that this process may be explained by employing classical continuum fracture mechanics, which might be important for tailoring the phenomenon for applying it to poststructuring of polymer brushes.

INTRODUCTION

In recent years, azobenzene molecules have found widespread use as polymer chain side groups that acted as triggers capable of altering the morphology and physical properties of the host bulk or film polymer system due to optically induced cis−trans photoisomerisation.1−4 When azo-groups are integrated into polymer chains, the pronounced physical differences between both isomers affect the properties of corresponding polymer blends or thin films over several length scales, with manifold conceivable applications in various fields.5−7

Among the many unexpected physical phenomena related toazo-modified polymers is the formation of so-called surface relief gratings (SRG) within photosensitive polymer films upon irradiation with an interference pattern.8−10 The material flow associated with SRG, triggered by absorption of UV-light, can even occur at room temperature and in air, i.e., when the polymer is supposed to be in a solid, glassy state.11−14 This phenomenon has been reported for the case of physisorbed polymer films prepared by drop- or spin-casting the polymer onto a solid surface. The SRG formation in polymer chains attached covalently to a substrate at high grafting density, i.e., in the polymer brush regime, has not been studied in great detail until now. Due to the high-density of these grafted polymer chains, one could expect the SRG formation to differ relative to physisorbed polymer films. For instance, the geometrical constraints within the brush could lead to a preferred overall orientation (director) of the azobenzene groups. This might change considerably, for instance, the kinetics of the material response to external stimuli.

The polymer brush geometry itself, even without being photosensitive, is employed widely in a broad range of applications,15 ranging from tuning wettability to controlling adsorption of proteins and biological systems.16−27 The main advantages of polymer brushes, relative to physisorbed films, include their high stability and high concentration of reactive centers per units area of the coating. Since the chains are covalently tethered to the substrate, exposure of the chains to a good solvent does not result in delamination or desorption of the material from the solid surface. While the degrafting of polymer brushes under certain conditions has recently been reported, the PMMA-b-PMAA brushes studied here have proven stable under the conditions applied in this work.28 Seki et al. were first to synthesize photosensitive brushes.29,30 In their work, azobenzene-containing monomers were polymerized by the “grafting from” method using the atom transfer radical polymerization (ATRP) scheme. The researchers could...
Seki et al. did not consider further how the topography of such brushes could possibly be controlled by light.

Experiments from our laboratory indicate that photosensitive brushes, at sufficiently high degree of polymerization, exhibit topographic changes under inhomogeneous irradiation with external UV-intensity patterns similar to photosensitive physisorbed films. We have reported that the mass transport in azobenzene modified brushes should be much more pronounced and faster than in physisorbed films. Furthermore, we have shown that extensive rupturing of polymer chains from the substrate takes place, implying that covalent bonds along the chains are broken. This happens exclusively in regions where the polymer material depletes. Such a process is quite remarkable, as the forces required to break a covalent bond are of the order of several nN. Usually, these can only be supplied by either strong hydrodynamic (viscous) stresses, or by direct application of so-called “nanoprobes” such as AFM tips or optical tweezers. In many processes in biology and material science, where chemical bonds are mechanically broken by self-organized processes, special conditions are required, such as given with the particular dendritic geometries of cylindrical brushes.

In our previous study, we have found that up to 70% of the polymer chains can be ruptured locally due to opto-mechanical stress. One important question that has not been answered so far is where along a polymer chain rupturing actually occurs. To answer this question, a new approach is needed. Conventional methods such as ellipsometry, FTIR, or SPR spectrosopies are not able to resolve local variations in molecular weight of the brush. AFM could uncover only an effective thickness of the remaining polymer film of 5–20 nm in the region where chain rupturing took place. This method cannot establish whether the remaining polymers comprise a high density of short chains or a low density of longer chains, or a mixture thereof.

Considering that the brush is in a glass-like state, it important to examine the locus of the rupture along a single chain. We assume that we could prepare a diblock-copolymer brush with the upper block made entirely of photosensitive polymer material. If only the upper block were subjected to rupturing, this would give rise to the photosensitive polymer trying to relocate on top of a rigid lower block. Mass flow and polymer reorganization are then completely restricted to the azobenzene-containing part. The rupturing of chains comprising parts of both blocks would either indicate a mean field picture, where a chain is embedded in a continuum of polymer material, or a crack mechanism, where stresses generated within the azobenzene-containing block are collectively redistributed across the whole layer and lead to rupturing in regions of imperfections (a local high grafting density, for instance). The above reasoning rules out using homopolymer brushes in answering these questions. Instead, by refining the composition of a diblock- or mixed brush, one might learn about the mechanisms of force generation and distribution within these systems.

In this work, we describe the synthesis and characterization of photoresponsive diblock-copolymer brushes consisting of poly(methylmethacrylate-b-methacrylic acid) (PMMA-b-PMAA) chains, where the PMMA block is attached covalently to a solid surface. At pH >5, the PMAA block is negatively charged and can be loaded by the azobenzene containing cationic surfactant. We describe the response of the resulting photosensitive polymer brushes to illumination with UV interference patterns as a function of irradiation intensity. We analyze the topography of the irradiated films before and after exposure to a good solvent for the polymer (PMAA block) and find that rupturing takes place at the interface between the PMMA and PMAA blocks.

EXPERIMENTAL SECTION

Deposition of ATRP Initiator on Silicon Wafers. The backside of a silicon wafer was first roughened using a sandblaster to allow characterization using IR-VASE. The wafer was cleaned of residual blast media and broken into smaller pieces for individual samples. No observable damage to the polished side of the silicon wafer could be detected.

Deposition of ATRP initiator (11-(2-bromo-2-methyl)propionyloxyundecyltrichlorosilane, BMPUS) onto the silicon wafer segments followed a previously reported protocol. Briefly, the segments were rinsed extensively with methanol, and then dried under a stream of N2 gas. Freshly cleaned segments were treated in a UV-Ozone chamber for 20 min, followed by immersion directly into a 1% (v/v) solution of BMPUS in anhydrous toluene. This system was held at −10 °C in a freezer for 20 h. After 20 h, the substrates were removed from the initiator solution, rinsed extensively with methanol, and then dried with a stream of N2 gas. Modified wafers were stored in the dark until further use.

Synthesis of PMMA Brushes. PMMA brushes were synthesized following a previously reported method. In short, 47 mL of MMA was passed through a column to remove inhibitor. The monomer was combined with 50 mL of a 1:4 H2O:MeOH solution and degassed by bubbling with nitrogen while stirring in a 250 mL round-bottom flask.

Figure 1. (a) Chemical structure of the azobenzene-containing surfactant. (b) Scheme of the PMMA-b-PMAA brush before exposure to surfactant solution and (c) after loading with surfactants.
therefore, the spectra do not change considerably after the irradiation.π

were placed in a surfactant solution of a given concentration for 16 h at conjugated benzene rings present in both isomers.

and attached hydrophobically or ionically to the brush. Any unbound nm. The spectrum of the cis isomer is characterized by two absorption allowed to proceed for 20 min, at which point the wafer was removed, under N2 gas. Based on evolution of the brush thickness, the reaction tri PMMA-b-PtBMA brushes were exposed to a 50% (v/v) of coe surfactant. All experiments were carried out below the critical micelle concentration (CMC, c)

to the micelle formation. All experiments were carried out in a related to the micelle formation. All experiments were carried out in a room with yellow light to avoid any premature isomerization of the surfactant.

The photosomerization behavior of the surfactant is described in detail elsewhere.π In short, the surfactant in the dark state is characterized by an absorption band (π–π transition of the azobenzene unit in the trans conformation) with a maximum at 353 nm. The spectrum of the cis isomer is characterized by two absorption bands with maxima at 313 nm (π–π transition) and at 437 nm (n-πtransition). The lifetime of the cis isomer in the brush is ~22 h; therefore, the spectra do not change considerably after the irradiation is turned off.π Irradiation at 325 nm results in an intermediate ratio of the trans and cis isomers, defined by the ratios of the extinction coefficients at the corresponding wavelengths. The band with maximum at ~290–295 nm corresponds to the absorption of the π-conjugated benzene rings present in both isomers.

Binding of Photosensitive Surfactants. PMMA-PMAA brushes were placed in a surfactant solution of a given concentration for 16 h at room temperature. The surfactant molecules diffused into the brush and attached hydrophobically or ionically to the brush. Any unbound surfactants were removed by placing the sample in a water bath for 15 min. The thickness of a sample increased due to absorption of the surfactant. The degree of binding (β) was determined by the following formula.π

where \( h_b \) and \( h_b^{\text{am}} \) are the dry thicknesses before and after complex formation, respectively, and \( M_{\text{PMMA}}^{\text{MAA}} (=86 \text{ Da}) \) and \( M_{\text{PMAA}}^{\text{MAA}} (=481 \text{ Da}) \) are the molecular weights of the repeat units before and after complexation with surfactant, respectively. The degree of binding gives the number of surfactant molecules per methacrylic acid (MAA) monomer units in the brush. This quantity can be interpreted as the total absorption of a surfactant into brush.

We have established that the surfactant molecules adsorb only into the PMMA block by performing a control experiment. Here the PMMA brush was exposed to surfactant solution and post treated as described above for the case of diblock-copolymer brush. No change in the thickness of the PMMA brush was observed, indicating the absence of the surfactants in the brush.

Methods. IR spectra of the attached polymer layers were recorded using an IR variable angle spectroscopic ellipsometer (VASE; J.A. Woollam Co., USA). Data were collected at an incidence angle of 70° (relative to the normal) over a range of 500–6000 cm⁻¹. The characterization of the real part of the total reflection coefficient, \( \rho \), reveals vibrational peaks that correspond precisely to those found in an FT-IR transmission spectrum. The spectra of the brush after each step of modification, i.e., (i) synthesis of the first block (PMMA), (ii) synthesis of the second block (PtBMA), (iii) conversion of PtBMA to PMAA block, and (iv) loading of the PMMA-b-PMAA brush with azobenzene containing surfactant are shown in SP-1 (Supporting Information, SP-1). The characterization of surface topography of PMMA-PMAA brushes was carried out with atomic force microscopy (AFM; Nanoscope V, Bruker, USA). The microscope was operated in tapping mode, using commercial tips (NanoSensors) with a resonance frequency of ~300 kHz, and a spring constant of ~50 N/m. The AFM micrographs were recorded in air at a temperature of around 23 °C and overall humidity of 55%. For thickness measurements, the brushes were scratched by a glass pipet to remove the material, and the step height between the top of the brush and the carried substrate was measured from the AFM cross-section analysis. All experiments were carried out in a room with yellow light to avoid any premature isomerization of the surfactant.

The Lloyd’s mirror scheme with He–Cd laser (Kimpton) operating at \( \lambda = 325 \text{ nm} \) (total power of ~3 mW) was used as UV interference lithography.π The periodicity of the interference pattern is given by \( d = \lambda / \sin(\theta/2) \), where \( \lambda \) is the wavelength of the incident light, and \( \theta \) is the angle between the incoming laser beam and the mirror surface. Irradiation time of 15 min and the periodicity of interference pattern of 1.4 µm were kept constant for all experiments.

**Table 1. Molecular Parameter of the PMMA-PMAA Diblock-Copolymer Brushes**

<table>
<thead>
<tr>
<th>( \sigma, \text{nm} )</th>
<th>( h_{\text{PMMA}}, \text{nm} )</th>
<th>( M_{\text{PMMA}}, \text{10}^2, \text{Da} )</th>
<th>( h_{\text{PMAA}}, \text{nm} )</th>
<th>( M_{\text{PMAA}}, \text{10}^2, \text{Da} )</th>
<th>( \Delta h_{\text{PMMA}} )</th>
<th>( \Delta h_{\text{PMAA}} )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I 0.4</td>
<td>5 ± 1</td>
<td>0.8</td>
<td>16 ± 1</td>
<td>2.7</td>
<td>21 ± 1</td>
<td>73 ± 4</td>
<td>4.6</td>
</tr>
<tr>
<td>II 0.4</td>
<td>10 ± 1</td>
<td>1.7</td>
<td>16 ± 1</td>
<td>2.7</td>
<td>26 ± 1</td>
<td>80 ± 4</td>
<td>5.0</td>
</tr>
<tr>
<td>III 0.4</td>
<td>18 ± 1</td>
<td>3.0</td>
<td>13 ± 2</td>
<td>2.2</td>
<td>31 ± 1</td>
<td>62 ± 4</td>
<td>4.8</td>
</tr>
<tr>
<td>IV 0.4</td>
<td>20 ± 1</td>
<td>3.4</td>
<td>16 ± 1</td>
<td>2.7</td>
<td>36 ± 1</td>
<td>80 ± 5</td>
<td>5.0</td>
</tr>
<tr>
<td>V 0.4</td>
<td>22 ± 1</td>
<td>3.7</td>
<td>18 ± 1</td>
<td>3.0</td>
<td>38 ± 1</td>
<td>86 ± 5</td>
<td>4.8</td>
</tr>
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"The grafting density, \( \sigma \), is determined as described elsewhere.π The number average molecular weight, \( M_{\sigma} \) is calculated according to the known height of the brush: \( M_{\sigma} = (h_{\text{PMMA}})/\sigma \), where \( \rho \) is the density, 1 g/cm³. \( h_{\text{PMMA}} \) = (\( h_{\text{PMMA}}^{\text{am}} - h_{\text{PMMA}} \)) is the height of the PMMA block after loading the brush with azobenzene surfactants. \( \Delta h_{\text{PMMA}}, \) the ratio between the height of the pure PMMA block, \( h_{\text{PMMA}} \) and loaded with surfactant, \( h_{\text{PMMA}}^{\text{am}} \), is determined as described elsewhere.π The number average molecular weight, \( M_{\text{PMMA}} \) and \( M_{\text{PMAA}} \) is the density, 1 g/cm³.

Under positive nitrogen pressure, 1.565 g of 2,2′-bipyridyl was dissolved completely, followed by 0.5088 g of CuCl. The entire solution was degassed for a further hour, then charged to a large, sealed vessel under nitrogen purge containing a silicon wafer modified with surface-bound BMPUS ATRP initiator. The polymerization was allowed to proceed for 20 min, at which point the wafer was removed, washed extensively with methanol, and dried with dry \( N_2 \) gas. Ellipsometric measurements were collected before proceeding with tBMA polymerization.

**Synthesis of PMMA-b-PtBMA Diblock-Copolymer Brushes.** For synthesis of PtBMA blocks, 15 mL of tBMA was passed through a column of inhibitor remover. The monomer was charged to a round-bottom flask containing 15 mL of DMSO. This solution was degassed by bubbling with nitrogen while stirring. Under positive nitrogen pressure, 12 µL of PMDETA was charged to the flask, followed by 17.7 mg of CuCl2, then 2.5 mg of CuCl2. After degassing the combined solution for a further hour, the mixture was charged to sealed vessels under nitrogen purge containing PMMA-modified wafer segments. Samples were removed from the polymerization solution at certain time intervals to achieve different length blocks of PtBMA. The samples were rinsed extensively with isopropanol, and then dried under a stream of \( N_2 \) gas.

**Synthesis of PMMA-b-PMAA Diblock-Copolymer Brushes.** PMMA-b-PtBMA brushes were exposed to a 50% (v/v) of trifluoroacetic acid in dichloromethane followed by rinsing with dichloromethane, isopropanol, then dichloromethane, and then dried under \( N_2 \) gas. Based on evolution of the brush thickness, the reaction appeared complete within 30 min of exposure time.

**Cationic Azobenzene Containing Surfactant.** Azobenzene-containing trimethylammonium bromide surfactants (Figure 1) with six CH2 groups in the alkyl spacer between the polar headgroup and the azobenzene unit were synthesized as described elsewhere.π The surfactant was dissolved in water (Milli-Q) and kept in the dark for several days to ensure complete relaxation to the trans conformation. All experiments were carried out below the critical micelle concentration (CMC; \( c_{\text{CMC}} = 0.5 \text{ mM} \)) to avoid influence of effects related to the micelle formation. All experiments were carried out in a room with yellow light to avoid any premature isomerization of the surfactant.
RESULTS AND DISCUSSION

We have investigated five PMMA-b-PMAA brushes of similar grafting density, differing in the length of the bottom PMMA block. The brushes can be viewed as bilayered polymer laminates consisting of PMMA and PMAA polymers (Figure 1a). The height of the bottom layer varies from 5 to 22 nm (Table 1), while the height of the second PMAA block is ~16 nm thick for all brushes (Table 1). The slight deviation of the height of the second block for brushes III and V is in the range of the experimental error.

To render the diblock-copolymer brush photosensitive, we attach azobenzene-containing cationic surfactants to the PMAA block of the brush by exposing the sample to a surfactant solution of concentration \( c = 0.1 \text{ mM} \) for 16 h (Figure 1a).

After exposure to the surfactant solution, the height of the brush increased significantly (Table 1). We have found that the azobenzene surfactant couples only to the PMAA block of the copolymer brush. This could be inferred from a control experiment where only the PMMA brush was exposed to the surfactant solution under identical conditions. No increase in thickness of the PMMA brush was observed, ruling out simple physical absorption of surfactants inside the brush. Taking into account that the increase in brush thickness is only due to change in PMAA thickness, the binding constant, \( \beta = 0.8 \), remains constant for all brushes showing that there are 0.8 surfactant molecules per one carboxyl group within the brush. This value found experimentally is the highest that could be achieved with the brushes presented in this paper.

Figure 2a shows the topography of brush V after irradiation with an interference pattern of periodicity \( D = 1.4 \text{ \( \mu \text{m} \) } \), for 15 min at \( \lambda = 325 \text{ nm} \) and \( I = 20 \text{ mW/m}^2 \). While the topography is smooth before exposure to the UV light, the formation of a surface relief grating (SRG) is observed after UV irradiation. The height of the formed gratings is 12 nm, the SRG periodicity equals exactly the optical periodicity of the interference pattern (Figure 2). In contrast to the previous study, where the photosensitive brushes were made utilizing azobenzene molecules in the Disperse Red (DR1) configuration covalently attached as a side chains to tethered polymers, further irradiation of the PMMA-b-PMAA-azo-surfactant complex for 1 h does not lead to any increase in the SRG height.

This observation can be explained by the photoisomerization kinetics of the surfactant molecules. It is well-known that irradiation of azobenzene with polarized light leads to reorientation of the photosensitive units perpendicularly to the polarization of the incident light. This effect is one of the driving mechanisms of the SRG formation. We have found that in the complexes formed by the PMAA brush and the photosensitive surfactants, there is no preferred orientation when irradiating with polarized light. Although certain anisotropy might be expected during irradiation, the equilibrium in-plane isotropic state is immediately achieved in the brush after the irradiation is stopped. One can conclude that in the complex featuring photosensitive surfactants complexed with polymer brushes, pure isomerization of the azobenzene units of the surfactant is realized; multiple cis—trans transitions, which would be necessary for a preferred orientation, do not occur. The DR1 molecules used in a previous study can be distinguished from the azobenzene containing surfactants by a very short lifetime of the cis-form. Hence, during irradiation multiple photoisomerizations from trans to cis and back occur, resulting in the reorientation of the azobenzene groups with their long axis perpendicular to the electrical field vector. In contrast, here the photoisomerization of surfactants appears only as a single event during irradiation, implying moderate changes in orientation of the azobenzene molecules.

The structured topography can be reverted to a flat state by exposing the brush to light of homogeneous intensity at 442 nm (Figure 2). At this wavelength, the cis isomers undergo reverse photoisomerization to the trans form, which leads to a redistribution of the polymer mass resulting in the initial flat state. We should emphasize that the topography change is related to the mass transport, and is not due to a simple change in thickness of the polymer film that occurs along with the change in free volume. It is known that the cis-isomer requires more free volume, resulting in an increase of polymer film thickness under illumination. However, this increase is only ~2% of the total thickness, i.e., ~1 nm. This could be concluded by measuring the AFM cross-sectional profile during continuous irradiation while alternating the wavelength of the incoming light.

In our previous study we have reported that polymer chains can be ruptured off the surface during the SRG formation. In the present study, we check the stability of the irradiated brush as well. For this we treat the irradiated brush with good solvent, dimethylformamide (DMF), for 10 min, and dry the specimens by nitrogen gas. Figure 3a shows the topography of the brush thereafter. The height of the topography grating increases from 12 to 53 nm and the profile resembles that of a ramified bush, where the PMAA chains spread on the PMMA film (scheme in the Figure 3). A straightforward explanation of this phenomenon is that some of the polymer chains have been ruptured from areas where the SRG topography assumes a minimum. This can be concluded from recording the change in topography at the same place on the brush after irradiation and subsequent treatment with a good solvent.

During the exposure to DMF, the ruptured chains are desorbed from the brush, resulting in an increase of the SRG
height. To further elaborate on this point, an identical sample was treated with UV light under homogeneous illumination followed by exposure to DMF. In this case, no change in the thickness of the polymer layer occurred, as can be inferred from the AFM cross-sectional analysis of the brush. We emphasize that during the exposure of the photosensitive brush to DMF a partial desorption of azobenzene-containing surfactants takes place, which results in decrease of the brush thickness (Table 1, $h_{PMAA}^{azo}$). The process takes place with a similar kinetic in both irradiated and nonirradiated brushes. This is not surprising since the lifetime of the cis-isomer in the brush is 10 min, which means that within this time a back relaxation to the trans-form occurs. Because the time between the UV irradiation and the subsequent treatment with DMF is typically 20 min, the surfactant molecules are all in trans conformation during the DMF treatment.

Additionally, DMF treatment of a nonirradiated brush loaded with the azobenzene surfactants results in partial desorption of surfactants from the brush. Consequently, the height of the PMAA azobenzene film, $h_{PMAA}^{azo}$, decreases to 53 nm for brush V (cf. Table 1). Measuring the total height of the brush by an AFM scratching experiment reveals that the height of the first PMMA layer remains unchanged. These observations reveal that the height of the stripes in the SRG corresponds to the height of the PMAA layer loaded with azobenzene surfactants. This finding indicates that the rupturing of the polymer chains occurs at the interface between the PMMA and PMAA blocks.

Figure 3b shows the same area on the brush after subsequent exposure to DMF and water solution. The periodicity and the height of the two gratings shown remain the same, but the morphology of the side walls and the area in between the grating changes. After treatment with DMF, a good solvent for both blocks, the upper polymer chains spread in between the gratings, and even single chains are visible on the AFM micrograph (Figure 3b, upper right picture). However, after exposure to water (a poor solvent for PMMA) the polymer chains of the upper block dewet back to the grating maxima. This indicates that PMMA resides in between the stripes.

To check whether the areas between the SRG indeed consist only of PMMA, we performed the following experiment. The sample in Figure 4b that was irradiated and subsequently washed once with DMF, was irradiated in the second step under identical conditions (i.e., $\lambda = 325$ nm, $I = 5$ mW/m$^2$, $D = 1.4$ $\mu$m, and $t = 15$ min), but with the intensity pattern oriented perpendicular to the first one. This we refer to as the so-called cross-irradiation. No response of the brush topography between the SRG was observed, indicating the absence of the PMAA-azobenzene complex. After exposure of the brush to DMF, a square periodicity of the PMAA bushes was generated (Figure 4c). The height of this structure decreased to 34 nm, which

Figure 3. (a) AFM micrographs of the PMMA-b-PMAA brush after irradiation with IP and subsequent treatment with good solvent (DMF). The corresponding scheme of the brush is shown in (b). Further treatment of the brush with water that is good solvent for the PMAA block and a poor solvent for PMMA, results in dewetting of the PMAA chains from the PMMA surface, as shown in the scheme (b). The corresponding AFM micrographs are shown on the right.

Figure 4. AFM micrographs of the brush topography (a) just after irradiation with an interference pattern, (b) after subsequent treatment with good solvent (DMF), and (c) after subsequent cross-irradiation and exposure to DMF. (d) The AFM cross-sectional analysis of the brush height.
corresponds to the height of the nonirradiated brush exposed to DMF, while the height of the first PMMA layer stays at the initial value of 22 nm. With this additional experiment we demonstrate that only the photosensitive PMAA block is ruptured near the PMMA interface, i.e., likely at the connecting point between the PMMA and PMAA blocks. The very same results are observed for all brushes presented in Table 1. The nonfunctionalized PMMA block stays intact through all presented thicknesses, i.e., 5, 10, and 20 nm.

We indicate that the height of the stripes formed depends on the amount of energy fed into the system. To change the energy we irradiate brush IV for 15 min while varying irradiation intensity in between (Figure 5). The SRG height measured just after the irradiation remains 12 ± 2 nm, independent of the irradiation intensity. However, after removal of the ruptured chains the formed stripes differ in height and cross-sectional profile. The height of the SRG first increases with energy (Figure 5) from 20 to 40 nm and to 53 nm and then drops down to 10 nm.

Starting from energy of 2.3 J/cm² (cases 2, 3, and 4), the cross-sectional analysis shows that the height of the brush in between the stripes corresponds to the height of the PMMA layer. In the case of lower intensity the height in between the stripes is larger than the initial height of the PMMA layer, implying that many PMAA chains have not been ruptured during the SRG formation. The cartoon in Figure 5 illustrates schematically the resultant morphology of the brush. For the irradiation dose of 2.3 J/cm², the height of the formed stripes is equal to the thickness of the PMMA layer loaded with surfactant, indicating that rupturing of the chains takes place only within those areas where the polymer material has receded, i.e., at the minima of the SRG topography. At higher irradiation doses, scission of polymer chains commences also near the topography maxima resulting in a decrease of the stripe height. Knowing the values of total brush thickness before irradiation and the height and cross-sectional profile after irradiation and solvent exposure, one can calculate the total number of ruptured chains as follows: number of ruptured chains = [(S₁ - S₀)/S₀]100%, where S₀ is the AFM cross-section area of the initial brush profile and S₁ is the AFM cross-section area of the brush after irradiation and subsequent treatment with DMF solvent (Figure 5). The cross-sectional profile for all measurements was measured over 14 µm, i.e., 10 SRG periods, near the scratched area (see, for instance, Figure 4d). For case 4, one sees that more than 90% of the PMAA chains have ruptured, while the thickness of the layer formed by the first block (PMMA) stays constant. This means that the opto-mechanical stress generated during irradiation cannot induce a “popping up” of the inert block, that has not been functionalized with photosensitive groups.

The question, as to, at which exact position along a single polymer chain the scission takes place, still remains open, and possibly is ill-posed. However, we can postulate safely that the rupturing must occur at or close to the interface between the PMMA and PMAA blocks. This claim is simply based on the experimental observations reported in this work: Brushes with different total thicknesses and with a constant chain length of the second, photosensitive block (equipped with azo side chains) are seen to always shed a layer comparable to the azo-modified block under UV illumination. This finding points to a collective phenomenon where the generation of forces takes place in the photosensitive block and stresses concentrate, due to the mismatch of material properties, at the (rough) interface between first and second block. While this is rather a very general conclusion, it tends to make a mean field picture less probable, where the forces generated can be thought to act on single chains. Finally, the continuum picture suggests that we may apply a very simple estimate from the theory of fracture. The dissociation energy of a C–C bond is ~346 kJ/mol, implying a covalent bond strength of around 3 nN. Taking into account the grafting density of the brush, one may roughly estimate a fracture stress of ~1.2 GPa. The tensile strength of the PMMA is ~52 MPa, indicating that material failure due to the continuum interpretation should definitely occur.

## CONCLUSIONS

In this study we have functionalized PMMA-b-PMAA diblock-copolymer brushes to render them light-sensitive by loading the upper PMMA block with cationic azobenzene-containing surfactants. The complex formation results in nearly a 5-fold increase of the thickness of the PMAA block. Under irradiation with an UV interference pattern the brush topography deforms into a surface relief grating (SRG). The height of the SRG reaches 12 nm (15% of the total thickness of photosensitive PMAA block) during the first 15 min of irradiation and does not increase further with increasing irradiation time. This behavior is related to the photoisomerization kinetics of azobenzene surfactants. During irradiation at 325 nm, after undergoing the trans–cis transition the surfactant molecule remains in the cis-form. In this case no reorientation of the azobenzene molecules takes place; as a consequence, mass transport is not promoted. However, the structuring appears not only in the form of a topography change but is further modified by the scission process observed at the interface between the nonphotosensitive PMMA block and the functional PMAA block. By washing out the ruptured chains and

Figure 5. Dependence of the number of ruptured chains on the irradiation intensity. Schemes of the brush cross-section are exerted for each irradiation spot. Red and blue colors represent the PMMA and the PMAA block, respectively. AFM micrographs of the corresponding topographies are presented above the plot.
characterizing the change in brush height, we calculate the number of ruptured chains as a function of irradiation intensity. We find that nearly 90% of the PMAA chains can be removed from the brush while the nonfunctional PMMA block remains intact. The evolving physical picture is that of two material continua, within the one of which opto-mechanical forces are generated that lead to rupture of chains in that block. We may postulate familiar concepts from materials science to apply, in that stresses generated in one phase accumulate at imperfections, that is, the (mesoscopic) boundary between the two blocks, and lead to excessive local stresses, resulting in mechanical fracture.

ASSOCIATED CONTENT

Supporting Information

Figure showing the evolution of IR peaks at each synthetic step. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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