Macromolecules
ARTICLE
pubs.acs.org/Macromolecules

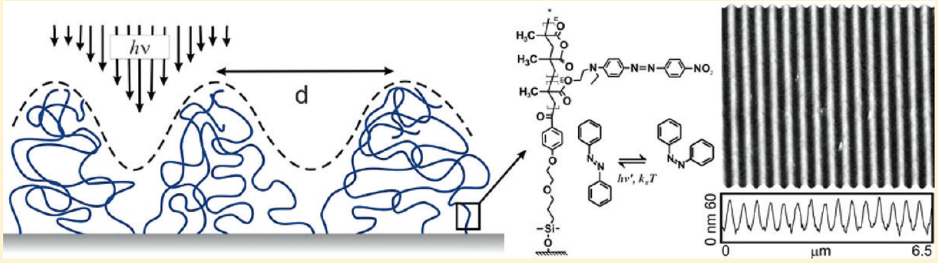
Light-Induced Chain Scission in Photosensitive Polymer Brushes

Nino Lomadze,[†] Alexey Kopyshev,[‡] Jürgen Rühe,[†] and Svetlana Santer*,[§]

[†]Department of Microsystems Engineering (IMTEK), University of Freiburg, 79110 Freiburg, Germany
[‡]Institute for Advanced Studies (FRIAS), University of Freiburg, 79104 Freiburg, Germany
[§]Institute of Physics and Astronomy, University of Potsdam, 14476 Potsdam, Germany

S *Supporting Information*

ABSTRACT:



We report on a process inducing photomechanical fracture of chemical bonds in photosensitive PMAA polymer brushes. The photosensitive PMAA polymer brushes were prepared by covalent attachment of azobenzene groups to poly(methylacrylic acid) (PMAA) chains generated by surface-initiated polymerization. While homogeneous irradiation leaves the polymer topography unchanged, the azo-PMAA brushes show a strong response upon irradiation with UV interference patterns. The photoisomerization process in the surface-attached polymer films results in the irreversible formation of surface relief gratings (SRG), which are strongly enhanced upon washing with a good solvent for the polymer. The photomechanical forces during mass transport induced by the irradiation lead to the scission of covalent bounds and accordingly to a degrafting of the polymer chains in areas where the polymer is receding from. It is observed that the number of ruptured chains depends strongly on the amount of azo side chains in the polymer.

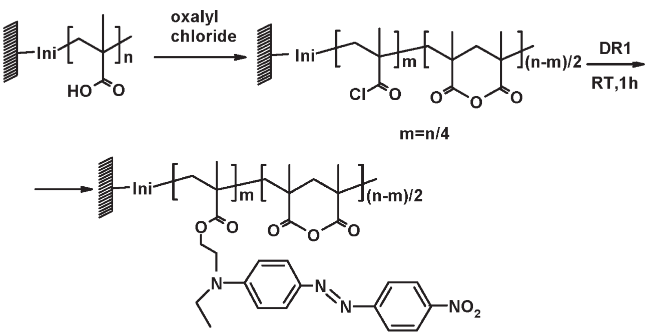
INTRODUCTION

Polymer brushes consisting of densely and covalently attached polymer chains to a solid surface can be employed in a broad range of applications, from tuning wettability to controlling adsorption of proteins and biological systems.[1] The brushes consisting of two different polymers are of special interest.[2] The topography of these brushes can be switched between two different states: patterned and flat, during nanophase separation when exposed to solvents or vapors of different selectivity.[3] In a variety of experimental and theoretical works it is described how the brush topography can be tuned among different metastable states by changing the solvent quality and/or temperature.[4] On the other hand, there are also several publications how the surface polarity and wetting of brushes can be influenced by external stimuli.[5] However, there is so far no report on how the topography of a brush can be controlled by using light as the only external stimulus.

Physisorbed azo-group -containing thin polymer films on the other side have been widely used to assemble photoresponsive surfaces utilizing mass migration and orientational effects, as they show reversible changes of physical properties upon light irradiation.[6] It is well-established that substituted azobenzene molecules undergo a reversible trans–cis–trans isomerization when irradiated with polarized light of an appropriate wavelength. This leads to a quasi-permanent molecular reorientation in a direction perpendicular to the direction of polarization.[7] Irradiation of an azo-polymer thin film with an interference pattern of UV light can be used to reversibly write in certain topographic features into the polymer film, resulting in formation of so-called surface relief gratings (SRGs).[8,9] This initiation of material flow by absorption of UV light can even occur at room temperature in air, i.e., in glassy state, when the polymer is supposed to be a solid. This is interesting, as not only the local properties of the azo content are changed but the whole matrix and polymer structure changes itself. Following the pioneering work of Nathanson and Kumar,[8,9] a lot of studies have been conducted clarifying the details of writing and erasing such relief structures as well as understanding the physical origins of the transport mechanisms.[10] Still a lot of open questions remain. A common starting point of all proposed mechanisms so far is the reorientation of azo-molecules according to the direction of the electric field vector, to which they preferentially orient perpendicularly.[11] Taking this evidence, one can develop models along various lines, for instance, changes in free volume of the azo-molecules and orientational phase changes such as in a nematic liquid crystals that also may be related to significant changes in strain within the polymer leading

Received: May 5, 2011
Revised: June 29, 2011
Published: August 23, 2011

Scheme 1. Synthesis of PMAA−DR1 Ester Brushes



to a viscoelastic response. In this respect, azo-modified polymer brushes may prove to be useful for further experimental studies, as due to the geometrical constraints of the high-density grafted polymer chains, considerable preorientation of azo-groups can be achieved.

Recently, end-grafted polymer layers have been used as carriers for photoresponsive molecules and exhibit surprisingly different properties from spin-casted films.[12] It was shown that the orientation of azo-groups within the thin polymer film is preferentially parallel to the surface in the case of polymer brushes, whereas in the case of nongrafted films, the azo-groups are oriented mostly perpendicularly.

In this work we present the synthesis and characterization of photoresponsive polymer brushes by attaching azobenzene chromophores to surface-attached PMAA chains. We describe the response of the resulting azo-polymer brushes to illumination with UV interference patterns. We study the topography of the irradiated films before and after exposure to a good solvent for the polymer and compare the behavior of these films to the corresponding physisorbed azo-containing polymer films. We investigate the photomechanical scission of polymer chains within the brush during SRG formation.

■ EXPERIMENTAL SECTION

Materials. All chemicals were purchased from Aldrich and used without additional purification. Silicon wafers with a 2.5 nm thick silicium oxide layer (Si-Mat; Germany), polished on both sides, were used for growth of polymer brushes.

Synthesis of Azo-PMAA Brushes. Poly(methacrylic acid) brushes were generated by surface-initiated photopolymerization following a method described elsewhere.[13] PMAA brushes were treated with oxalyl chloride in dimethylformamide (DMF) (0.2 vol %) at room temperature for 3 h (Scheme 1). The obtained acid chloride-co-anhydride brushes were treated with DR1 in DMF at room temperature for 1 h. The obtained functionalized brushes were extracted with DMF for 16 h.

Methods. Transmission FT-IR spectra of the attached polymer layers were recorded using a Bio-Rad Excalibur spectrometer. The characterization of surface topography of azo-PMAA brushes was carried out with atomic force microscopy (AFM) (Nanoscope IIIa, Veeco). 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.

The Lloyd's mirror scheme with He−Cd laser (Kimmon) operating at λ = 442 nm (total power of about 60 mW) was used as UV interference lithography setup (Figure 1).

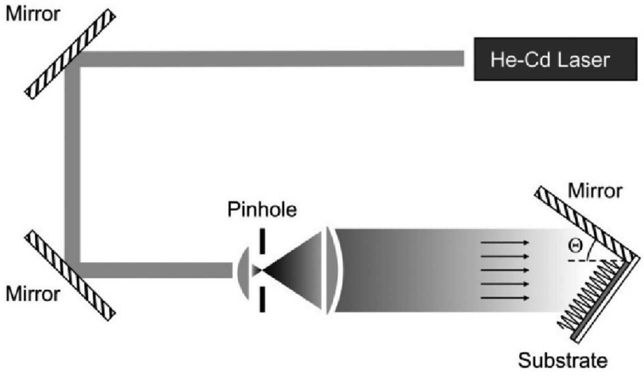


Figure 1. Scheme of the Lloyd's setup used for structuring of photosensitive polymer brushes.

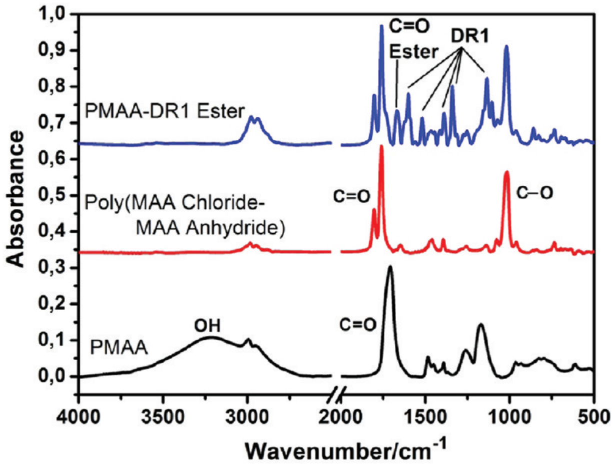


Figure 2. FT-IR spectra of PMAA (black), poly(MAA chloride−MAA anhydride) (red), and PMAA−DR1 ester brushes.

The beam of the circular polarized light is cleaned by a lens−pinhole unit and then split into two coherent beams by the mirror, interfering at the sample position to create a regular line pattern. The periodicity of the interference pattern is given by $d = \lambda/\sin(\theta/2)$, where λ is the wavelength of the incident light and θ is the angle between the incoming laser beam and the mirror surface. Irradiation times vary between several minutes and 2 h.

■ RESULTS AND DISCUSSION

To introduce photosensitive azobenzene groups into a polymer brush, we chose in this study the polymer-analogous esterification reaction between the poly(methacrylic acid) brush (PMAA) and disperse red (DR-1) as the azobenzene compound (Scheme 1 and Figure 3a), as the corresponding azobenzene group containing monomer gave only low molecular weight polymer and thus very thin brushes.

Chlorination of PMAA brushes with oxalyl chloride yielded a copolymer brush containing both acid chloride and anhydride groups as described for bulk PMAA.[14,15] The FT-IR spectra of PMAA brush and of its chlorination product are presented in Figure 2. The strong double bands at 1756 and 1802 cm^{-1} can be assigned to overlapping absorption bands of acid chloride and anhydride carbonyl groups.[16] From the loss of the adsorption band of the acid group it might be concluded that an almost

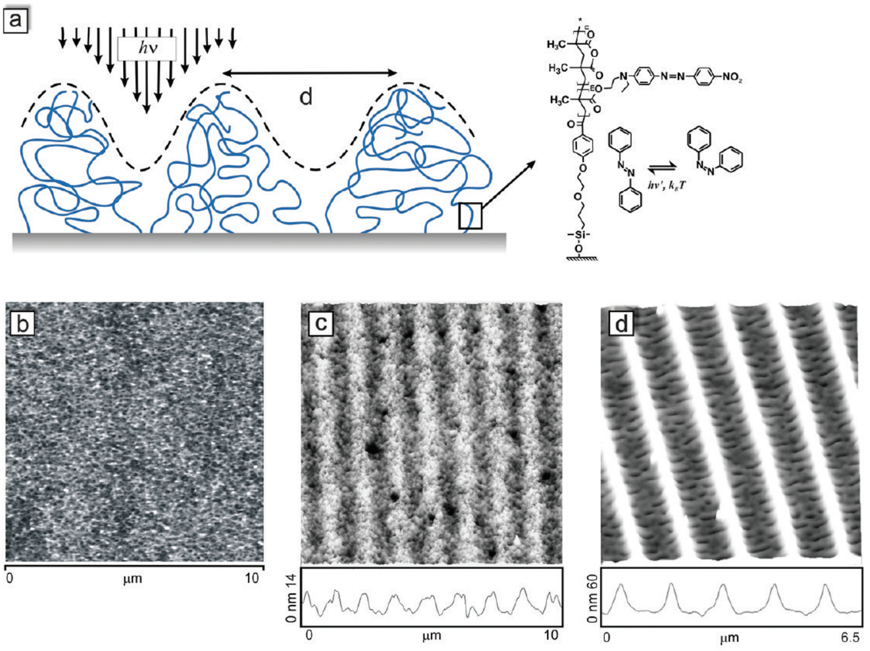


Figure 3. (a) Schematic depiction and chemical structure of the photosensitive azo-PMAA polymer brush. (b) Tapping mode AFM micrograph of the azo-PMAA brush before irradiation with interference pattern. (c) The topography of the brush after irradiation with the UV interference pattern at λ = 442 nm during 10 min. (d) After irradiation during 30 min, the depth of the formed pattern increases to almost total height of the brush; that is, areas of small height are almost at substrate level.

complete conversion of the acid groups of PMAA into the acid chloride/anhydride takes place although detection of an absorption band of acidic carbonyl groups in the FT-IR spectrum could be complicated by the presence of chloride and anhydride. In addition to the FT-IR analysis, the relative content of acid chloride and acid anhydride groups can be estimated from the reactivity of the activated brush during the esterification with DR1. While acid chloride groups react relatively rapidly with DR1 the corresponding reactions with anhydrides is much slower. Rapid esterification of ∼25% of the functional groups takes place at room temperature, as analyzed using the decreasing of integral of carbonyl group absorption band of FT-IR spectrum. The remaining functional groups undergo a rather slow esterification at higher temperature in the presence of a catalytic amount of TEA. By varying the reaction time, the azo-content of the brushes can be controlled. The FT-IR spectrum of DR1 ester-functionalized brush shown in Figure 2 with 25% azo-content shows characteristic absorption bands of the azo compound at 1601 cm^{-1} (C=C), 1518 cm^{-1} (NO_2 assym), 1389 cm^{-1} (N=N), 1339 cm^{-1} (NO_2 symm), and 1142 cm^{-1} (CN) as well as those of ester-carbonyl group at 1688 cm^{-1}.

While homogeneous UV-irradiation left the polymer topography practically unchanged, irradiation with an interference pattern yielded a very strong response of the film topography to the irradiation. The topography follows the intensity distribution of these patterns and deforms, resulting in a surface relief grating (SRG). Before irradiation, the topography of the azo-brushes is flat with a roughness of 0.5 nm (rms taken over an area of 10 μm × 10 μm) (Figure 3b). After an irradiation time of 10 min the depth of the stripes is 10 nm, and the periodicity of the formed pattern is 1.2 μm (Figure 3c). By increasing the irradiation time to 30 min, it was possible to almost completely remove the polymer material from certain areas on the brush. The pattern of mass redistribution follows the irradiation pattern (Figure 3d). However, it is difficult to make a statement how the material redistribution is correlated with the light intensity. It is not clear whether a concentration of mass proceeds into areas of minimum or maximum irradiation intensity (as it may appear from Figure 3a).

The brush shown in Figure 3b−d has 65% of its monomer units substituted by DR-1. The thickness of the brush in this case is 60 nm, while the depth of the stripes is 55 nm after 30 min irradiation. Characteristic almost regular longitudinal cracks perpendicular to the direction of mass transport are observed (Figure 3d). They have distances between 200 and 600 nm and typical lengths around 600 nm.

The depth of the stripes formed depends on the amount of the attached azo-groups, when irradiation time and intensity were kept constant. For this study, we cut a poly(MAA chloride−MAA anhydride) brush with a thickness of 117 ± 5 nm into several pieces and treated it with DR1. The modified brush with an azo-contents of 16% resulted in an increase of the thickness to 140 ± 5 nm, while a 25% contents of DR-1 lead to a thickness increase to 152 ± 5 nm, as determined from AFM measurements.

The irradiation time was kept at 15 min, corresponding to a dose of 90 J/cm^2. Figure 4 shows that the stripe depth increases from 1 nm for the polymer with 16% of (DR-1) substituted repeat units to 2 nm for 18%, 4 nm for 21%, and 7 nm for 25% monomer substitution with azo side chains. To check whether the SRG formation is reversible, i.e., whether it is possible to make the brush material to refill the voids, the brushes were treated with dimethylformamide, which is a good solvent for the polymer. Surprisingly, instead of returning to the flat state, we find that the depth of patterns does not decrease but increases from 12 to 15, 25, and 55 nm for azo-contents of 16%, 18%, 21%, and 25%, respectively (Figure 4).

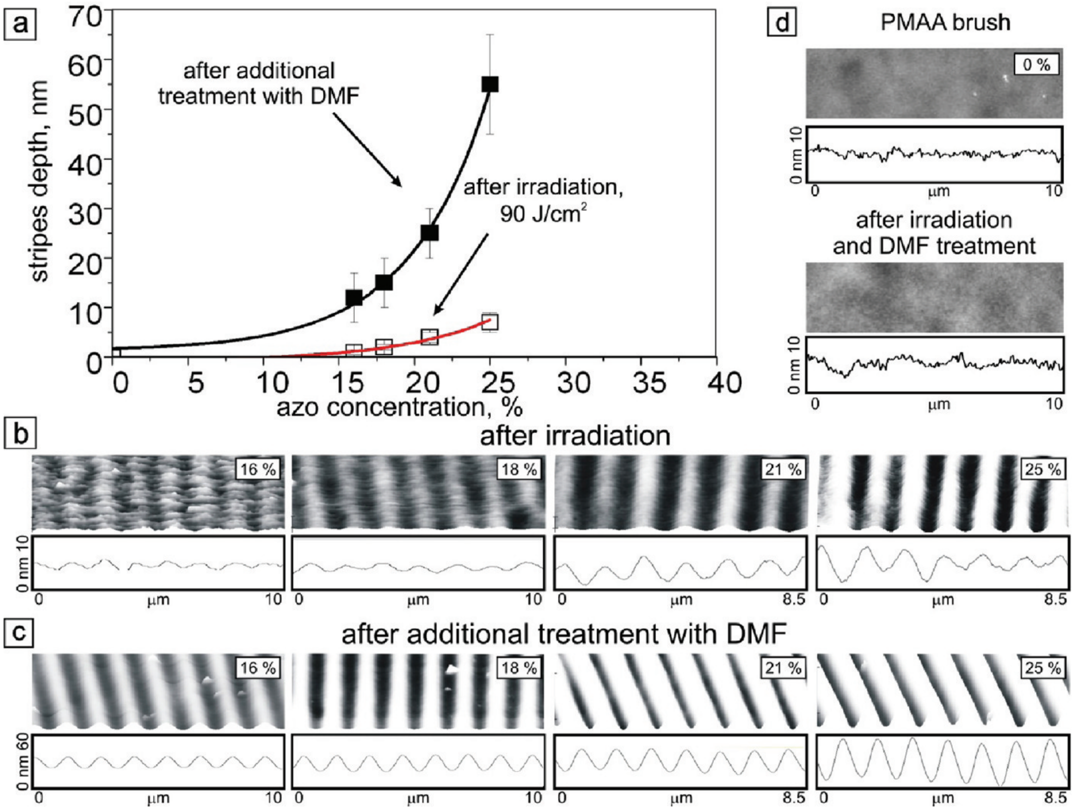


Figure 4. (a) Stripe height of azo-PMAA brushes after irradiation with UV interference patterns as a function of azo concentration of the polymer film. The red curve corresponds to the height directly after irradiation (15 min, with an irradiation dose of 90 J/cm^2), while the black one shows the same pattern after additional treatment of the brush with DMF. (b) and (c) show the corresponding AFM micrographs. (d) shows the topography of a PMAA brush just before irradiation and after 1 h of irradiation with UV interference pattern followed by DMF treatment.

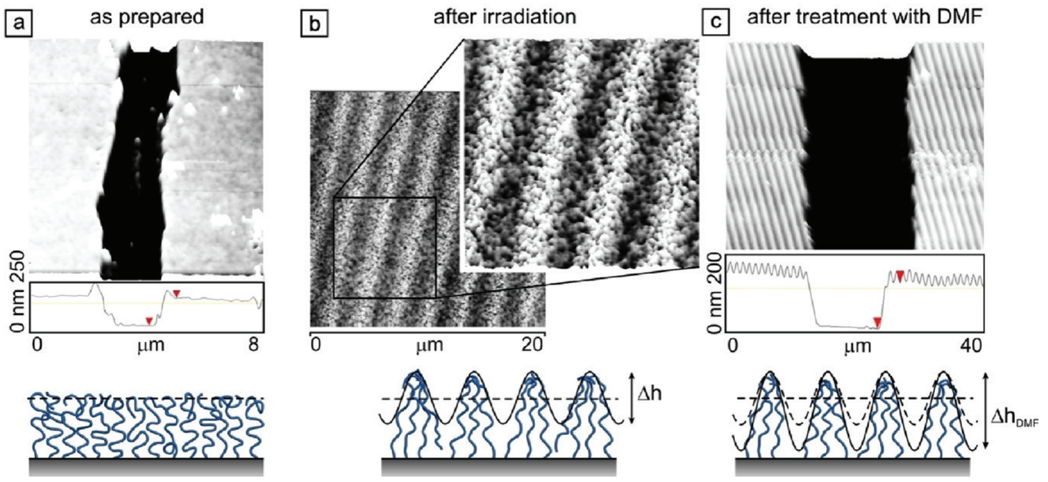


Figure 5. AFM micrographs with corresponding schemes of chain elongation clarifying the AFM procedure for estimating the fraction of ruptured chains. The black areas in (a) and (c) are due to a scratch, which allows a thickness determination.

An explanation of this phenomenon is that some of the polymer chains have been ruptured from areas of low light intensity. To further elucidate this point, an identical sample was treated with UV light under homogeneous illumination followed by exposure to DMF solution. In this case no change in thickness of the polymer layer occurs as can be inferred from the AFM cross-sectional analysis of the brush (see Supporting Information). In a second experiment it was shown that also the irradiation of the pure PMAA brush with a UV-intensity pattern does not result in topography changes (Figure 4d). There was no drop in overall film thickness measured after intense treatment with DMF solvent. This result rules out a simple photochemical degradation mechanism involving an absorption process under UV-irradiation. This can be taken as clear evidence that the scission of the

Table 1. Height Modulations before and after DMF Treatment and Fraction of Ruptured Chains on the Azo-Contents of the Brushes[a]

azo, %	Δh_0, nm	Δh_{DMF}, nm	$\Delta\sigma_{min}$, %
0	0 ± 0.5	0 ± 1	0
16	1 ± 0.5	12 ± 1	57
18	2 ± 0.5	15 ± 1	59
21	5 ± 0.5	25 ± 1	62
25	7 ± 0.5	55 ± 1	72

[a] Δh_0 is the depth of the stripes after irradiation with interference patterns (irradiation time 15 min), Δh_{DMF} is the stripe depth after treatment with DMF, and $\Delta\sigma_{min}$ is the percentage of ruptured chains.

polymer chains off the silicon substrate takes place only due to mass transport and is not caused by photochemical degradation.

From the AFM measurements it is possible to estimate the number of ruptured chains using

$$\Delta\sigma_{min} = 1 - \frac{h_{min}}{h_0}$$

where h_0 is the initial thickness of the brush, h_{min} is the thickness of the grooves after treatment with DMF, and $\Delta\sigma$ is the percentage of ruptured chains (Figure 5).

Even at low content of azo-groups (16%), more than 50% of the chains are ruptured, while at 25% monomer substitution it increases up to 72% (Table 1).

One might speculate about the very nature of the scission process. On the one hand, there are chain scission theories for laminar flow assuming that the drag force experienced by the chain rises until it will eventually break the molecular bond when a certain critical strength is exceeded. In our case, we would have to overcome the bond strengths of either Si−O, Si−C, C−C, or C−O bonds that are relevant for the brush chain attachment. However, it is not clear at this point whether the energy change per volume built up through the light-induced gradient forces suffices to directly break the rather strong covalent bonds (Si−O, 452 kJ/mol; Si−C, 318 kJ/mol; C−C, 346 kJ/mol; C−O, 356 kJ/mol).[17] This will depend on the density of grafting points compared to the energy changes per volume within the polymer film and is at the present stage hard to estimate.

In addition, the stripe depth and thus the fraction of ruptured chains seem to depend exponentially on the azo-contents. This could be explained if we assume that the energy deposited in the polymers by the irradiation intensity increases linearly with the azo-contents and that chain scission is a thermally activated process. When a simple Arrhenius behavior is considered, a linear increase in the energy would lead to a corresponding exponential increase of the rate constant for the scission process.

However, it might well be that the scission process is more complex than suggested above, where forces act on an independent single chains embedded in some mean-field environment. In addition, collective behavior may occur where large local tensions capable of breaking single bonds are built up from large scale mechanical strains. There is at least an indication toward this picture, arising from the occurrence of nanoscale cracks in the films shown in Figure 4c. The photodegrafting process will depend on many parameters, such as the irradiation time and also the aspect ratio (periodicity of the stripe pattern with respect to the maximum film thickness possible) which still need to be studied more comprehensively.

CONCLUSIONS

Azobenzene-group-containing PMAA brushes were generated by surface-initiated polymerization and a polymer analogous reaction. The maximum content of azo side chains introduced into the PMAA chains that could be achieved was 65%. While the photogroup containing film was very stable against photodegradation, it exhibits a very strong response upon radiation with UV-light interference patterns, leading to inhomogeneous intensity distributions. We observe formation of a pronounced periodic structure of the polymer film following the periodicity of the intensity pattern of the UV light. The topography change is related to a redistribution of polymer mass induced by the cis−trans isomerization of the azobenzene moieties that most likely proceeds from areas of low toward high light intensity. We find that this mass redistribution is irreversible under certain conditions. It can be attributed to a photomechanically induced scission of polymer chains, leading to a degrafting of polymers off the substrate. This is further substantiated by the fact that upon solvent treatment a significant fraction of the polymer is washed out and that the topography modulations are strongly enhanced. The degrafting process increases very strongly with the azo-contents of the polymer. However, even at small azo-contents, more than 50% of the chains are ruptured, predominantly within areas of receding polymer material.

The surprising strength of the photomechanical scission process could not be inferred from surface relief grating formation in simple physisorbed photosensitive films and is still lacking a detailed understanding. This question, however, is interesting because it directly challenges the understanding of optically induced phase changes in photosensitive films as a whole.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Figure 1. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: santer@uni-potsdam.de.

ACKNOWLEDGMENT

This research is supported by the DFG (SA1657/3-1). We thank Dr. Wolfgang Mönch and Bernd Aatz for their help with the laser setup.

REFERENCES

(1) (a) Yerushalmi-Rozen, R.; Klein, J.; Fetters, L. J. *Science* **1994**, *263*, 793–795. (b) Mansky, P.; Liu, Y.; Huang, E.; Russell, T. P.; Hawker, C. *Science* **1997**, *275*, 1458–1470. (c) Raphael, E.; de Gennes, P. G. *J. Phys. Chem.* **1992**, *96*, 4002–4007. (d) Chen, C. S.; Mrksich, M.; Huang, S.; Whitesides, G. M.; Ingber, D. E. *Science* **1997**, *276*, 1425–1428. (e) Ito, Y.; Ochiai, Y.; Park, Y. S.; Imanishi, Y. *J. Am. Chem. Soc.* **1997**, *119*, 1619–1623.

(2) (a) Matyjaszewski, K.; Patten, T. E.; Xia, J. H. *J. Am. Chem. Soc.* **1997**, *119*, 674–680. (b) Zhulina, E. B.; Singh, C.; Balazs, A. C. *Macromolecules* **1996**, *29*, 6338–6348. (c) Advincula, R. C.; Brittain, W.; Caster, K. C.; Rühe, J. *Polymer Brushes*; Wiley-VCH: New York, 2004. (d) Usov, D.; Gruzdev, V.; Nitschke, M.; Stamm, M.; Hoy, O.; Luzinov, I.; Tokarev, I.; Minko., S. *Macromolecules* **2008**, *40*, 8774–8783.

(3) (a) Santer, S.; Kopyshev, A.; Donges, J.; Rühe, J.; Jiang, X.; Zhao, B.; Müller, M. *Langmuir* **2007**, *23*, 279–285. (b) Santer, S.;

Kopyshev, A.; Donges, J.; Yang, H.-K.; Rühe, J. *Adv. Mater.* **2006**, *18*, 2359–2363. (c) Santer, S.; Kopyshev, A.; Yang, H.-K.; Rühe, J. *Macromolecules* **2006**, *39*, 3056–3061. (d) Santer, S.; Rühe, J. *Polymer* **2004**, *45*, 8279–8297. (e) Santer, S.; Kopyshev, A.; Donges, J.; Yang, H.-K.; Rühe, J. *Adv. Mater.* **2006**, *18*, 2359–2362. (f) Santer, S.; Kopyshev, A.; Donges, J.; Yang, H.-K.; Rühe, J. *Langmuir* **2006**, *22*, 4660–4667. (g) Schuh, C.; Santer, S.; Prucker, O.; Rühe, J. *Adv. Mater.* **2009**, *21*, 1–5.

(4) (a) Zhao, B.; Brittain, W. J. *J. Am. Chem. Soc.* **1999**, *121*, 3557–3558. (b) Zhao, B.; Haasch, R. T.; MacLaren, S. *J. Am. Chem. Soc.* **2004**, *126*, 6124–6134. (c) Müller, M. *Phys. Rev. E* **2002**, *65*, 030802(R). (d) Minko, S.; Mueller, M.; Usov, D.; Scholl, A.; Froeck, C.; Stamm, M. *Phys. Rev. Lett.* **2002**, *88*, 035502. (e) Rühe, J.; Knoll, W. In *Supramolecular Polymers*; Ciferri, A., Ed.; Marcel Dekker: New York, 2000; p 565. (f) Paik, M. Y.; Xu, Y.; Rastogi, A.; Tanaka, M.; Yi, Y.; Ober, Ch. K. *Nano Lett.* **2010**, *10*, 3873–3879.

(5) Minko, S.; Müller, M.; Motornov, M.; Nitschke, M.; Grundke, K.; Stamm, M. *J. Am. Chem. Soc.* **2003**, *125*, 3896–3900.

(6) (a) Seki, T. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2084–2109. (b) Natansohn, A.; Rochon, P. *Chem. Rev.* **2002**, *102*, 4139–4176. (c) Barrett, C. J.; Mamiya, J.; Yager, K. G.; Ikeda, T. *Soft Matter* **2007**, *3*, 1249–1261. (d) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847–1874. (e) Yager, K. G.; Barrett, C. J. *J. Photochem. Photobiol., A* **2006**, *182*, 250–261. (f) Yager, K. G.; Barrett, C. J. *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 487–494. (g) Ichimura, K.; Oh, S. K.; Nakagawa, M. *Science* **2000**, *288*, 1624–1626.

(7) (a) Rau, H. In *Photochemistry and Photophysics*; Rebek, J., Ed.; CRC Press: Boca Raton, FL, 1990; Vol. 2, pp 119—141. (b) Todorov, T.; Nikolova, L.; Tomova, N. *Appl. Opt.* **1984**, *23*, 4309–4312. (c) Jones, C.; Day, S. *Nature* **1991**, *351*, 15. (d) Loucif-Saibi, R.; Nakatani, K.; Delaire, J. A.; Dumont, M.; Sekkat, Z. *Chem. Mater.* **1993**, *5*, 229–236. (e) Sekkat, Z.; Knoll, W. *Photoreactive Organic Thin Films*; Academic: New York, 2002.

(8) (a) Rochon, P.; Batalla, E.; Natansohn, A. *Appl. Phys. Lett.* **1995**, *66*, 136–138. (b) Kim, D. Y.; Tripathy, S. K.; Li, L.; Kumar, J. *Appl. Phys. Lett.* **1995**, *66*, 1166–1168. (c) Lefin, P.; Fiorini, C.; Nunzi, J. M. *Opt. Mater.* **1998**, *9*, 323–328.

(9) (a) Barrett, C. J.; Natansohn, A. L.; Rochon, P. L. *J. Chem. Phys.* **1996**, *100*, 8836–8842. (b) Bellini, B.; Ackermann, J.; Klein, H.; Grave, Ch.; Dumas, Ph.; Safarov, V. *J. Phys.: Condens. Matter* **2006**, *18*, 1817–1835. (c) Kumar, J.; Li, L.; Jiang, X. L.; Kim, D. Y.; Lee, T. S.; Tripathy, S. K. *Appl. Phys. Lett.* **1998**, *72*, 2096–2098.

(10) (a) Barrett, C. J.; Rochon, P. L.; Natansohn, A. L. *J. Chem. Phys.* **1998**, *109*, 1505–1516. (b) Bian, S.; Williams, J. M.; Kim, D. Y.; Li, L.; Balasubramanian, S.; Kumar, J.; Tripathy, S. *J. Appl. Phys.* **1999**, *86*, 4498–4508. (c) Lefin, P.; Fiorini, C.; Nunzi, J.-M. *Pure Appl. Opt.* **1998**, *7*, 71–82. (d) Pedersen, T. G.; Johansen, P. M.; Holme, N. C. R.; Ramanujam, P. S.; Hvilsted, S. *Phys. Rev. Lett.* **1998**, *80*, 89–92. (e) Baldus, O.; Leopold, A.; Hagen, R.; Bieringer, T.; Zilker, S. J. *J. Chem. Phys.* **2001**, *114*, 1344–1349. (f) Baldus, O.; Zilker, S. J. *Appl. Phys. B: Laser Opt.* **2001**, *72*, 425–427.

(11) (a) Geue, T. M.; Saphiannikova, M. G.; Henneberg, O.; Pietsch, U.; Rochon, P. L.; Natansohn, A. L. *Phys. Rev. E* **2002**, *65*, 052801/4. (b) Saphiannikova, M.; Neher, D. *J. Phys. Chem. B* **2005**, *109*, 19428–19436.

(12) (a) Seki, T. *Curr. Opin. Solid State Mater. Sci.* **2006**, *10*, 241–248. (b) Uekusa, T.; Nagano, S.; Seki, T. *Macromolecules* **2009**, *42*, 312–318.

(13) Konradi, R.; Rühe, J. *Macromolecules* **2004**, *37*, 6954–6964.

(14) Cornaz, J. P.; Hutschneker, K.; Deuel, H. *Helv. Chim. Acta* **1957**, *40*, 2015–2019.

(15) Manecke, G.; Heller, R. *Makromol. Chem.* **1958**, *28*, 185–196.

(16) (a) Grant, D. H.; Grassie, N. *Polymer* **1960**, *1*, 125–134. (b) Lai, J. H. *Macromolecules* **1984**, *17*, 1010–1012.

(17) Huheey, E. Keiter, E.; Keiter, R. *Anorganische Chemie*; Walter de Gruyter: Berlin, 2003.