

# Fabrication of Thiol–Ene “Clickable” Copolymer-Brush Nanostructures on Polymeric Substrates via Extreme Ultraviolet Interference Lithography

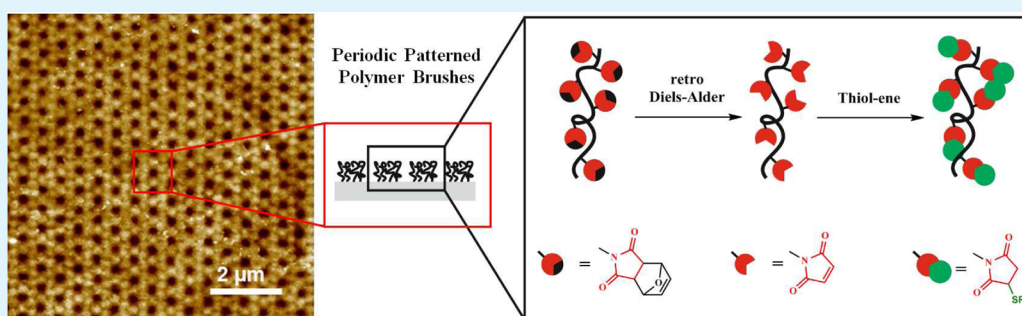
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## S Supporting Information



**ABSTRACT:** We demonstrate a new approach to grafting thiol-reactive nanopatterned copolymer-brush structures on polymeric substrates by means of extreme ultraviolet (EUV) interference lithography. The copolymer brushes were designed to contain maleimide functional groups as thiol-reactive centers. Fluoropolymer films were exposed to EUV radiation at the X-ray interference lithography beamline (XIL-II) at the Swiss Light Source, in order to create radical patterns on their surfaces. The radicals served as initiators for the copolymerization of thiol–ene “clickable” brushes, composed of a furan-protected maleimide monomer (FuMaMA) and different methacrylates, namely, methyl methacrylate (MMA), ethylene glycol methyl ether methacrylate (EGMA), or poly(ethylene glycol) methyl ether methacrylate (PEGMA). Copolymerization with ethylene-glycol-containing monomers provides antibiofouling properties to these surfaces. The number of reactive centers on the grafted brush structures can be tailored by varying the monomer ratios in the feed. Grafted copolymers were characterized by using attenuated total reflection infrared (ATR-IR) spectroscopy. The reactive maleimide methacrylate (MaMA) units were utilized to conjugate thiol-containing moieties using the nucleophilic Michael-addition reaction, which proceeds at room temperature without the need for any metal-based catalyst. Using this approach, a variety of functionalities was introduced to yield polyelectrolytes, as well as fluorescent and light-responsive polymer-brush structures. Functionalization of the brush structures was demonstrated via ATR-IR and UV–vis spectroscopy and fluorescence microscopy, and was also indicated by a color switch. Furthermore, grafted surfaces were generated via plasma activation, showing a strongly increased wettability for polyelectrolytes and a reversible switch in static water contact angle (CA) of up to 18° for P(EGMA-co-MaMA-SP) brushes, upon exposure to alternating visible and UV-light irradiation.

**KEYWORDS:** polymer brushes, polymeric materials, click chemistry, nanostructures, EUV lithography, thiol–ene, functional surfaces, light-responsiveness

## 1. INTRODUCTION

Patterned functional polymeric surfaces with reactive groups that can be modified under mild conditions without employing any metal catalyst open a broad field of applications and are of particular interest for the bioconjugation of polymeric materials.<sup>1</sup> Such patterns need to be fabricated with properties and characteristics that enable them to interact with their environment in a desired manner. Polymer brushes are ideal candidates for such applications, since polymers can be readily synthesized to be multifunctional by the incorporation of several monomers with different properties and functions.

Post-polymerization modification of a functional precursor polymer facilitates the establishment of libraries of functional polymers, without the need to optimize the individual polymerization conditions for varieties of monomers carrying different functional groups.<sup>2,3</sup> Often, reactions on surfaces proceed with poor efficiency due to slow kinetics and undesired side reactions, caused by the heterogeneity of the system. In

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contrast, efficient and chemospecific transformations,<sup>2,4,5</sup> collectively grouped as “click” reactions,<sup>6–12</sup> have drawn tremendous attention in recent decades. Among these efficient reactions, many, like the copper-catalyzed alkyne–azide cycloaddition,<sup>13–17</sup> are limited in terms of their biocompatibility, as the metal ions are toxic to cells. As a consequence of this, “click” reactions that avoid the use of metal catalysts have experienced a major increase in their utilization.<sup>18–22</sup> Another coupling reaction that is often referred to as “click” chemistry is the nucleophilic thiol–ene reaction.<sup>22–26</sup> Due to its usually fast reaction kinetics, this Michael-type hydrothiolation of a C=C bond is a very robust technique, leading to high or quantitative yields, with little or no byproduct, under ambient, nonstringent reaction conditions.<sup>27,28</sup>

Thiol-reactive polymeric materials that contain maleimide groups for conjugation have been developed recently.<sup>20,29–33</sup> Maleimides are versatile functional groups for thiol–ene reactions, as they show fast kinetics because of their two electron-withdrawing carbonyl groups in a cis-configuration, combined with bond-angle relaxation and release of strain in the ring upon thiol-addition.<sup>27,28,34–36</sup> Since the maleimide group contains a polymerizable double bond, maleimide monomers require efficient protection during polymerization, as well as efficient deprotection after the polymerization.<sup>33,37,38</sup> The ability to reversibly deactivate/activate maleimides by means of Diels–Alder (DA) and retro Diels–Alder (rDA) reactions, respectively, is based on their high reactivity as dienophiles with a variety of dienes.<sup>39</sup> Notably, the simple DA/rDA reactions require no additional reagents and generate no byproducts,<sup>40,41</sup> thus making them attractive for obtaining masked polymers and reactivating dormant polymers into “clickable” form. Maleimide–furan adducts have been applied for the generation of reversible covalent assemblies,<sup>42–44</sup> self-healing polymers,<sup>45,46</sup> thermally responsive dendrons,<sup>47</sup> segmented block dendrimers,<sup>48</sup> and polymers with a tunable cross-linking density.<sup>31,49</sup> The thiol–maleimide reaction, which is fast, facile, and selective, has been exploited intensively for coupling functional moieties to biomolecules.<sup>50–52</sup> Although many examples of self-assembled monolayers of maleimide conjugates on various metallic and glass surfaces have been described,<sup>53</sup> reports of polymer surfaces functionalized with maleimides are rare.<sup>54</sup>

Maleimide-containing polymer brushes were fabricated on silicon oxide surfaces using copper-mediated atom transfer radical polymerization (ATRP).<sup>55</sup> This approach entails immobilization of specific radical initiators on the silicon-based substrate, followed by metal-mediated polymerization. Needless to say, development of a universal method for fabrication of thiol-reactive brushes on polymeric substrates will expand their versatility. In particular, to date, there are no reports of fabrication of thiol-reactive copolymer brushes on polymeric substrates. The rapid increase in the utilization of polymeric substrates due to their cost-effectiveness for high-throughput usage in a disposable manner necessitates the development of protocols that will allow rapid production of patterned reactive platforms on polymeric substrates, e.g., for biological assays.

A precise definition of domain sizes and architectures in soft-material systems provides a basis for controlling interactions of the environment with a surface. A technology for radiation-induced grafting of micro- and nanostructured polymers by free-radical polymerization (FRP) has been established in past years.<sup>56–59</sup> In this approach, nanostructured patterns of

polymer brushes are grafted from activated polymeric surfaces such as polyolefins and fluoropolymers. The activation is carried out via interference exposure with extreme ultraviolet (EUV) light. Precise control over the creation of radical patterns, down to the nanometer scale, allows grafting of nanostructured brushes in a subsequent polymerization process. The process is very simple compared to controlled radical polymerization (CRP) methods, such as atom transfer radical polymerization (ATRP),<sup>60</sup> reversible addition–fragmentation chain transfer (RAFT),<sup>61</sup> or nitroxide-mediated polymerization (NMP),<sup>62</sup> where initiators need to be immobilized at the surface. Furthermore, the FRP-approach yields periodic brush structures, even at short reaction times, with more than an order of magnitude higher thickness compared to brushes produced by CRP.<sup>56</sup>

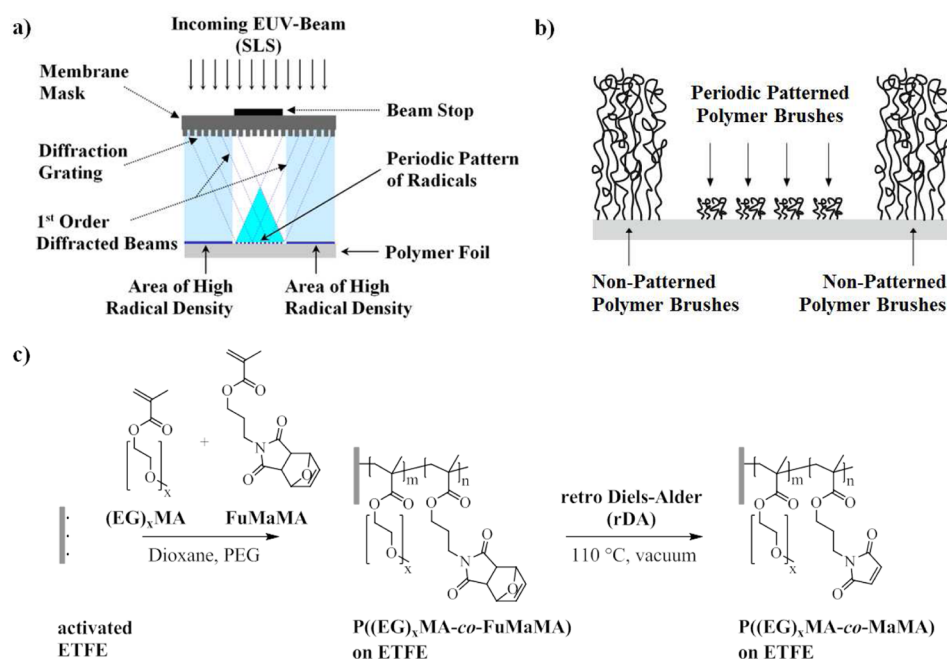
In this article, we demonstrate grafting of patterned copolymer-brush structures on a polymeric substrate, namely, poly(ethylene-*alt*-tetrafluoroethylene) (ETFE), which could easily be functionalized at room temperature via metal-free thiol–ene reaction. In particular, copolymers containing furan-protected maleimide side chains as reactive groups and different pendant side chains were synthesized. Poly(methyl methacrylate), ethylene glycol methyl ether methacrylate, and poly(ethylene glycol) methyl ether methacrylate were used as the comonomers yielding the copolymers P(MMA-*co*-FuMaMA), P(EGMA-*co*-FuMaMA), and P(EGMA-*co*-FuMaMA), where the latter two provided antibiofouling properties to the brushes. Thereafter, activation of masked maleimide groups via the rDA reaction, as well as a facile fabrication of functional surfaces via thiol–ene reactions, was carried out. Successful modification of the patterned brushes was displayed via modification with different thiols generating polyelectrolytes, as well as fluorescent and light-responsive polymer-brushes on a polymeric substrate.

## 2. MATERIALS AND METHODS

**2.1. Materials.** Hot-pressed, flat 100- $\mu\text{m}$ -thick ETFE foils (Nowoflon, ET-6235 Nowofol GmbH, Siegsdorf, Germany) were used as the substrates. Chemicals were purchased from Sigma-Aldrich (Buchs, Switzerland), VWR (Zurich, Switzerland) or Fluka (Buchs, Switzerland). The monomers methyl methacrylate (MMA), ethylene glycol methyl ether methacrylate (EGMA), and poly(ethylene glycol) methyl ether methacrylate (PEGMA, molecular weight 300 Da) were passed through an alumina column before use. All other chemicals were used as received. The furan-protected monomer was synthesized according to a procedure described in the literature.<sup>63</sup> The synthesis and NMR characterization of the spiroopyran thiol are in the Supporting Information (Scheme S1). The precursor molecule SP-PFP was prepared as previously reported.<sup>56</sup>

**2.2. Sample Activation.** This has been described in detail in a previous publication.<sup>56</sup> In brief, ETFE samples were exposed to EUV light with a central wavelength of 13.5 nm under vacuum. Patterns of radicals were created on the polymeric surfaces by irradiation through silicon nitride masks with chromium gratings of different periods in a dedicated interference lithography setup at the Swiss Light Source. For large-area activation, flat-pressed samples were activated with low-pressure argon plasma (Femto, Diener Electronics, Jettingen, Germany) operated with 40 kHz/30 W for 1–10 min.

**2.3. Brush Preparation. Grafting of Copolymer Brushes.** Activated samples were placed in a monomer solution (3 mmol) of the furan-protected maleimide methacrylate and ethylene glycol monomethyl ether methacrylate in 3 mL of dioxane containing 20% vol poly(ethylene glycol), degassed with nitrogen and heated for 2 h to 70 °C. Copolymerization with methyl methacrylate, or with poly(ethylene glycol) monomethyl ether methacrylate, was carried out analogously. The mole fraction of the different monomers in the



**Figure 1.** (a) EUV interference lithography, as performed at SLS. Patterns of radicals were created by interference of photon beams (92.5 eV) diffracted at grating structures. (b) Cross-section of nonpatterned and periodic patterned polymer-brush nanostructures grafted from areas of high radical density and periodic pattern of radicals, respectively. (c) Synthetic strategy for copolymer brushes via grafting of P((EG)<sub>x</sub>MA-co-FuMaMA) and the subsequent retro Diels–Alder (rDA) reaction used to activate the maleimide groups.

solution was varied, but the total monomer concentration remained the same.

**Retro Diels–Alder Reaction.** The deprotection of the maleimide moieties was carried out by heating the substrates under vacuum for 1 h at 110 °C.

**Thiol–Ene Reactions.** The Michael-additions of the different thiols (0.1 mmol) were carried out in 3 mL of *N,N*-dimethylformamide (DMF) at ambient temperatures overnight.

**2.4. Nuclear Magnetic Resonance Spectroscopy.** <sup>1</sup>H NMR spectra were recorded on a Bruker 300 MHz spectrometer using deuterated chloroform or dimethyl sulfoxide (DMSO) as a solvent and trimethylsilane as the reference.

**2.5. Atomic Force Microscopy.** AFM scans in height and peak force mode were acquired via ScanAssistMode in air on a Dimension Icon instrument (Bruker, Karlsruhe, Germany) as follows: ScanAssist Air silicon nitride (Si<sub>3</sub>N<sub>4</sub>) cantilevers with a tip radius of 12 nm, a spring constant of 0.4 N m<sup>-1</sup>, and a resonance frequency of 70 kHz (Bruker, Karlsruhe, Germany). First-order flattening procedures (NanoScope Analysis 1.5 software, Bruker, Karlsruhe, Germany) were applied to all measured data.

**2.6. Attenuated Total Reflection Infrared Spectroscopy.** The measurement strategy using a Hyperion 3000 IR microscope (Bruker, Fällanden, Switzerland) equipped with an ATR objective with a circular contact area with 100 μm diameter has been described in detail in previous work.<sup>56</sup>

**2.7. Water Contact Angle Determination.** A G2 & DO3426 contact angle measuring system (Krüss GmbH, Hamburg, Germany) was used for determination of static contact angles of 3 μL water droplets. The error in the values evaluated with the proprietary Krüss software is estimated to be in the range ±2°.

**2.8. Fluorescence Microscopy.** An Olympus IX81 fluorescence microscope (Olympus Deutschland GmbH, Hamburg, Germany) equipped with an OBS MegaView camera and cell<sup>R</sup> software was used for acquisition and evaluation of fluorescence images.

**2.9. UV–Vis Spectroscopy.** UV–vis transmission spectra in a range from 200 to 800 nm were acquired on a UV–vis–NIR spectrometer (Lambda19, PerkinElmer, Schwerzenbach, Switzerland) equipped with a deuterium lamp and a halogen light source.

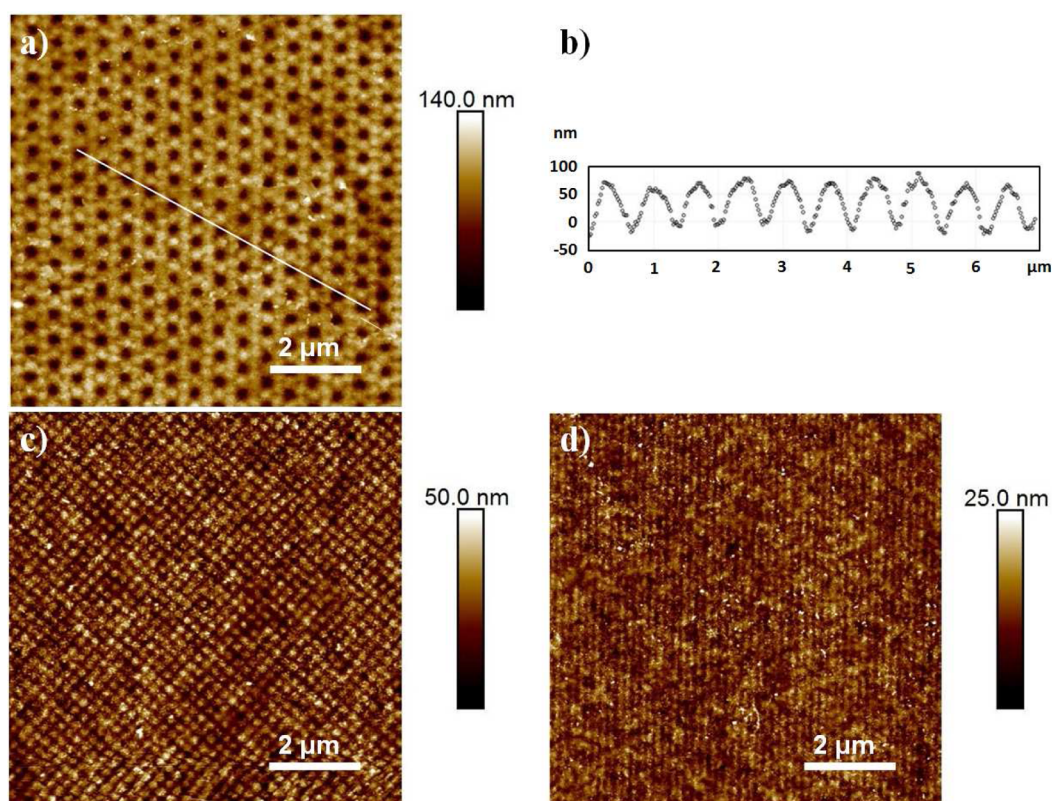
### 3. RESULTS AND DISCUSSION

**3.1. Fabrication of Patterned Copolymer Brushes via Interference Lithography.** Patterned functional polymeric surfaces with chemoselective groups open up a broad field of applications in various areas, such as diagnostic microarray fabrication. In this work, we used an established process, which has been developed in our institute, to produce nanostructured, functional polymer brushes showing high reproducibility in terms of achievable height-dose dependence and resolution.<sup>56–59</sup> In Figure 1a, a scheme of the EUV lithographic exposure step providing the basis for grafting nanostructured polymer brushes is shown.

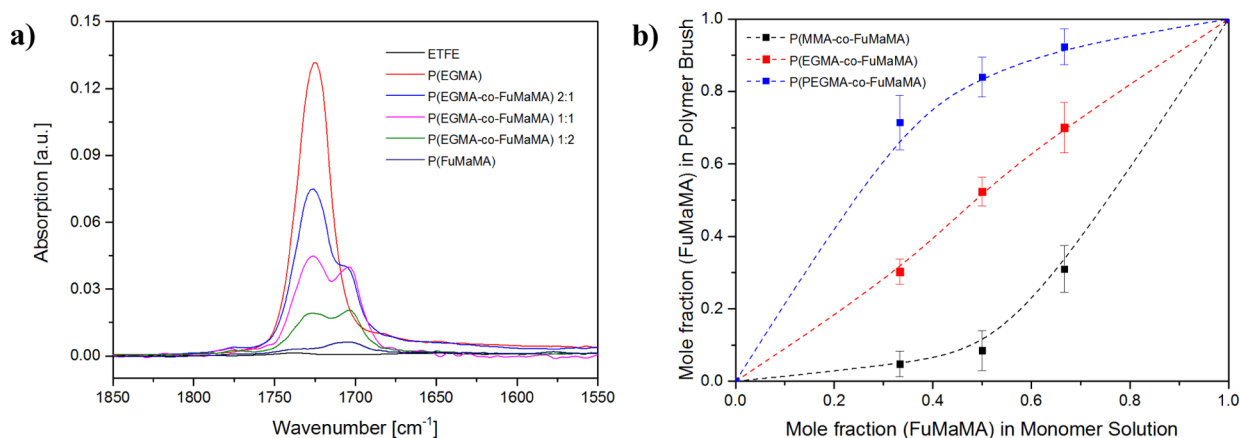
Undulator light with a wavelength of 13.5 nm (92.5 eV) was used to crack chemical bonds and, as a consequence, to create radicals at polymer surfaces. The interference setup used generates periodic radical patterns on the surface of ETFE foils via diffraction at grating structures in the mask. The formed radicals were used as initiators in a subsequent polymerization reaction, to graft micro- and nanostructured polymer brushes covalently from substrate polymer surfaces (Figure 1b). The masks used here allowed the production of line and dot arrays or hexagonal patterns with 100 nm to 1.5 μm resolution on areas as large as 200 μm<sup>2</sup> based on two, four, or six beam interference, respectively.

The aim of this work was the fabrication of functionalizable maleimide-containing polymer brushes on geometrically well-defined areas and with a defined thickness. For the copolymerization, we have chosen methacrylates with 0, 1, or, on average, 4.5 ethylene glycol units as side groups mixed in different ratios with the protected maleimide monomer (Figure 1c). This gave us control over the concentration of reactive centers in the grafted brush structures and provides additional antibiofouling properties to these patterned surfaces.

Atomic force microscopy (AFM) images of areas covered with brush nanostructures grafted using free-radical polymer-



**Figure 2.** AFM images of P(EGMA-*co*-FuMaMA) copolymer nanostructures grafted from ETFE. (a) Structure with hexagonal symmetry defined by six interfering beams and (b) line profile along the line indicated in part a. High-resolution structures were achieved using interference of (c) four beams, resulting dots with 280 nm period, and (d) two beams, resulting in 200 nm period lines.



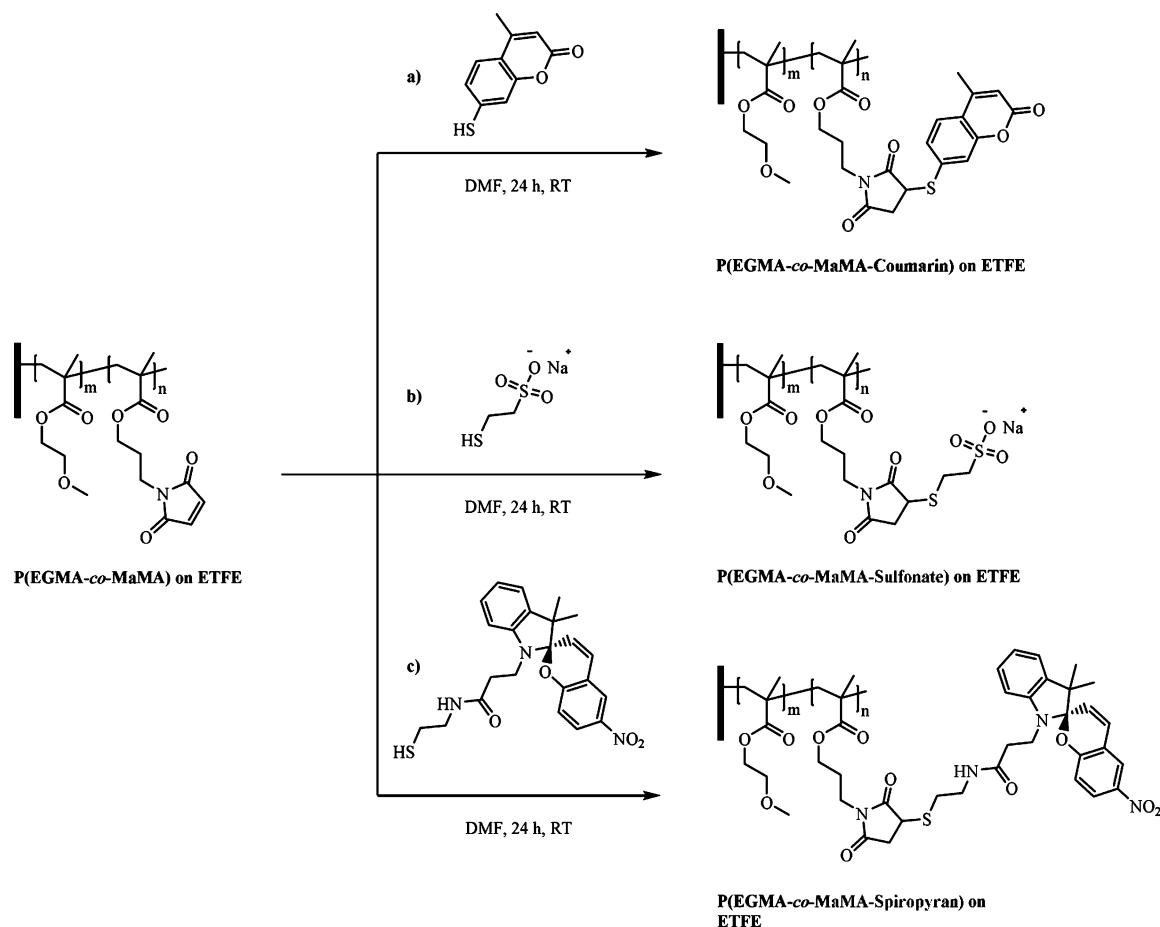
**Figure 3.** (a) ATR-IR spectra of P(EGMA), P(EGMA-*co*-FuMaMA), and P(FuMaMA) brush microstructures grafted from ETFE. (b) Mole fraction of FuMaMA in MMA, EGMA, and PEGMA copolymer-brush structures grafted from ETFE as it depends on the mole fraction of FuMaMA in the comonomer solution. Determination was performed via the relative ratios of the carbonyl vibrations of the ester and imide groups in ATR-IR spectra.

ization are shown in Figure 2. Patterns were defined by two, four, or six interfering EUV-beams using the established lithography setup and grafted at an EGMA:FuMaMA-ratio of 2:1. Two interfering EUV-beams led to nanopatterned line structures, four interfering EUV-beams led to dot structures, and six interfering EUV-beam led to hexagonal structures of P(MMA-*co*-FuMaMA), P(EGMA-*co*-FuMaMA), and P(PEGMA-*co*-FuMaMA). Homogeneous copolymer hexagonal nanopatterned structures with a strong contrast could be grafted, as indicated also in the cross-section profile (Figure 2b). In this case cavities of 100–200 nm in diameter were formed by six dots, hexagonally arranged, 650 nm in width.

Representative of all maleimide-containing copolymer combinations, P(EGMA-*co*-FuMaMA) copolymer-brush structures are shown in Figure 2a. Furthermore, dot and line nanopatterns with a period down to 280 nm (Figure 2c) and down to 200 nm (Figure 2b), respectively, were achieved. P(MMA-*co*-FuMaMA) as well as P(PEGMA-*co*-FuMaMA) copolymer nanostructures led to similar dimensions, differing only in their dose dependence and reaction times according to their grafting behavior described before.

To gain a better understanding of the grafting kinetics, homopolymers grafted with each ethylene glycol derivate monomer were analyzed individually. Evaluation of the dry

Scheme 1. Examples for Thiol–Ene Post-Polymerization Modification of Grafted P(EGMA-*co*-FuMaMA) on ETFE: (a) Coumarin-Containing Fluorescent Brushes, (b) Sulfonate-Containing Polyelectrolytes, and (c) Spiropyran-Containing Light-Responsive Brushes



thickness of grafted micropatterns of poly(methyl methacrylate) P(MMA), ethylene glycol methyl ether methacrylate P(EGMA), and poly(ethylene glycol) methyl ether methacrylate P(PEGMA) showed a roughly square-root dependence on dose, consistent with the brush-like configuration for all three polymers. Using FRP conditions, microstructures were accessible that exceeded 1  $\mu\text{m}$  in thickness for MMA, 650 nm for EGMA, and 200 nm for PEGMA brushes. These different findings for the different monomers may be explained by the polymerization kinetics, which were influenced by the number of ethylene glycol units on the monomer and therefore its size. This led to a 2–5 times faster grafting process for P(MMA), i.e., the monomer without ethylene glycol compared to P(EGMA) with one or P(PEGMA) with 4.5 ethylene glycol groups, respectively. Another aspect that may influence the grafting kinetics is the occurrence of side reactions such as hydrogen-abstraction reactions. (Oligo)ethylene glycol-based monomers bear abstractable hydrogens, which can drastically reduce the reaction rates and yields by the formation of radicals of low reactivity in the glycol side chains, leading to termination reactions.<sup>64</sup>

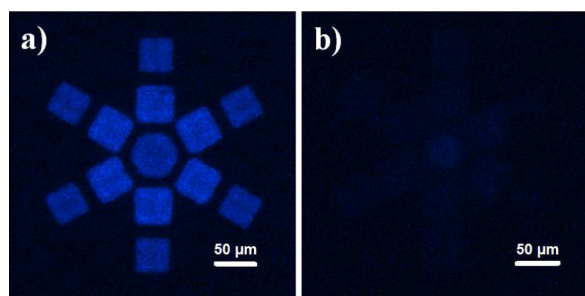
**3.2. Copolymerization.** The furan-protected maleimide-containing monomer (FuMaMA) was copolymerized with MMA, EGMA, or PEGMA (Figure 1c). Polymerization temperature needed to be kept moderate (typically below 90  $^{\circ}\text{C}$ ) in this case in order prevent rDA reactions and to avoid *in situ* cross-linking which would result in gelation.<sup>32</sup> We

quantified the monomer compositions on the copolymer-brush structures via the intensity ratios of the carbonyl vibrations at 1726 and 1705  $\text{cm}^{-1}$  for the ester and imide groups appearing in the ATR-IR spectra of the individual copolymers (Figure 3a, Supporting Information Figures S2 and S3). Their relative intensities of P(MMA), P(EGMA), P(PEGMA), and P(FuMaMA) homopolymers were used to define the mole fractions of FuMaMA for having no FuMaMA on the ethylene glycol or full FuMaMA homopolymer brushes, respectively. The relative intensities for copolymers were fitted in terms of the carbonylic vibrations for esters from the backbone of the FuMaMA fraction. With increasing content of FuMaMA in the brush, the C=O vibration for esters was reduced, while that for imides was enhanced. The experimentally obtained monomer compositions of the copolymer-brush structures showed that the incorporation of the masked monomer was not equal to its mole fraction in solution. This discrepancy can be assigned to the steric hindrance of the pendant bicyclic group in the monomer. Thus, again, size appeared to determine the stoichiometry, as two different monomer types always compete for the free radicals on the surface or in the growing chains. As a result of this, the mole fraction of FuMaMA was much lower on the P(MMA-*co*-FuMaMA) and much higher on the P(PEGMA-*co*-FuMaMA) brush structures than its mole fraction in the monomer solution (Figure 3b). Interestingly, when grafted in a copolymer with

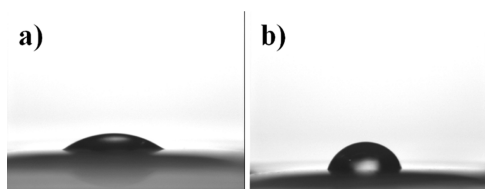
EGMA, the stoichiometry was almost identical to that in the monomer solution.

**3.3. Deprotection.** The deprotection of the maleimide groups was achieved using heat treatment under vacuum to remove the furan moiety via the retro Diels–Alder (rDA) reaction (Figure 1c). This reaction step is expected to be nearly quantitative.<sup>55</sup> It could be detected as a minor shift in the ATR-IR spectra of the imide C=O vibration of the conjugated amide rDA product (Supporting Information Figure S4) and the appearance of strong bands at 830 and 696  $\text{cm}^{-1}$  for cis-conjugated  $\text{sp}^2$  C–H vibrations, respectively (Supporting Information Figure S5).

**3.4. Thiol–Ene Functionalization.** Our strategy was to create functionalized polymer-brush structures via covalent binding of different thiols to surface grafted maleimide-containing brushes via the thiol–ene reaction (Scheme 1). Effective functionalization was demonstrated by the coupling of a thiol-containing coumarin, resulting in fluorescent brushes (Figure 4), as well as coupling of sulfonated thiols resulting in polyelectrolytes (Figure 5).



**Figure 4.** Fluorescence emission ( $\lambda_{\text{Em}} = 390$  nm) of (a) coumarin-containing P(EGMA-*co*-MaMA-Coumarin) and (b) negative control of non coumarin-containing P(EGMA-*co*-FuMaMA/Coumarin) brush structures grafted from ETFE under an excitation with UV-light ( $\lambda_{\text{Ex}} = 360$  nm).



**Figure 5.** Static water contact angle (CA) measurements on large-area brush structures of (a) sulfonate on P(EGMA-*co*-MaMA-Sulfonate) polyelectrolytes and (b) negative control of sulfonate on P(EGMA-*co*-FuMaMA/Sulfonate) brushes grafted from plasma activated 100- $\mu\text{m}$ -thick ETFE foil.

Figure 4 shows the fluorescence images for patterned surfaces after rDA and Michael-addition of a blue fluorescent coumarin-thiol dye.

The effective thioether formation was demonstrated via the strong blue fluorescence detected only on the patterns of grafted brushes, indicating a covalent attachment of the dye and the absence of physisorption on the unmodified ETFE surface. The control experiment using protected FuMaMA brush structures resulted in negligible fluorescence intensity in the structured areas (Figure 4b).

In order to analyze macroscopic properties, such as the wetting behavior of mercaptoethanesulfonate (MES)-containing polyelectrolyte surfaces, ETFE foils were activated in argon

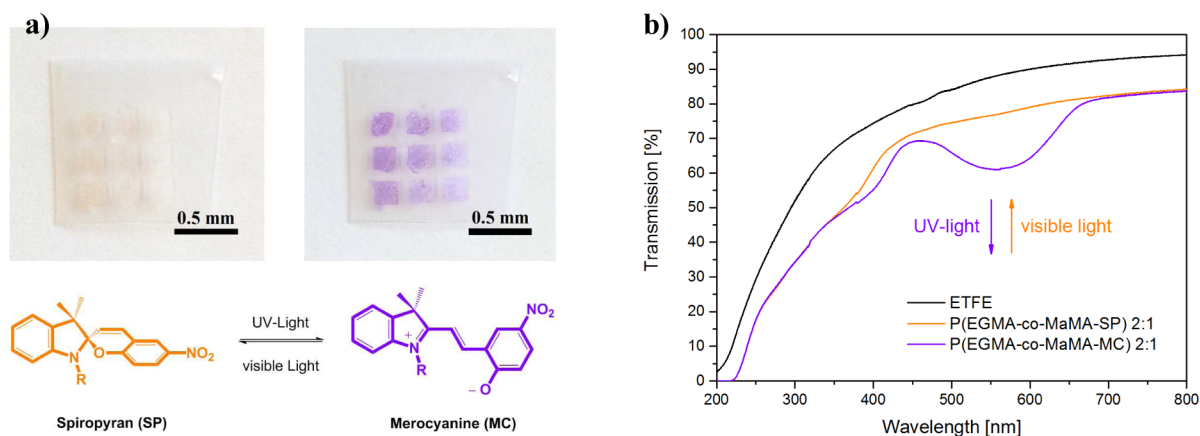
plasma to create  $\text{cm}^2$ -scale areas of radicals suitable to initiate graft polymerization of P(EGMA-*co*-FuMaMA). After modification of the maleimide-containing brushes with MES, a substantial increase in surface wettability was evident since the water contact angle decreased from 73° to 31°, as expected from the transformation of the neutral polymer into a negatively charged polyelectrolyte brush. On the protected brush, no reaction with MES was observed (Figure 5). The Michael-addition of the thiols to the unprotected maleimide could also be detected via ATR-IR microscopy. The appearance of strong characteristic bands for the C=O, C=C, and C–H vibrations of the aromatic coumarin (Supporting Information Figure S6), as well as  $\text{SO}_3^-$  vibrations for the sulfonate (Supporting Information Figure S7) after the thiol–ene reaction, showed covalent attachment to the brush structures. Furthermore, the disappearance of the characteristic peaks at 830 and 696  $\text{cm}^{-1}$  for cis-conjugated  $\text{sp}^2$  C–H vibrations demonstrated very high to quantitative yields for the hydrothiolation reactions. A detailed analysis of the IR bands is listed in Supporting Information Table S1. In summary, the nucleophilic thiol–ene reaction offers a highly efficient and specific methodology for modification of polymeric surfaces coated with maleimide-containing polymer brushes.

To demonstrate that the copolymer brushes on a polymeric substrate can be used as a platform to fabricate a stimuli-responsive system, light-responsive spiropyran (SP)-containing polymer brush structures for smart surface applications have been created via conjugation of a newly synthesized thiol-containing SP to the reactive maleimide groups along the polymeric backbone (Scheme 1). For this purpose, ETFE foils have been irradiated on a large area with EUV-light (92.5 eV) in an exposure without an interference mask, to achieve sufficiently thick areas to detect a visible color change (Figure 6).

The almost transparent SP-containing P(EGMA-*co*-MaMA-SP) brushes switched to a deep purple color when exposed to UV-light (Figure 6a). The color switch could also be detected in the appearance of a strong absorbance band in the transmission spectra around 570 nm, which is in the typical range for spiropyrans (Figure 6b).<sup>56</sup> The heterocyclic spiropyrans carry a chromene moiety, which is orthogonally linked through a spiro-carbon atom. UV-light causes the reversible heterolytic cleavage of the  $\text{sp}^3$  carbon–oxygen bond, forming the planar zwitterionic open form of the deeply colored merocyanine.<sup>65–67</sup>

Furthermore, sample spectra of P(EGMA-*co*-MaMA) and spiropyran-functionalized P(EGMA-*co*-MaMA-SP) brush structures acquired with ATR-IR and the listed appearing peaks with assignments can be found in the Supporting Information (Figure S8 and Table S1). After the post-polymerization modification, strong characteristic bands for N–H and  $\text{NO}_2$  stretching, as well as C–H, C=C, and C–O vibrations from the aromatic skeleton of the SP could be detected. The complete disappearance of the peaks for cis-conjugated  $\text{sp}^2$  C–H vibrations, which are characteristic for maleimides, indicated a highly efficient post-polymerization modification (>95% yield).

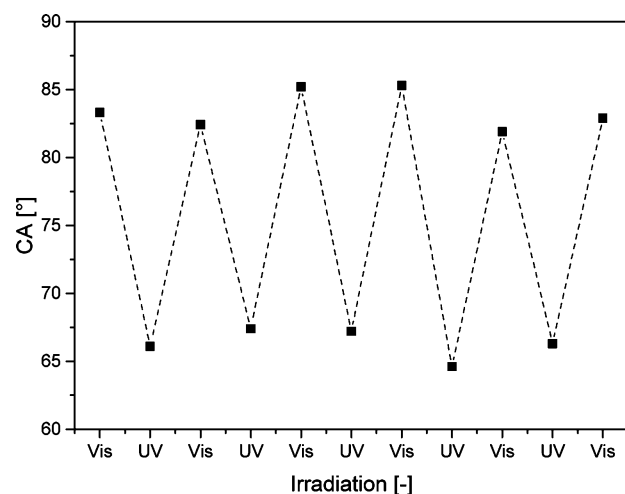
In the next step, argon-plasma activation was used to graft large areas of P(EGMA-*co*-FuMaMA) brushes from ETFE foils for analyzing the switching of wettability of photoresponsive polymer brushes. The grafting process led to an enhanced surface free energy and therefore to a more hydrophilic surface



**Figure 6.** (a) Reversible color switching and (b) transmission spectra of thick microstructured P(EGMA-co-MaMA-SP) brushes on ETFE upon exposure to visible and UV-light showing the reversible switch in absorption around 570 nm. The switch in color and transmission was originating from the transition of colorless spiropyran (SP) to zwitterionic merocyanine (MC).

as indicated by a water contact angle reduction from  $104^\circ$  to  $60^\circ$  (Supporting Information Table S2).

The deprotection via the rDA to the maleimide-containing P(EGMA-co-MaMA) resulted in an increase of the CA to  $73^\circ$ , explicable by the more hydrophobic nature of the conjugated maleimide. After the binding of the spiropyran moieties yielding P(EGMA-co-MaMA-SP) brushes, a static contact angle of  $84^\circ$  was reached. The static contact angle of these modified surfaces could now reversibly be switched between  $84^\circ$  (P(EGMA-co-MaMA-SP)) and  $66^\circ$  (P(EGMA-co-MaMA-MC)) by alternating irradiation with UV and visible light (Figure 7). The reversible change of up to  $18^\circ$  was close to values observed for nonpolymeric spiropyran-containing surfaces.<sup>33,39,68</sup> Switching was reversible for at least 10 cycles.



**Figure 7.** UV and visible light-induced switching of the static contact angles of P(EGMA-co-MaMA-SP) brush surfaces measured with  $3 \mu\text{L}$  water droplets.

The above-mentioned functionalization was carried out to demonstrate how polymeric substrates could be modified in nanostructured as well as in large-area form by using maleimide-containing copolymer brushes. The benign, metal-free polymerization and post-polymerization modification steps allowed preservation of properties of the appended functional molecules without the threat of any metal-ion contamination.

The effective functionalization in a facile manner demonstrates the versatility of this approach.

#### 4. CONCLUSIONS

A method for functionalization of polymeric substrates with thiol-reactive copolymer brushes via extreme ultraviolet (EUV) radiation and their subsequent functionalization using nucleophilic thiol-ene conjugation was demonstrated. In particular, free-radical polymerization of masked maleimide monomers from initiator patterns created with EUV interference was used to grow brush structures, which could be deprotected and modified via thiol-ene coupling, to yield fluorescent, polyelectrolytic, and light-responsive polymer brushes on fluoropolymer surfaces. A successful copolymerization was carried out with short (MMA), medium (EGMA), and long (PEGMA) comonomers. Grafting of furan-protected maleimide-containing copolymer-brush structures of P(MMA), P(EGMA), and P(PEGMA) was clearly evident from ATR-IR spectra.

Attachment of thiols via thiol-ene reactions to the deprotected maleimide side chains was chemoselective and specific. Additionally, patterned, spiropyran-containing polymer brushes were demonstrated to behave as smart surfaces reacting to light as an external stimulus by switching of contact angle, fluorescence, and color. The UV-light-induced wettability switch of  $18^\circ$  caused by spiropyran-merocyanine isomerization was in the characteristic range for spiropyran-modified surfaces.

The three presented examples of functionalization of maleimide-containing copolymer brushes on polymeric substrates demonstrate the versatility of this approach. Further expansion of the concept toward multifunctional and multi-responsive systems may, for instance, be achieved by copolymerization of two reactive monomers that will allow orthogonal modification with different functional moieties.

Different activation methods have been used to control the creation of radicals on the surface, taking advantage of plasma activation for large-area activation and of the EUV interference lithography setup at the Swiss Light Source to access micro- and nanopatterns. Exposure and grafting parameters allowed us to control the grafting density and thickness of the brush structures. Furthermore, copolymerization regulated the density of the attached functional centers on the structures to help control other additional properties for the brushes. For instance, the hydrophobicity or hydrophilicity could be

influenced by varying the number of ethylene glycol moieties in the side chains of the comonomer. Especially, hydrophilic PEG-containing functional brushes will be interesting in future projects as they provide antibiofouling properties along with the potential for selective bioconjugation.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Detailed organic synthesis of spiropyran thiol (SP-SH), AFM step-height measurements of methacrylate homopolymers, and ATR-IR spectra of copolymer-brush structures on ETFE, as well as static CA measurements on plasma-activated polymer surfaces. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b01804.

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### Notes

The authors declare no competing financial interest.

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