Photopolymerization of Poly(Ethylene Glycol) Diacrylate on Eosin-Functionalized Surfaces

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We describe a new method that allows photopolymerization of hydrogels to occur on surfaces functionalized with eosin. In this work, glass and silicon surfaces were derivatized with eosin and photopolymerization was carried out using visible light (514 nm). This mild condition may have advantages over methods that use ultraviolet (UV) light (e.g., for encapsulation of cells and proteins, in drug screening, or in biosensing applications). The hydrogel formed on the modified surface is remarkably stable for an extended period of time. The resultant hydrogel was hydrated for more than 18 months without suffering delamination from the substrate surface. This strongly suggests covalent attachment of the hydrogel to the surface. Contact angle titration measurements and X-ray photoelectron spectroscopy analysis of eosin surfaces before and after irradiation in the presence of triethanolamine suggest that the eosin radical is responsible for the covalent attachment of the gel onto the substrate surface. This method allows for 2-D patterning of hydrogels, which is demonstrated here using the microcontact printing technique. However, noncontact photolithography could be used to form similar patterns by directing light through a mask. This method can be easily implemented to form arrays of fluorophores and proteins in situ.

Introduction

Poly(ethylene glycol) (PEG) is an exceptional polymer with excellent properties and widespread use in biomaterials, biotechnology, and medicine.[1] It is biocompatible, nontoxic, non-immunogenic, hydrophilic, and can be chemically cross-linked into hydrogels for a variety of applications.[2,3] Degradable PEG hydrogels have been prepared for their use as drug carriers for release of proteins and low-molecular-weight compounds.[4] PEG hydrogels have also been used for wound-covering applications, and they can be formed in situ under mild photopolymerization conditions.[3] Due to their biocompatibility and semipermeable properties, cross-linked PEG hydrogels have been used as immunoprotective barriers in tissue engineering for therapeutic cell transplantation to prevent the rejection of transplanted cells by the host's immune system.[5] Hydrogel membranes with these properties provide efficient immunoprotection because they exclude large biomolecules, such as antibodies and immune surveillance cells, that could compromise the viability of encapsulated cells. Yet, at the same time, the semipermeable membrane allows the diffusion of small molecules, such as nutrients (e.g., oxygen, glucose, and amino acids) and metabolism products. In the case of applications involving treatment of type I diabetes, encapsulated islets are able to secrete insulin in response to varying levels of glucose in the body and this insulin can permeate through the membrane. As a result, islet cells encapsulated in hydrogels do not lose their viability or insulin secretion capabilities.[5−8] The semipermeable properties of cross-linked hydrogels made by interfacial photopolymerization of PEG diacrylate were studied by Cruise et al. by forming hydrogels upon poly(vinylidiene fluoride) microporous filters. This approach allowed them to study the effect of molecular weight and concentration of the PEG diacrylate on the diffusivity of biological molecules.[7]

Hydrogels have also been used for the development of electrochemical and optical sensors.[9] Revzin et al. fabricated PEG hydrogel microstructures based on UV-initiated free-radical polymerization and incorporated fluorophore-labeled acetylcholine esterase in hydrogel microstructures to investigate the potential use of these PEG-based microstructures in optical sensors.[10]

This type of photopolymerization also has a number of medical applications in vivo. Elisseeff et al. demonstrated the potential use of transdermal photopolymerization for cartilage tissue engineering applications by using a PEG hydrogel.[11] The validity of the model was established by delivering chondrocytes and PEG precursor through a needle, and after minutes of skin exposure to light, liquid biomaterials would be converted to hydrogel. In this application, the wavelength of light needed to initiate

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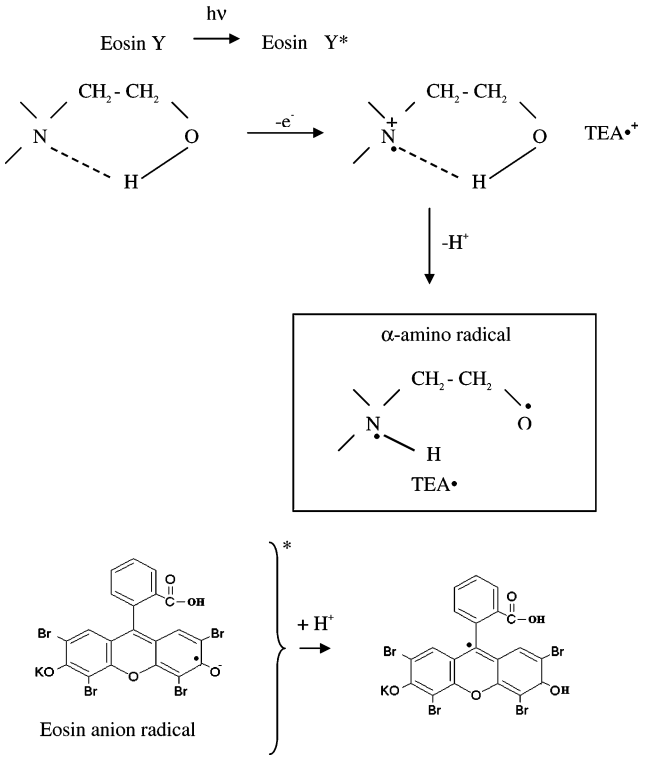
Scheme 1. Schematic Representation of the Photoinitiation Process



photopolymerization is of utmost importance since living tissue transmits very little UV light, whereas its transmittance increases at longer wavelengths. Hydrogels formed by this technique could be used for implantation of biomaterials for plastic surgery applications, as well as for cell and drug encapsulation purposes without the need for invasive surgical intervention.[11]

This study describes a new technique for the formation of PEG diacrylate hydrogels on surfaces. The most essential step in this technique involves the immobilization of an initiator onto the substrate followed by surface-initiated photopolymerization to generate the polymer.[12] The process of hydrogel formation involves the modification of a glass surface by silanization followed by derivatization with an initiator and, finally, forming the hydrogel by irradiating the precursor solution. Eosin was used as the photoinitiatior because of its spectral properties that perfectly suit its use as an initiating system for an argon ion laser.[13] In the presence of an electron donor such as triethanolamine (TEA), which acts as a co-initiator, eosin initiates acrylate polymerization when irradiated.[14,15] It is generally accepted that polymerization occurs as a result of the formation of free radicals originating from triethanolamine. The photoinitiation mechanism, as described in Scheme 1, involves irradiation with green light (514 nm), as a result of which, eosin is excited to the triplet state. Subsequently, electron transfer from triethanolamine to the excited triplet state of the eosin dye produces an eosin anion radical and a triethanolamine cation radical. This is followed by rapid proton loss from the triethanolamine radical cation ($TEA^{\bullet+}$), resulting in a neutral α-amino radical ($TEA^{\bullet}$), which is generally assumed to initiate free-radical polymerization.[13−16] Simultaneously, the proton released from the triethanolamine cation radical is transferred to the eosin anion radical, yielding a neutral eosin radical.[16]

Surface immobilization of an initiator that promotes stable attachment of a hydrogel onto a surface, as presented here, also allows for the formation of 2-D patterns of hydrogels, which can be generated with a variety of techniques, such as microcontact printing (μCP),[17] photolithography,[18] and dip-pen lithography.[19]

Experimental Section

Materials. Eosin (98%), 1-vinyl-2-pyrrolidinone (99+%), poly(ethylene glycol) diacrylate (MW = 575 Da), 3-aminopropyltriethoxysilane (99%), Woodward's reagent K (2-ethyl-5-phenylisoxazolium-3′-sulfonate, 95%) were obtained from Aldrich. Triethanolamine (>99.5%) was obtained from Fluka. Toluene (99.5+%), ethyl alcohol, hydrogen peroxide (30%), sodium hydroxide, sulfuric acid, phosphoric acid, acetic acid, sodium acetate, sodium phosphate monobasic, sodium phosphate dibasic, and sodium carbonate were obtained from Sigma. All chemicals were used as received. Premium quality glass slides (75 × 25 mm) were purchased from Fisher Scientific. Silicon wafers were purchased from TTI Silicon (Sunnyvale, CA). Silicone elastomer stamps for μCP were a gift from Prof. Chilkoti at Duke University. Teflon filters (0.2 μm) were obtained from Corning.

Buffers. All buffer solutions were prepared at 10 mM concentration as follows: pH 3, phosphoric acid/sodium phosphate monobasic; pH 5, acetic acid/sodium acetate; pH 7, sodium phosphate monobasic/sodium phosphate dibasic; pH 8, sodium phosphate dibasic; pH 9, sodium phosphate tribasic; pH 11, sodium carbonate. Exact pH values for buffer solutions were obtained using an Accumet AB15 pH meter. Deionized (DI) water (electric resistivity > 18 MΩ cm) was obtained from a Barnstead Nanopure Infinity UV/UF water-purification system. All glassware and silicon coupons used were cleaned with "piranha solution" (3:7 (v/v), 30% hydrogen peroxide/concentrated sulfuric acid; CAUTION: *piranha solution reacts violently with most organic materials and should be handled with extreme care*).

Amine Functionalized Surfaces. A 7.5 mL aliquot of 3-aminopropyltriethoxysilane (APTES) in toluene solution (10% v/v) was added to a 20 mL clean scintillation vial under a N_2 atmosphere. A maximum of two pre-cleaned glass substrates were added to each vial and sealed. The samples were incubated at room temperature for 2 h to allow the formation of an APTES monolayer. The modified substrates were then removed from the solution and rinsed several times with toluene. In addition, to remove unbound deposited materials, the substrates were placed in toluene in the ultrasonic bath for five minutes. This procedure was repeated at least five times. Finally, the substrates were rinsed with ethanol, water, and ethanol again and then dried with nitrogen. Freshly prepared APTES monolayers were used in these experiments in order to minimize reaction between NH_2 groups and CO_2 present in air.[20]

Surface Derivatization with Eosin. A 1 mM eosin solution was prepared, and the solution was adjusted to pH 7. The eosin solution was mixed with an equal volume of 100 mM Woodward's reagent (WRK) for 5 min to allow the reaction of carboxylic groups present on eosin with WRK. Silanized glass substrates with amine groups were then immersed in this solution for 10 min in order to allow coupling through amide bond formation. After this, the samples were thoroughly rinsed with water in order to remove unreacted eosin from the surface.

Hydrogel Formation through Photopolymerization. The hydrogel precursor solution was prepared with concentrations of 225 mM triethanolamine, 25% (w/w) PEG diacrylate (MW =

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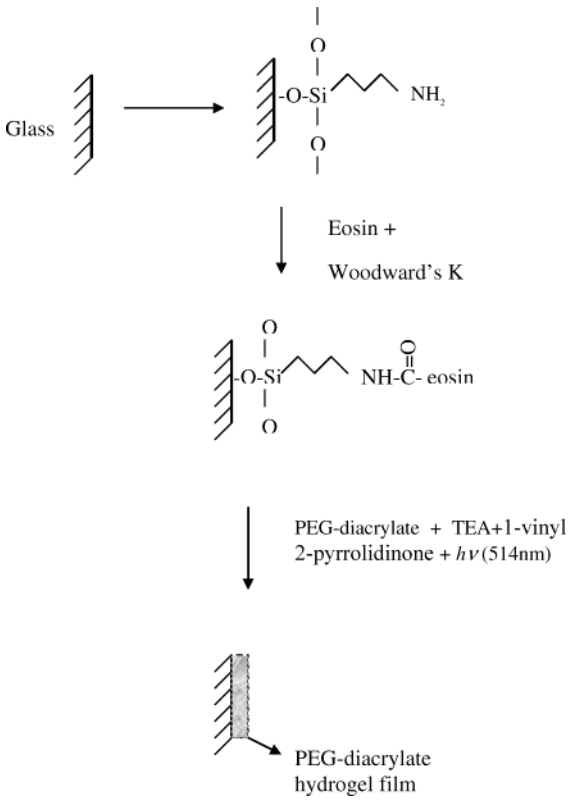
Scheme 2. Schematic Representation of the Surface Modification and Photopolymerization Process on Eosin-Functionalized Surfaces



575 Da), and 37 mM 1-vinyl-2-pyrrolidinone (NVP). The solutions were adjusted to pH 8 using HCl. Precursor solutions were filter sterilized using a 0.2 μm syringe Teflon filter. A 20 μL aliquot of this solution was placed onto the initiator-immobilized glass surface. The substrate was illuminated with an argon ion laser for 3 min ($\lambda = 514$ nm, P = 4.5 mW/cm^2) (Scheme 2). This resulted in fast polymerization (a thick hydrogel layer could be formed in less than 30 s) and formation of a cross-linked hydrogel on the glass substrate. The stability of the surface-bound hydrogel was challenged by prolonged incubation in water.

2-D Patterning of Initiator and Hydrogel using Microcontact Printing (μCP) and Surface-Initiated Photopolymerization. The surface of a poly(dimethylsiloxane) (PDMS) stamp with a pattern of circles (10 μm diameter and center-to-center distance of 40 μm) was oxidized for 30 s with an oxygen plasma to render it hydrophilic.[21] The oxidized stamp was then "inked" with the eosin solution that was activated with Woodward's reagent and placed in contact with the substrate. The amine groups in the regions that contacted the stamp reacted with the eosin molecules of the inked PDMS stamp. After this, 20 μL of PEG diacrylate precursor solution was added for subsequent photopolymerization on the initiator-patterned surface. Scheme 3 displays the procedure to prepare patterned surfaces by using μCP in combination with surface-initiated photopolymerization.

Surface Characterization. *Contact-Angle Titrations.* Contact-angle titration provides a convenient (if indirect) method for examining the state of ionization of functional groups on a surface.[22] Advancing contact angles were determined at room temperature using a Ramé-Hart goniometer, model 100 (Gilmant Inst., Barrington, IL). The measurements were recorded using the following procedure: the advancing contact angle was obtained by depositing an ~1 μL drop of a specific buffer on the surface; an additional 1 μL buffer droplet was added on top of the first drop, and this addition was repeated two times. Contact angles at both sides of the droplet were determined and the average value of these angles was recorded as the contact angle at that specific pH. All the values reported are the average of six measurements taken at the same location on both sides of the drop and have a maximum error of ±3°.

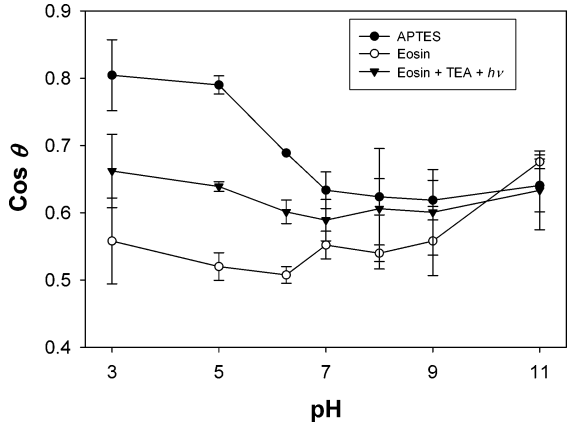


Figure 1. Contact-angle titration curves for different surfaces (●, APTES monolayers; ○, eosin functionalized surfaces; and ▼, eosin functionalized surfaces after exposure to 514 nm laser radiation in the presence of triethanolamine).

X-ray Photoelectron Spectroscopy (XPS). The surfaces were analyzed with a Surface Science Instruments model SSX-100 spectrometer at the National ESCA and Surface Analysis Center for Biomedical Applications (NESAC/BIO) at the University of Washington.

Survey scans from 0 to 1000 eV binding energy were performed to determine the elemental composition of the surfaces. High-resolution scans for carbon (C1s), oxygen (O1s), and nitrogen (N1s) (20 eV window) were also recorded. An Al K$\alpha_{1,2}$ monochromatized X-ray source ($h\nu = 1486.6$ eV) was used to stimulate photoelectron emission. Charge compensation was implemented during spectral acquisition using an electron flood gun operated at 5 eV. The residual pressure in the analysis chamber was on the order of 10^{-9} Torr or lower during spectral acquisition. The spectral envelopes were resolved into Gaussian peaks to fit the spectra, and the hydrocarbon C1s peak was referenced to 285 eV.

Ellipsometry. The thickness of the hydrogel films was determined using a UVISEL phase-modulated spectroscopic ellipsometer from Jobin Yvon, Thin Film Division.

Optical Microscopy. The PDMS stamp and the hydrogel pattern on the glass surfaces were observed with an optical microscope (Nikon Eclipse ME 600) equipped with a CCD camera.

Results and Discussion

Samples were prepared according to the procedures specified in the previous section. All surfaces were characterized using contact-angle titrations in the pH range of 3−11 at different stages of the surface-modification process. The contact-angle titrations of amine-functionalized surfaces (created by chemisorption of APTES on glass or silicon) are shown in Figure 1. The contact-angle behavior of APTES surfaces (filled circles) as a function of pH is consistent with ionization of surface functional groups. That is, these surfaces become more wettable at low pH values, which is an indication of reactive spreading due to ionization (protonation) of the amine groups at low pH. Reactive spreading occurs because the acid−base reaction at the interface contributes to reduce the interfacial free energy. An inflection point is seen in this curve around pH 6. This is a few units lower than the expected pK_a of amine groups but may be a result of a reduced dielectric constant near a surface, which makes deprotonation more difficult to occur (hence shifting the curve a few pH units lower). This inflection point in

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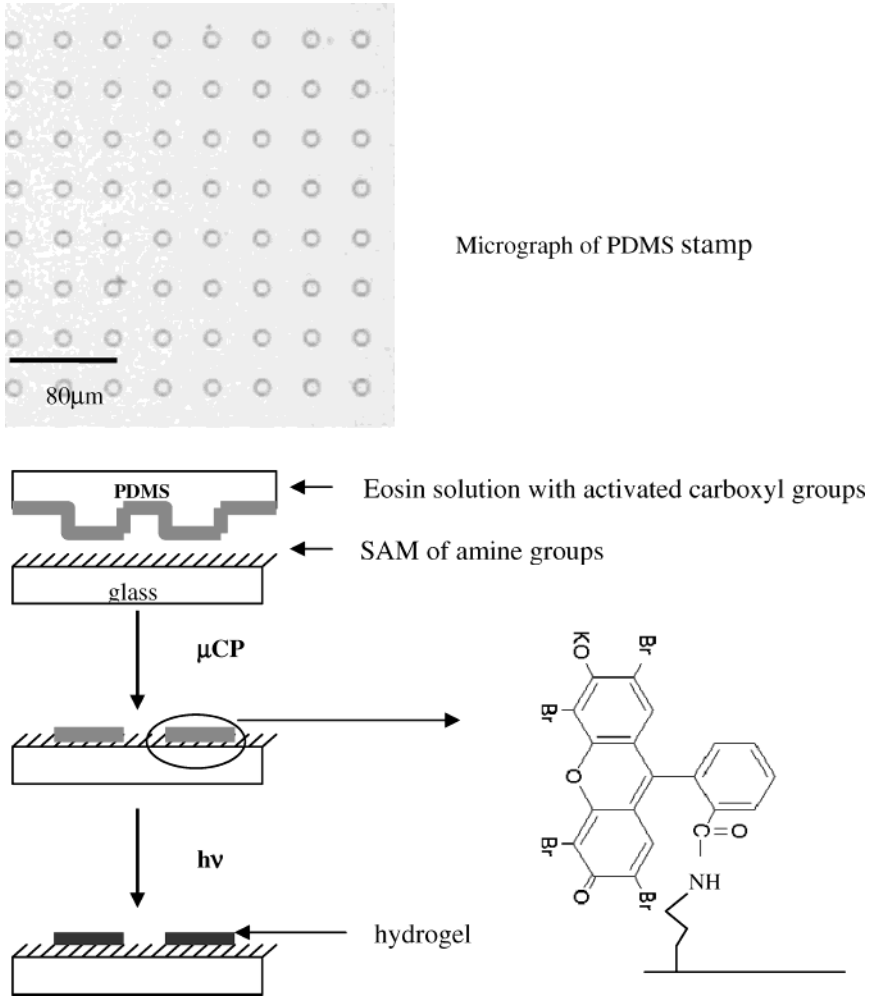
Scheme 3. Fabrication of Initiator-Patterned Surfaces by Microcontact Printing (*μ*CP)



the curve is sometimes referred to as p$K_{1/2}$ by some authors to emphasize the fact that it does not represent the true pK_a.[22]

The amine-functionalized surfaces were further reacted with eosin according to Scheme 2. This derivatization proceeded through reaction between the amine groups of the APTES surface and the carboxyl groups of the eosin molecule. Since this reaction would eliminate the ionizable amine groups, these surfaces were reexamined using contact-angle titrations. The contact-angle titration curve for the eosin functionalized surfaces does not show a dependence on pH, except at the highest pH value employed in these measurements (Figure 1). The disappearance of a threshold trend, where the wettability suddenly decreases when going from low to high pH, is an indication that the ionizable NH_2 groups have been eliminated through surface reaction with the eosin molecule.

It was found that the eosin-functionalized surfaces were suitable for photopolymerization of PEG diacrylate in aqueous medium. This polymerization reaction occurred at the solid−liquid interface upon irradiation with the 514 nm line of an argon laser in the presence of the electron-donor molecule triethanolamine (Scheme 1). Control experiments demonstrated that the polymerization reaction could only occur in the presence of eosin, triethanolamine, PEG diacrylate, and the irradiation provided by the laser at 514 nm. Furthermore, when eosin was covalently attached to the APTES surfaces, the thin hydrogel film formed through photopolymerization remained firmly attached to the surface. In fact, these hydrogel films remain attached to the solid substrates after being immersed in aqueous solutions for more than 18 months. In contrast, when eosin does not form a covalent bond with the surface, the formed hydrogel quickly delaminates upon immersion in water or aqueous solutions (usually in a matter of minutes). The latter was determined by forming eosin monolayers on APTES surfaces through electrostatic interaction only. This was accomplished by exposing the APTES surfaces to the eosin molecule without the peptide-coupling reagent (WRK). In this case, an amide bond is not formed and the carboxyl groups of eosin interact with the amine groups of APTES through electrostatic interactions only. A second control consisted of staining hydrophobic surfaces, such as polystyrene Petri dishes and poly(vinylidiene fluoride) filtration membranes with ethyl eosin. Further controls consisted of bovine serum albumin adsorbed onto the latter surfaces prior to staining with ethyl eosin. Although all these methods yielded eosin-stained surfaces capable of initiating hydrogel formation at the solid−liquid interface, none of them produced hydrogel films that would remain attached to the surface following incubation in aqueous solutions.

Eosin in the presence of electron donors is capable of forming free radicals following electron transfer (such as TEA) and has been widely used for photopolymerization reactions. Published reports using this system ascribe polymerization to the free radicals formed upon electron transfer and deprotonation of the TEA following irradiation with visible light. This is consistent with interfacial

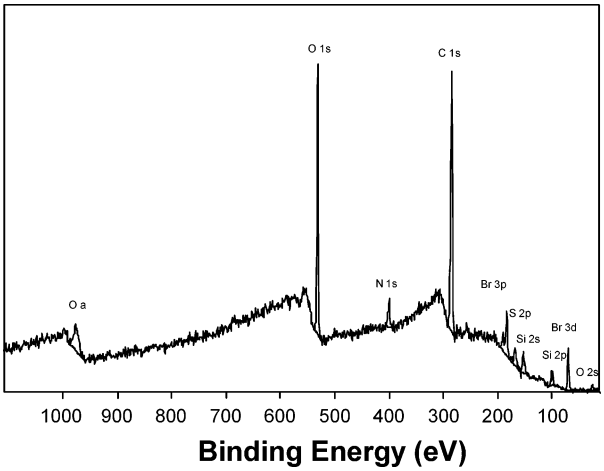
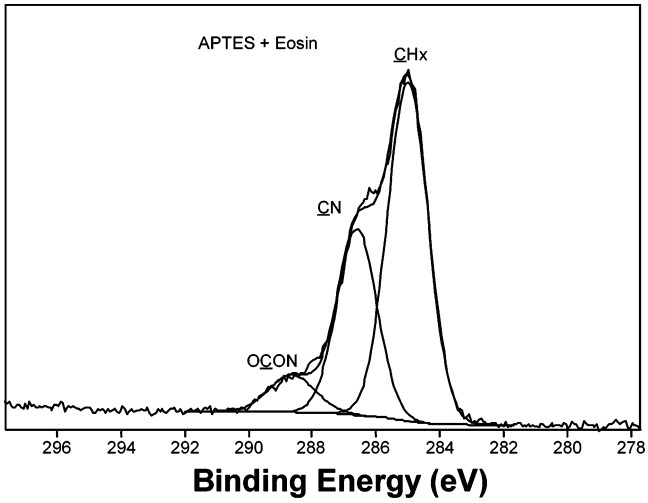


Figure 2. Wide-scan XPS analysis of an eosin functionalized surface.

polymerization since the TEA• radicals are generated through interaction with surface-immobilized eosin (Scheme 1). However, the free radicals originated are not bound to the surface and thus can diffuse into the bulk. Therefore, the formation of TEA• radicals cannot explain the stable attachment of the hydrogels to the surface. As determined from the control experiments, it is the presence of surface-immobilized eosin that promotes stable attachment of the hydrogels. Thus, the hypothesis that interaction of the hydrogel with the surface-bound eosin radical occurs offered a plausible explanation for the strong and stable attachment of the hydrogel films formed by interfacial photopolymerization. An eosin radical could interact with the hydrogel to form covalent bonds either through initiation of polymerization or by termination through addition of "live" hydrogel chains to surface-bound eosin radicals. In fact, it has been reported that eosin can initiate photopolymerization without the electron donor. However, polymerization of acrylates with eosin alone proceeds very slowly.[23]

To prove that the surface-bound eosin radicals can interact with other free radicals (e.g., TEA•, or those from a growing polymer chain), surfaces with covalently attached eosin were illuminated in the presence of triethanolamine for 3 min. The resulting surfaces were examined by contact-angle titrations and XPS. If the formed eosin radicals can react with triethanolamine radicals, this would result in the combination of both at the surface. Contact angles measured for this surface show a slight change in wettability (Figure 1). This indicates surface modification has occurred, possibly as a result of reaction between eosin and triethanolamine radicals. Data obtained by XPS further supports this hypothesis (vide infra).

XPS analysis. Surface analysis by XPS of the substrate with covalently attached eosin shows the presence of Br atoms on the surface (Figure 2), which is evidence for the presence of eosin on the surface (Br is not present on the APTES surface). After illuminating these surfaces in the presence of triethanolamine for 3 min and rinsing the surface, XPS analysis shows significant changes in surface composition. A comparison of the high-resolution C1s spectra of eosin-functionalized surfaces before and after illumination with 514 nm light in the presence of TEA shows an increase in the intensity of the peak at 286.5 eV (Figure 3). This peak is generally ascribed to C−N and C−O groups. The fact that this peak increases upon



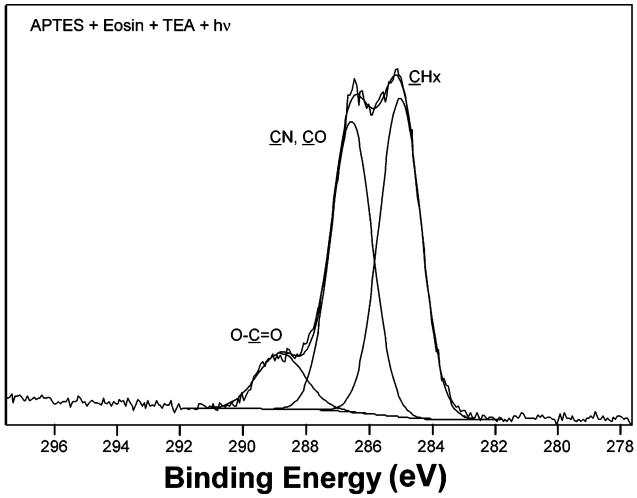


Figure 3. High-resolution C1s spectra of (a) an eosin functionalized surface and (b) an eosin-functionalized surface illuminated (514 nm) in the presence of triethanolamine.

Table 1. Compositional Values of Carbon Peaks for All Samples

	sample	binding energy (eV)	atomic %	peak assignment
1	APTES	285	49.1	$C-H_x$
		286.6	40.7	$C-N$
		288.7	10.2	−OCON−
2	APTES + eosin	285	60.2	$C-H_x$
		286.6	32.3	$C-O$, $C-N$
		288.6	7.5	$N-C=O$
3	APTES + eosin + TEA + *hν*	285	47.6	$C-H_x$
		286.6	43	$C-O$, $C-N$
		288.8	9.4	N−C=O
4	APTES + eosin + hydrogel	285	12.9	$C-H_x$
		286.2	77.7	$C-O$
		288.7	9.3	$O-C=O$

illumination in the presence of TEA suggests that the TEA• radical reacted with the eosin radical on the surface, resulting in its incorporation to the surface. This would offer one possible explanation to the mechanism of attachment of the hydrogels. The hypothesis that the eosin radical can initiate polymerization is more difficult to prove since the eosin radical only forms in the presence of TEA (which results in formation of TEA• radicals). Thus, it would be impossible to quantify the separate role of eosin radicals during polymerization.

Table 1 shows the compositional values of C1s peaks for all samples. The CH_x functionality composition of the

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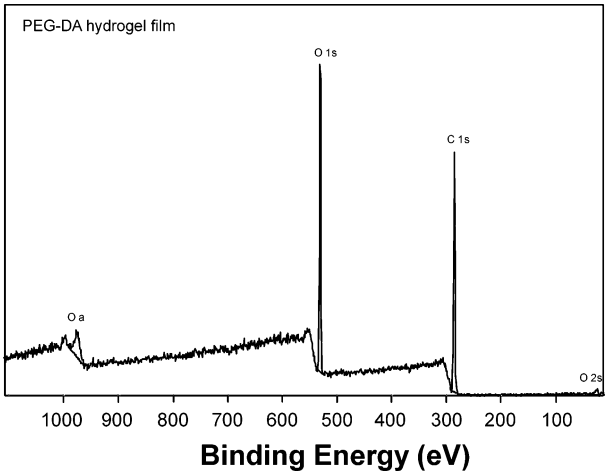

Figure 4. Wide-scan XPS analysis of a PEG diacrylate film formed by photopolymerization on an eosin-functionalized surface.

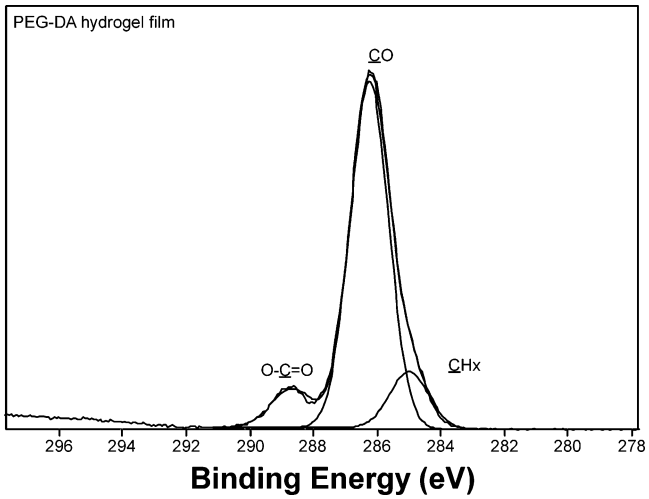

Figure 5. High-resolution C1s spectrum of a PEG diacrylate film formed by photopolymerization on an eosin-functionalized surface.

surface containing eosin (APTES + eosin) is higher than that of the surface containing amine groups (APTES). The reaction of amine groups on the APTES surface with activated eosin solution results in higher compositional values of C−C functional unit for this surface, as eosin has more C−C functionalities in its molecular structure.

The analysis of the sample with the formed PEG diacrylate hydrogel is in perfect agreement with the molecular structure of PEG diacrylate. The theoretical and experimental carbon-to-oxygen ratio is found to be equal to 2 for this sample. The theoretical composition of PEG diacrylate structure is 78.6% C−O groups, and it is experimentally proven by XPS that this functional unit in fact comprises 78% of the surface (Figures 4 and 5). This is further evidence for the presence of PEG diacrylate hydrogel on the surface. The disappearance of the Si peaks from this sample indicates that the hydrogel thickness was greater than 100 Å, the sampling depth of XPS.

Ellipsometric measurements indicate the formation of a thick hydrogel on the surface (in the hydrated state this thickness can be larger than 100 μm). This is much larger than the typical thicknesses obtained through surface-initiated polymerization of linear polymers. For example, recent work by Ista et al. reports the formation of ultrathin polymer films (~130 Å) on surfaces derivatized with the free radical initiator, 2,2′-azobis(2-amidinopropane) hydrochloride.[24] Thicker films could be a result of the cross-linked nature of these hydrogels. In the case of surface-initiated polymerization of linear polymers, the growth of the linear chain at the surface can be terminated by processes such as chain transfer, combination, or disproportionation. However, during polymerization of multifunctional polymers (such as the cross-linked PEG-DA hydrogels) the growing polymer can have multiple reactive groups (pendant double bonds). Termination of the growth process at the surface will occur only after all the reactive groups on the surface-bound polymer are terminated. This, together with the fact that the polymer is cross-linked and can have multiple attachment sites to the surface, may explain the large difference in thickness obtained. Additionally, entanglement of unbound polymers can occur within the cross-linked hydrogels. Therefore, the technique presented offers different characteristics to surface-initiation processes reported before and allows the formation of thicker surface-bound polymer films. This may then offer an alternative method for those applications where thicker films are required and not possible to achieve with conventional surface-initiated polymerization of linear polymers. Also, the thickness of the hydrogel films can be controlled by varying the exposure to laser irradiation or the composition and concentrations of the precursor solution.

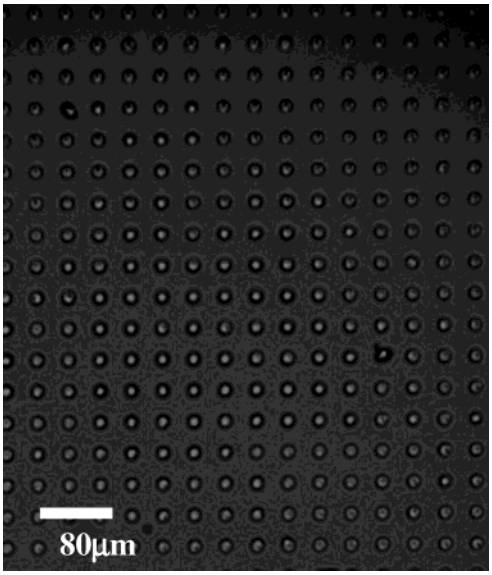

Figure 6. Optical microscope image of patterned hydrogel microstructures on a glass surface. These were created by forming an eosin pattern on a glass surface using μCP followed by photopolymerization of a hydrogel precursor mixture (see text) using the 514 nm line of an argon laser.

2-D Patterning of PEG hydrogels. Defined regions of an APTES surface were reacted with eosin using μCP. This surface was then exposed to the hydrogel precursors and exposed to 514 nm light in order to produce hydrogel films on the regions derivatized with eosin. Figure 6 displays the image of the patterned hydrogel microstructures. It is evident from the figure that the surface was successfully functionalized by patterned eosin, and this in turn resulted in the formation of patterned hydrogel regions that are attached to the substrate surface. Light areas in the figure are the regions where hydrogel formed. This micrograph also indicates that the hydrogels attach in such way that, even if they were adherent to only a few

(24) Ista, L. K.; Mendez, S.; Pérez-Luna, V. H.; López, G. P. *Langmuir* **2001**, *17*, 2552.

spots on the surface, the length scale between these contact points is smaller than 10 μm.

This technique also offers the potential for creating hydrogel microstructures of various geometries by illuminating through a photomask placed on top of the precursor solution. The latter could be used to produce an array of hydrogels with varying properties on the same surface in noncontact mode.

Conclusion

We have described the photopolymerization of PEG diacrylate on eosin-modified surfaces and generated hydrogel patterns on glass and silicon surfaces. The hydrogels formed on the modified surfaces did not delaminate from the surface even upon hydration for more than a year. This attachment suggests that the gel becomes covalently bonded to the surface during photopolymerization. The simplicity of this technique provides potential for use in biotechnology applications. The mild photopolymerization conditions that can be carried out at 514 nm may be advantageous over methods that use UV light. The advantages of mild photopolymerization conditions are elimination of cytotoxicity and loss of functionality (e.g., when living cells are encapsulated with hydrogels). The method is amenable for 2-D patterning of hydrogels in aqueous solution, thus it can be implemented to pattern proteins in situ not only with μCP technique but also with noncontact photopatterning. Such surfaces could be useful to control shape, morphology, and function of mammalian cells through localization of cells into patterns or arrays or for biosensing applications. Gel attachment to the surface can be utilized to determine the swelling behavior of photopolymerized thin hydrogel films by measuring the height increase of the swollen hydrogel that will allow for determination of cross-link density.[9,10] Since the photopolymerization reaction occurs very rapidly, it is possible to study the earlier events in hydrogel formation at limited exposure times, within miliseconds or microseconds. Also, in this regard, we have developed a mathematical model capable of simulating the progress of polymerization and film formation for this system; results from this effort will be reported elsewhere. The simplicity of the technique presented here provides potential for a multitude of applications.

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