Chem. Mater. **2009,** *21,* 399–403

Thin Hydrogel Films With Nanoconfined Surface Reactivity by Photoinitiated Chemical Vapor Deposition

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Received October 8, 2008. Revised Manuscript Received November 25, 2008

Several property requirements have led to the modification of hydrogels by incorporating functional groups. The current work seeks to achieve graded functional group incorporation into hydrogel thin films using the one-step technique of photoinitiated CVD (piCVD). The functional group pentafluorophenylmethacrylate (PFM) is copolymerized with hydroxyethyl methacrylate (HEMA). Because PFM reacts easily with amine groups, the incorporation of PFM results in a platform for subsequent functionalization. The graded copolymer confines the PFM to the near surface region (~20 nm) allowing the control of the hydrogel film properties independently of the surface reactivity. Although homogeneous incorporation of PFM in the hydrogel matrix inhibits swelling, the swollen water content of pure pHEMA is nearly preserved in the graded copolymer. FTIR spectroscopy shows that the absorption peaks corresponding to the fluorinated phenyl ring in the graded copolymer disappear after functionalization with O,O-bis (2-aminoethyl) polyethylene (PEG-diamine), suggesting a nearly complete conversion of the PFM bonds.

Introduction

Hydrogels are polymer networks that have the capability of absorbing large amounts of water without dissolving.[1,2] Some hydrogels are able to achieve similar water content to human tissue and exhibit excellent biocompatibility, and as a result, have gained strong acceptance in bioengineering.[3,4] Hydrogels have been modified by many available chemistries and techniques to incorporate functional groups.[5−11] Kawaguchi et al. investigated active esters in quaterpolymer microspheres that were allowed to undergo hydrolysis or aminolysis.[12] Functionalized dextrans were studied by Maire and co-workers for bearing coboxylate, benzylamide and sulfate groups, which exhibit binding capacity.[13] Such functionalized hydrogels have been used for varied applications such as targeted cell adhesion,[14−16] selective functional protein binding,[11,17,18] and drug delivery carriers.[5]

Because of the limited ability of large molecules such as proteins or other biologically relevant ligands to diffuse into polymers, functional groups at the surface react most readily. Unreacted functional groups within a hydrogel matrix are problematic because they can negatively impact bulk properties and generate undesired reactions, particularly over long time scales.[19] Thus, some groups have centered their attention on changing only the near-surface properties of hydrogel films. Burnham et al. presented a method for creating a surface-patterned streptavidin-conjugated polyacrylamide hydrogel that can be used to generate biofunctionalized templates.[20] The penetration depth of the streptavidin was 4 μm, which was approximately one-quarter of the thickness of the film, and fewer than 2% of the binding sites were successfully utilized. Zhu et al. grafted carboxyl groups onto polycaprolactone membranes surface under UV light to create surfaces functionalizable via carbodiimidization chemistry.[21] Hu and co-workers presented a procedure to covalently link polymers to the surface of poly(dimethylsiloxane) by ultra-

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10.1021/cm802737m CCC: $40.75

violet graft polymerization.[22] Each of these processes requires two steps: one to create the bulk material and a second to introduce the desired functionality onto the surface.

The current work seeks to achieve both homogeneous and graded functional group incorporation into hydrogel thin films using the one-step technique of photoinitiated CVD (piCVD). Previously, piCVD was demonstrated as a means of systematically controlling the cross-link density of hydrogels deposited from hydroxyethylmethacrylate (HEMA) and the resultant the degree of swelling.[23] Here, the functional comonomer pentafluorophenylmethacrylate (PFM) is copolymerized with HEMA. The solubility contrast of the hydrophilic HEMA monomer and the hydrophobic PFM monomer makes this copolymer difficult to achieve via solution phase techniques. Previous work demonstrated that the PFM group can be successfully incorporated into films by plasma enhanced CVD[24] and initiated CVD.[25] Because the ester group of PFM reacts easily with amine groups,[17] the incorporation of PFM results in a platform for subsequent functionalization with a multitude of amine containing compounds.

Although pentafluorophenylesters have been widely used to create functional surfaces, the piCVD technique is, to the best of our knowledge, the first one-step process to create surface functional groups without requiring any modification of the substrate surface. Chilkoti and co-workers reported MAPS, a multistep solvent-based procedure to modify polymer surfaces with functional pentafluorophenyl esters at the surface.[26,27] However, this process requires the underlying polymer layer to undergo an overnight carboxylation step involving a number of corrosive or toxic reagents. Such reagents may not be compatible with biologically relevant substrates, such as sensors or tissue scaffolds, or may be of potential concern for materials destined for physiological implantation.

Polymer CVD techniques are compatible with any substrate not affected by reduced pressure and can coat fragile substrates such as sensors[23] and complex geometries such as particles[23,28] or trenches.[29] Paracyclophanes functionalized with pentafluorophenyl esters have been deposited previously by CVD.[30,31] However, the nanoconfinement of these functional groups to the near-surface area via a graded copolymerization has not yet been demonstrated.

Because piCVD is a vapor phase process involving the continuous flow of reactant gases, the introduction and distribution of functional groups can be controlled simply by varying the composition of the incoming feed gas. As the growth rate of films is monitored in situ by interferometry, we are also able to demonstrate nanoscale control over the incorporation of the functional groups throughout the depth of the film.

Hydrogels with homogeneous incorporation of functional groups, here termed homogeneous copolymers, are synthesized by maintaining constant flow rates of both HEMA and PFM throughout the course of the deposition. The strategy for achieving graded layers in which PFM is confined to the near surface region (~20 nm) is to flow the PFM monomer into the CVD reactor only during the final period of growth. The continuity in growth with the first pure HEMA layer creates a gradient in functional group incorporation without the need for physically stacking chemically dissimilar layers. Because the pure HEMA layer does not need to be chemically modified in order to incorporate the functional groups, no lengthy carboxylation step is required, and the total deposition time for the entire structure is approximately 15 min.

We directly compare the homogeneous copolymer, the graded copolymer, and the pure HEMA films, providing insight into the importance of functional group distribution on reactivity and properties. Graded functional layers via piCVD offer several potential benefits. First is the ability to independently control bulk film properties, like swellability and modulus, and surface reactivity. Here, we show that the swellability of a hydrogel can be maintained by incorporating the functional comonomer only within the near-surface region. Second is the elimination of functional groups in the bulk of the film which have limited ability to react yet can degrade bulk film properties. In this study, the reactivity of the both the homogeneous and the graded films with PEG-diamine is monitored by Fourier transform infrared (FTIR) spectroscopy. Finally, the graded films enable reduced usage of the expensive functional monomer.

Experimental Section

Hydrogel Preparation. The piCVD process and reactor have been described in detail previously.[23] All samples were deposited on silicon wafers (Waferworld) maintained at 30 °C through backside coolant circulation. PFM (95%, Monomer Polymer) and HEMA (99%+, Sigma Aldrich) monomers were utilized without further purification. HEMA was heated to 80 °C in a temperature-controlled crucible and its vapors were metered into the reactor through a mass flow controller (MKS, 1152). The flow rate of PFM, which was heated to 60 °C in a separate crucible, was also metered with a mass flow controller. No separate photoinitiator was used. A throttling butterfly valve (MKS, 653B) was used to control the pressure inside the chamber. The film growth was initiated by exposing the substrate to 50 μW/cm^2 ultraviolet light of 254 nm wavelength. Film growth was observed in situ through interferometry and used to obtain the desired film thickness.

Two types of films were deposited in this work: homogeneous copolymers and graded copolymers. For the homogeneous copolymers, both monomers, HEMA and PFM, were introduced into the reactor simultaneously during the polymerization. The HEMA flow rate was held constant for all the homogeneous copolymer depositions, while the PFM flow rate was systematically varied between

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Table 1. Experimental Conditions for the Copolymer Synthesis[a]

samples	HEMA flowrate (sccm)	PFM flowrate (sccm)	P_{total} (mTorr)	molar composition (% PFM)
H0 and G0	2.0	0.0	100	0
H1 and G1	2.0	1.0	150	33
H2 and G2	2.0	3.0	250	60
H3 and G3	2.0	5.0	350	71

[a] For the homogeneous films (series H), all the indicated flowrates were used throughout the deposition. For the graded films (series G), no PFM is used at the start of the deposition.

samples. The reactor pressure was varied for each deposition to maintain the HEMA partial pressure at 100 mTorr. Film growth was terminated at approximately 115 nm. For the graded copolymer, HEMA was initially introduced into the reactor and the polymerization proceeded until approximately 90 nm of film was deposited. Then, PFM was introduced into the feed gas while remaining constant the HEMA flow and the copolymer was deposited for an additional 25 nm of film deposition. The flow rates and pressures for both the homogeneous and graded copolymers are summarized in Table 1. It should be noted that although the copolymer composition is controlled by changing the feed gas composition, these values are not equal. This is because piCVD is a surface reaction,[23] and the monomers will be present on the substrate as adsorbed species as a function of their individual volatilities. In this paper, we report the composition of the feed gas unless otherwise noted.

Film Characterization. FTIR spectroscopy was carried out on a Nicolet Nexus 870 in normal transmission mode equipped with a MCT detector and KBr beamsplitter. Spectra were acquired over the range of 400−4000 cm^{-1} with a 4 cm^{-1} resolution for 256 scans. To allow for accurate comparison, all spectra were thickness normalized and baseline corrected; no other processing was performed.

The TOF-SIMS analysis reported here were performed on a ToF-SIMS type ION-TOF IV instrument, equipped with Bi polyatomic primary ion source, a Cs/electron impact dual source column (DSC), and a low-energy electron flood gun (for charge compensation of insulating samples). The incidence angle of both the Bi and Cs ion sources was 45°. Sputter etching of the surface was accomplished with a beam of 500 eV Cs+ ions (with a target current of 30 nA) rastered over a 400 mm × 400 mm area. A pulsed beam of 25 keV Bi3++ ions, scanned over a 100 mm × 100 mm region centered within the sputtered area, was used to generate secondary ions for analysis in negative ion mode. A high current beam of low energy (<20 eV) electrons was employed for charge compensation. Mass resolution (m/Dm) was higher than 5000 and full spectra from 1 to 800 amu were acquired for all depths profiles. The signals are plotted once they are completely stabilized; the initial period is due to a transient effect until a sputtering steady state is reached. The surface oxidation also contributes to this effect modifying the ionization at the first film nm.

Dry and swollen film thicknesses were measured via spectroscopic ellipsometry (M-2000, J.A. Woollam). All data were collected at a 75° incident angle for 220 wavelengths between 313 and 718 nm and fit to a Cauchy-Urbach isotropic model to obtain the thickness. First, the dry film thickness was determined. Then, the samples were then mounted in a liquid cell and immersed in pH 7.4 buffer. Data were collected 1, 3, 5, 7, and 10 min; for all films, the equilibrium swollen thickness was reached after 5 min. The swollen water content was determined by dividing the increase in film thickness by the total thickness of the swollen film. The procedure was repeated to test the stability of the polymer films and reversibility of the swelling response. The measurements were obtained again after having rinsed the films in deionized water and dried them overnight in a vacuum oven.

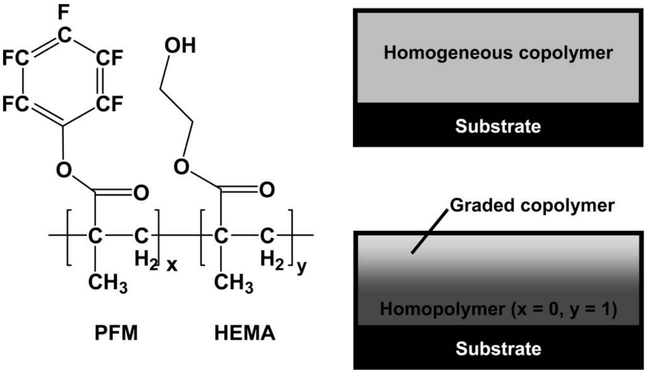

Figure 1. Schematic of the chemical composition (left) and physical structure of the homogeneous (top right) and graded (bottom right) copolymer films.

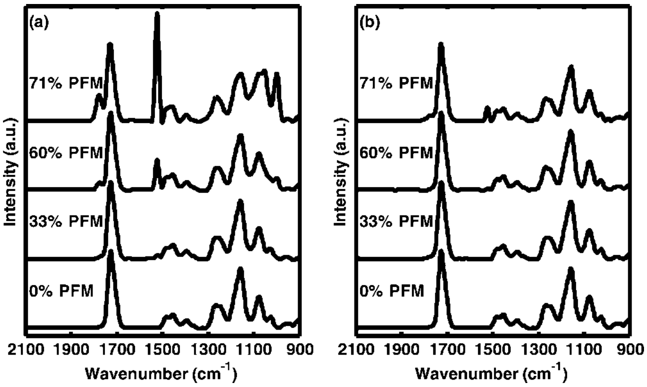

Figure 2. FTIR spectra of three copolymer compositions for (a) homogeneous copolymers and (b) graded copolymers, along with the spectra for pure pHEMA. The composition refers to gas phase molar composition during piCVD synthesis.

Sample Modification. Functionalization of the samples was performed with a 0.05 M solution of O,O-bis (2-aminoethyl) polyethyleneglycol (PEG-diamine) (Sigma Aldrich) in ethanol (100%, VWR). The hydrogels were immersed in the solution and maintained at 30 °C for 1 h. The sample then was rinsed with ethanol to remove any unreacted ligand and dried with room temperature nitrogen and analyzed by FTIR.

Results and Discussions

FTIR Characterization. Figure 2 compares the FTIR spectra of three homogeneous copolymers of varying compositions to three graded copolymers of the same near-surface composition. A pHEMA film synthesized with piCVD is shown for reference. The labeled mole percentages of HEMA and PFM represent the gas phase composition. In most cases, the film composition will be different, reflecting the differences in the volatility of the two monomers and their reactivity ratios.[32] The spectrum of the pure HEMA contains three main vibrational modes.[33] The most intense of these peaks is centered at ~1725 cm^{-1} and signifies the C═O stretching. The C−H bending appears in its normal range of 1500−1350 cm^{-1}. The peak centered at ~1260 cm^{-1} signifies the stretching vibrational mode of C−O. The presence of PFM is indicated by three main absorption

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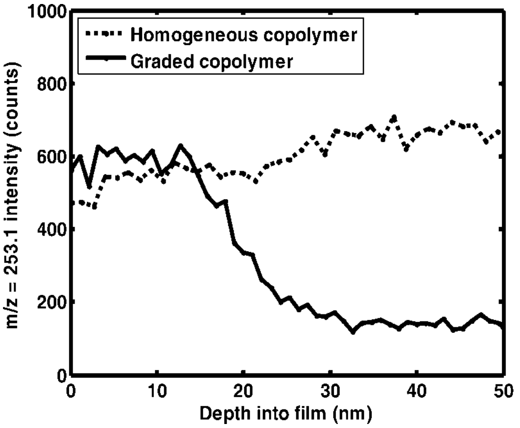

Figure 3. ToF-SIMS depth profile showing signal from *m/z* = 253.1, corresponding to a positively charged PFM fragment, as a function of film depth for both the homogeneous and graded copolymer (samples H3 and G3, respectively).

bands.[34] The narrow, weak peak that appears at 1774 cm^{-1} can be associated with the retention of the carbonyl group from the active ester. The fluorinated phenyl ring is expressed at 1522 cm^{-1} as a sharp peak with a high intensity. The C−F vibrations are also present at 1000 cm^{-1}. The PFM peaks in the FTIR spectra for the homogeneous copolymer are clearly expressed for all the ratios. There is a lower signal from the PFM peaks in the graded copolymer than in the homogeneous copolymer because it is only present near the surface of the film, as opposed to the homogeneous copolymer that has PFM incorporated throughout the hydrogel matrix.

Depth Profiles. Depth profiles of positive ion ToF-SIMS spectra confirmed the film structure of the homogeneous and graded copolymers. Figure 3 shows the intensity at *m/z* = 253.1, which corresponds to the charged PFM monomer fragment,[35] as a function of film depth for both the homogeneous and graded copolymers. The copolymer shows a relatively constant PFM content throughout the film depth. The graded copolymer shows PFM present in the first 20 nm of film, confirming that the functionality in the graded copolymer is nanoconfined to the near surface region. This is consistent with the fact that PFM was introduced only in the final stages of the deposition. The surface PFM content (at zero depth) is comparable to that in the homogeneous copolymer, indicating that both have a similar density of functional groups at the surface. However, the functionality in the graded copolymer is nanoconfined to the near-surface region. Positive ion ToF-SIMS spectra confirming retention of the PFM structure are available as Supporting Information.

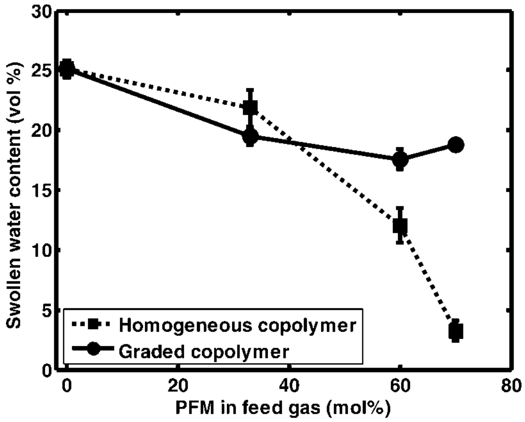

Figure 4. Swollen water content as a function of the increasing PFM content for both the homogeneous and graded copolymer.

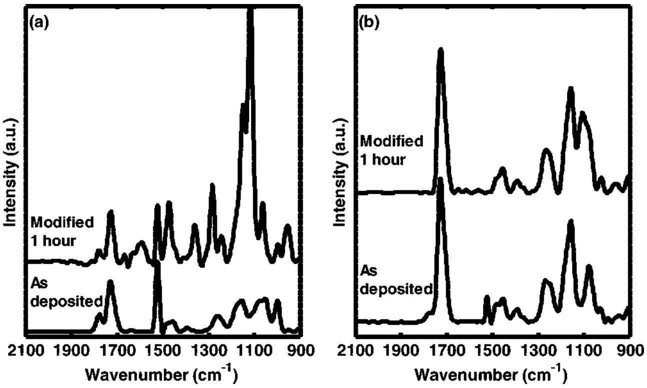

Figure 5. FTIR spectra of the copolymer synthesized by piCVD before and after the functionalization with H2N-PEG-NH2. (a) Homogeneous copolymer (sample H3); (b) graded copolymer (sample G3).

Degree of Swelling and Water Content. The ability to swell defines the nature and function of a hydrogel. Consequently, retaining its swelling properties while incorporating surface-active components is extremely important. Figure 4 displays the swollen water content for the homogeneous and graded copolymers for different degrees of PFM incorporation. It can be seen that with an increasing PFM content, the swollen water content decreases from 20% (pure pHEMA) to 3% (71% PFM). The homogeneous copolymer does not retain the swelling properties of the HEMA because of the hydrophobicity of PFM. However, for the graded copolymers, the swollen water content of pure pHEMA is mainly preserved even with increasing PFM content. These results suggest that physical swelling properties of a hydrogel can largely be maintained even after incorporating an ultrathin copolymeric layer. This decouples the underlying physical properties of the hydrogel from the chemical properties of the surface activity, allowing these two properties to be chosen independently.

Hydrogel Functionalization. The pentafluorophenyl ester moiety functionalizing the polymer surface easily reacts with amine groups. During the reaction, the pentafluorophenyl group is replaced by an amide bond.[17] This reactivity allows the functionalization of the hydrogel by any nucleophilic agent in a single-step reaction. Figure 5a shows the spectra of the homogeneous copolymer and Figure 5b shows the spectra of the graded copolymer before and after functionalization with PEG-diamine for 1 h.

After functionalization, a peak is expected to appear at 1107 cm^{-1}, a strong and a wide peak attributed to the C−O vibration of the PEG. In both the functionalized homogeneous and graded copolymers, PEG functionalization is confirmed by the presence of this peak in the FTIR spectra. There is far more PFM in the homogeneous copolymer so, as expected, there is far more PEG attached to the homo-

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geneous copolymer. However, the absorption peaks corresponding to the fluorinated phenyl ring only disappear completely in the case of the graded copolymer. This suggests that the functionalized homogeneous copolymer contains a significant fraction of unreacted PFM that can be susceptible to undesired subsequent reactions with nucleophiles. Unlike the homogeneous copolymers, the graded copolymer provides a nearly complete conversion of the PFM bonds. This phenomenon can be explained by the inability of the reactive amines to diffuse through the film. This could be especially important if the films are functionalized with large biomacromolecules, such as proteins. From this perspective, it is desirable to nanoconfine the PFM on the surface as in the graded copolymers to ensure its complete reaction.

Conclusions

This work has demonstrated that both homogeneous and graded copolymers can be successfully deposited by piCVD. FTIR and ToF-SIMS analyses confirm that the reactive pentafluorphenyl ester group (PFM) remains intact after the photopolymerization, allowing for the formation of thin films capable of postfunctionalization with primary amines. The distribution of PFM within the film depth has also been confirmed. In the graded copolymer films, the PFM signals in both XPS and ToF-SIMS decrease from a maximum at the top surface, confirming the nanoconfinement of the reactive moiety to the near-surface region. Because the piCVD process involves real-time tracking of film thickness, the compositional distribution can, in principle, be chosen arbitrarily.

For the graded polymer, the PFM is introduced into the feed gas only during the final ~20 nm of film deposition, thereby confining the functionality only to the near-surface region. In addition to reducing quantity of expensive functionalized monomer, there are two primary materials property benefits to this near-surface confinement. First, the hydrogel properties of the bulk region of graded copolymers are largely maintained. This is especially important when compared to the homogeneous copolymers, which exhibit markedly worse swelling properties than the graded copolymers. For the graded films, the underlying properties of the homopolymer can be chosen independently from the properties of the surface activity. Second, nearly all the PFM moieties in the graded copolymer are available for reaction. In the homogeneous copolymer, much of the PFM is occluded within the polymer matrix, resulting in low conversion of this functionality due to steric hindrance. It should be noted that any vinyl comonomer capable of being introduced into the reactor as a vapor can be used to form the graded functional film. Moreover, because the film thickness is monitored by in situ interferometry, it is in principle possible to create a copolymeric layer of controlled thickness, a feature not afforded by traditional solution methods. Future work will focus on engineering the thickness of the copolymeric layer based on the size of the ligand used in subsequent functionalizations.

Acknowledgment. The authors thank the Generalitat de Catalunya for the Research Consolidated Group grant: SGR-2005 to Grup d'Enginyeria de Materials (GEMAT), the Draper Laboratoires UiRAD, and the National Defense Science and Engineering Graduate Fellowship for providing funds to support this research. The authors are grateful for the assistance of Dr. Raúl Perez from the Nanotechnology Platform from the Parc Científic de Barcelona, Universitat de Barcelona, for performing the ToF-SIMS experiments.

Supporting Information Available: Positive ion ToF-SIMS spectra confirming retention of the PFM structure for both the homogeneous and graded copolymers (PDF). This material is available free of charge via the Internet from http://pubs.acs.org.

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