Modification of Poly(lactic acid) Films: Enhanced Wettability from Surface-Confined Photografting and Increased Degradation Rate Due to an Artifact of the Photografting Process

Amol V. Janorkar, Andrew T. Metters, and Douglas E. Hirt*

Department of Chemical Engineering and Center for Advanced Engineering Fibers & Films, Clemson University, Clemson, South Carolina 29634-0909

Received May 13, 2004; Revised Manuscript Received August 24, 2004

ABSTRACT: The major objective of this research was to modify PLA film surfaces with the ultimate aim of making a bioactive surface that will show faster degradation. The PLA film was solvent-cast, and the film surfaces were grafted with poly(acrylic acid) (PAA) and poly(acrylamide) (PAAm) using a UV-induced photopolymerization process. The film surface resulting from each reaction step was analyzed using ATR−FTIR spectroscopy and contact angle measurements. Results showed that PAA was grafted from PLA film surfaces in 2 or 3 h, while PAAm was grafted in 3 or 5 h depending on the method of activation. Films grafted with PAA and PAAm exhibited improved wettability. The neat and surface-modified films were incubated in different pH solutions, viz., pH = 4, 7, and 10, for specified time periods. The films resulting from each treatment were analyzed using atomic force microscopy (AFM). The molecular weights of the incubated films were measured using chloroform-based GPC. Results established that faster degradation of the PLA film when incubated in different pH solutions was achieved for PLA-*g*-PAA films; however, control studies revealed that the major contribution to the observed degradation was due to the entangled PAA chains resulting from acrylic acid monomer that migrated into the film bulk and not due to the surface-grafted layers.

Introduction

Poly(L-lactic acid) (PLA) is a biodegradable and bioabsorbable polyester with favorable biocompatibility and has been used as a bioabsorbable material in the medical and pharmaceutical fields. When implanted in living organisms, including the human body, PLA is hydrolyzed to its constituent α-hydroxy acid, which is then eliminated through general metabolic pathways.[1] Cargill Dow LLC produces PLA commercially by converting corn starch into lactic acid, which is then polymerized. Unlike other synthetic fiber materials with vegetable sources (e.g., cellulosics), PLA is well-suited for melt-spinning into fibers.[2,3] PLA sheets can also be prepared using a melt extrusion process.[4] However, the surface properties of PLA are not easily altered because it is a highly crystalline polyester with no chemically modifiable side-chain groups, limiting its use in many applications. In addition, the degradation of PLA is slow, often leading to a long lifetime in vivo. In some cases, a second operation has been required almost 3 years after implantation to remove a PLA-based implant.[5] Surface modification of PLA has the potential to expand the market for PLA into many more application areas. The major objective of this research was to modify PLA film surfaces by grafting hydrophilic polymers from the surface with an ultimate aim of making the surface bioactive while at the same time enhancing the degradation rate of the bulk polymer.

Researchers have used a variety of experimental techniques to introduce a desired chemical functionality in PLA. Kimura et al. synthesized a copolymer of glycolic acid and malic acid to give a carboxyl-functionalized poly(α-hydroxy acid) having a backbone similar to that of PLA.[1] To introduce reactive groups and lower the crystallinity, Ouchi et al. synthesized random and block copolymers of lactic acid and depsipeptides.[6] However, this strategy for PLA bulk modification may be problematic because it alters the molecular weight of PLA, often results in poor yields, introduces limited densities of the functional groups, requires synthesis of a new polymer type, and influences the bulk properties relative to neat PLA. Irvine et al. explored the use of surface segregation to modify the surface of polylactide-based devices by blending poly(methyl methacrylate-*random*-polyoxyethylene methacrylate) comb polymers with PLA.[7] The comb polymers were premodified with RGD peptides to create nanoscale ligand clusters to control cell responses. However, the comb polymers and the polylactide used had similar molecular weights (M_w ∼ 100 000), which may result in undesirable bulk properties. Cai et al. explored the surface modification of a PLA film with chitosan to improve its cell affinity. In their study, carboxyl (−COOH) groups were created on a PLA film surface by placing the film in a 1 M NaOH solution at 50 °C for 1 h.[8] These carboxyl groups were then activated using a water-soluble carbodiimide and later reacted with chitosan. However, placing a PLA film in a basic solution at an elevated temperature could catalyze the degradation of the film during the modification process itself. Our aim in this research was to surface modify PLA film without using migratory additives or copolymer variants of PLA. Our modification method involved the use of photopolymerization.

Photoinduced grafting is a useful technique well-known for its advantages: low cost of operation, mild reaction conditions, selectivity of UV light absorption without affecting the bulk polymer, and permanent alteration of the surface chemistry.[9] Photoinduced grafting of acrylic acid and its subsequent polymerization have been used extensively in the past.[9−13] Ma et al. used a sequential two-step photoinduced living graft

* Corresponding author: e-mail hirtd@clemson.edu.

10.1021/ma049056u CCC: $27.50
Published on Web 10/26/2004

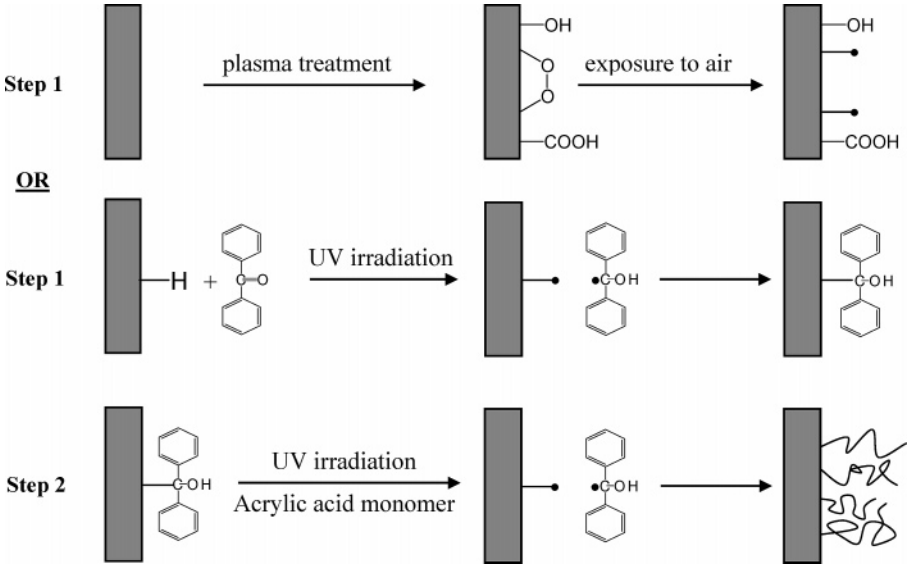

Figure 1. Reaction scheme for the photoinduced graft polymerization of acrylic acid onto a polymer film surface [benzophenone grafting route adapted from ref 9].

polymerization method to modify commercial porous polypropylene microfiltration membranes.[9] As shown in Figure 1, benzophenone abstracted hydrogen from the substrate to generate surface radicals and semipinacol radicals, which combine to form surface initiators in the absence of monomer solutions. These unique surface initiators remained photolabile under the UV irradiation. Subsequently, when the acrylic acid solution was added onto the active substrate, the graft polymerization was initiated under the same UV irradiation conditions used in the first step. A similar procedure was followed to obtain surface modification of the PLA film reported here. Figure 1 shows a schematic of the reaction procedure. For comparison, PLA films were activated using a plasma treatment procedure and subsequently subjected to photoinduced grafting of acrylic acid, as followed by Steffens et al.[14] PAAm was grafted by duplicating the procedures used for PAA grafting.

PLA degrades through hydrolysis of the backbone ester groups, and this hydrolysis is thought to be autocatalyzed by the polymer carboxylic acid end groups.[15] The degradation rate can be affected by many factors due to the complexity of the solid−liquid reaction system. These factors include polymer chemical structure, molecular weight, molecular weight distribution, morphology, water diffusion rate into the polymer, and water content in the polymer. The polymer degradation rate is determined mainly by polymer reactivity with water and accessibility of the ester groups to water and catalysts, i.e., carboxylic acid end groups. In addition, the degradation of the polyesters is accelerated by temperature and protons present in the solution.[15,16] Because of the vital importance of the degradation characteristics of a biomaterial, the degradation behavior of PLA and its copolymers has been widely studied. As PLA degradation can be acid or base catalyzed, the mechanism of degradation has been studied by placing the specimens in various buffer solutions (pH = 2−10) for several weeks.[15−20] Most of these degradation studies focused on PLA degradation at elevated temperatures (30−60 °C). Apart from its application as a biomaterial, PLA has also been used for agricultural mulch films and disposable thermoplastic products.[21] Degradation of PLA mulch films in well-characterized biotic and abiotic environments has been investigated.[22] Researchers have also studied PLA degradation by enzymes and microbes.[23−25] We studied the degradation of neat, surface-modified, and several "control" PLA films in buffer solutions with pH = 4, 7, and 10 at room temperature for a relatively short incubation period (up to 4 weeks).

Poly(acrylic acid) (PAA) and poly(acrylamide) (PAAm) were selected for the surface grafting because of their high water absorbent properties. Grafting such hydrophilic polymers is hypothesized to enhance the water content in the PLA film, which could potentially accelerate PLA degradation. In addition, PAA should provide a very large number of carboxylic acid groups that may lead to a faster degradation of PLA. Thus, an aim of this research was to study the degradation of neat vs surface-modified PLA films and to assess the enhancement in the degradation, if any, due to the carboxylic acid groups (in the case of PLA-*g*-PAA) vs the neutral amide groups (as with PLA-*g*-PAAm).

Experimental Section

Materials. PLA pellets were supplied by Cargill Dow LLC. Acrylic acid (99.5% w/w) was obtained from Acros Organics. Acrylamide (99% w/w) was obtained from Aldrich Chemicals. Benzophenone and H_2O_2 (30% w/w) were obtained from Fisher Scientific, and methylene chloride (CH_2Cl_2) was purchased from Aldrich Chemicals. All chemicals were used as received. Solutions with pH = 4 (biphthalate buffer), pH = 7 (borate buffer), and pH = 10 (phosphate buffer) were obtained from J.T. Baker.

Experimental Procedures. *Preparation of PLA Films.* The PLA films were solvent-cast in a glass Petri dish. The Petri dish was cleaned by exposing it to a solution of concentrated H_2SO_4 and 30% H_2O_2 (70:30 v/v) for 45 min. This piranha solution was handled with extreme care, as it reacts violently with most organic materials. The Petri dish was then rinsed with copious amounts of distilled water and dried with a stream of nitrogen. PLA pellets (approximately 1.1 g) were dissolved in 90 mL of CH_2Cl_2, and the solution was then poured into the cleaned Petri dish. The Petri dish was aligned to a horizontal position to facilitate formation of a cast film with uniform thickness. The assembly was kept in a chemical hood for 24 h, and CH_2Cl_2 was allowed to evaporate at a very slow rate. The film was removed from the dish using a razor blade. The nominal thickness of PLA film formed by this procedure was 125 μm (~5 mil).

Activation of PLA Films. The PLA film surface was activated by plasma treatment in air for 2 min using a Harrick Scientific Co. (model PDC-320G) plasma cleaner/sterilizer. The "high energy" setting available on the machine (~18 W) was used. A radio frequency of 10.5 MHz and vessel pressure of ~0.3−0.5 Torr were maintained during the treatment procedure. The plasma-treated PLA films were stored at atmospheric conditions for 30 min before subjecting them to the photografting of acrylic acid or acrylamide (see Figure 1).

Photoinduced Grafting of Benzophenone onto PLA Film Surfaces. A PLA film specimen (approximately 0.5 cm × 3 cm) was dip-coated in a 5% w/w solution of benzophenone in ethanol. The specimen was allowed to stand at room temperature for 30 min to ensure evaporation of ethanol. The film was then carefully transferred to a quartz cuvette in a nitrogen glovebox. UV irradiation of the film was performed for 10 min in a UV processor (model no. 60000; Oriel Corp.). The processor was equipped with a 100 W mercury arc lamp (model no. 8261; Oriel Corp.) having a wavelength range of 232−500 nm and intensity of ~25 mW/cm^2 at 365 nm. After irradiation, the substrate was removed from the quartz cuvette, sonicated in ethanol for 5 min to remove any unreacted benzophenone, and then dried at room temperature. A control film was prepared by the same procedure without the benzophenone.

Photoinduced Graft Polymerization of Acrylic Acid (or Acrylamide) from PLA Film Surfaces. The benzophenone grafted PLA film was put in a Pyrex test tube containing 10% v/v acrylic acid (or acrylamide) solution in ethanol, purged with nitrogen, and then exposed to the UV irradiation for a specified time. The Pyrex test tube used in the photopolymerization step prevented all wavelengths below 300 nm from reaching the samples. After irradiation, the substrate was sonicated in ethanol for 5 min to remove any unreacted acrylic acid (or acrylamide) and dried at room temperature for 24 h. A control film was prepared following the same procedure without the acrylic acid (or acrylamide). The resulting film was analyzed by ATR−FTIR and contact angle goniometry. Sonication of the control and grafted films in ethanol for more than 5 min did not affect the ATR−FTIR and contact angle goniometry results.

Degradation of Neat and Surface-Modified PLA Films. Films were incubated in buffer solutions with pH = 4, 7, and 10 for a specified time. The films were subsequently analyzed using AFM and GPC.

Analytical Techniques. *ATR−FTIR Spectroscopy.* Attenuated total reflectance (ATR) FTIR spectroscopy was used to monitor the grafting reactions on a film surface. ATR uses an evanescent field, which decays exponentially into the film, so the absorbance spectrum corresponds to a penetration depth that depends on the wavelength, angle of incidence, and the refractive indices of the sample and crystal.[26] The variables used in the experiments gave a penetration depth of approximately 0.4 μm. A Nicolet Avatar 360 with a horizontal, multibounce ATR attachment was used to conduct the experiments. The peak at wavenumber 1720 cm^{-1} corresponding to the −C═O stretches in the carboxylic acid of PAA, the peak at wavenumber 1661 cm^{-1} corresponding to the −C═O stretches in the amide functionality of PAAm, and the peak at wavenumber 1756 cm^{-1} corresponding to the −C═O stretching vibrations in PLA were used for characterization. Results will be reported as peak area ratio (PAR), e.g., peak area at 1720 cm^{-1} divided by the peak area at 1756 cm^{-1}. Graphical software (ORIGIN) was used to deconvolute peaks at 1720 and 1756 cm^{-1} in the case of PLA grafted with PAA and at 1661 and 1756 cm^{-1} in the case of PLA grafted with PAAm using limits for the area integration of 1500−1900 cm^{-1}. The reported PAR values are an average of at least three measurements with ±95% confidence intervals.

Contact Angle Goniometry. Contact angle measurements were performed on a Kruss G10 static contact angle apparatus. The data were analyzed by calculating the water contact angles using the sessile drop method. The reported contact angle values are an average of 10 readings with ±95% confidence intervals.

Table 1. Design of Experiments for Photografting from PLA Film Surface

	step 1		
expt no.	plasma treatment	benzophenone grafting	step 2 monomer
1	yes	yes	no[a]
2	no	no	yes
3	yes	no	yes
4	no	yes	yes

[a] Pure ethanol was used instead of 10% monomer solution in these experiments.

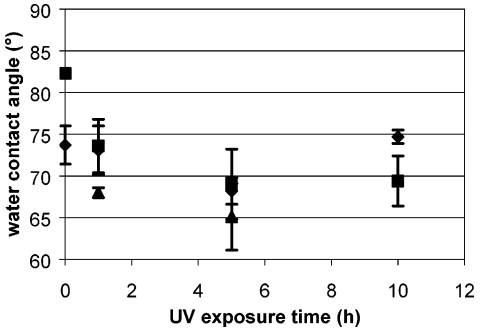

Figure 2. Effect of UV exposure time on water contact angle of the (◆) PLA film activated with plasma treatment, grafted with benzophenone, and exposed to UV irradiation in ethanol without acrylic acid monomer, (■) PLA film exposed to UV irradiation in 10% v/v acrylic acid solution in ethanol without plasma treatment and benzophenone grafting, and (▲) PLA film exposed to UV irradiation for various times in 10% v/v acrylamide solution in ethanol without plasma treatment and benzophenone grafting. The error bars represent 95% confidence intervals.

Gel Permeation Chromatography (GPC). The molecular weight of neat and surface-modified PLA films after incubation in buffer solutions was measured using a Waters Associates separation module (model 2695). The system was equipped with two consecutive Polymer Labs PLGel 5 μm Mixed-D and Mixed-E columns and a Waters Associates 2410 refractive index detector set at 35 °C. A sample of 5−10 mg was dissolved in an appropriate volume of chloroform to achieve a nominal concentration of 2 mg/mL. Chloroform was used as eluent at a flow rate of 1 mL/min. The molecular weights were calculated using the calibration data of polystyrene standards of narrow molecular weight distribution (Polysciences, Inc., M_w range ~580−377400 Da).

Atomic Force Microscopy (AFM). Atomic force microscopy (AFM) images were obtained using a Digital Instruments NanoScope IIIa in the tapping mode.

Results and Discussion

Grafting Studies. Table 1 shows the various experiments designed to compare the photografting induced via benzophenone grafting, which is a specific chemical reaction, with photografting induced by a nonspecific plasma activation process. Figure 2 shows results of the "control experiments" for photografting of PAA, namely, experiment 1 in which both the plasma treatment and benzophenone grafting were used without subsequent acrylic acid grafting and experiment 2 in which acrylic acid grafting was attempted without step 1. The neat PLA film had a water contact angle of 82 ± 1°. The contact angle of the initially unmodified PLA film was only slightly reduced in either experiment (shown by diamonds (experiment 1) and squares (experiment 2) in Figure 2). These results established that the absence of either one of the two steps in Figure 1 yielded a water contact angle much greater than that expected for a film

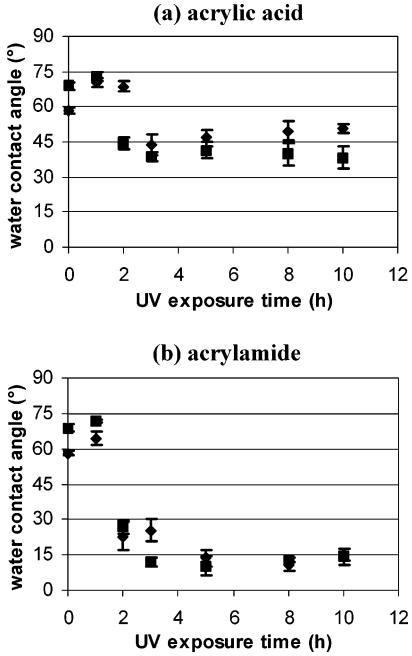

Figure 3. Effect of UV exposure time on water contact angle of the PLA film activated with plasma treatment (◆) or grafted with benzophenone (■) and exposed to UV irradiation in 10% v/v monomer solution in ethanol. The error bars represent 95% confidence intervals.

grafted with PAA,[12] from which we conclude that both reaction steps are necessary for successful grafting of PAA.

Similarly, the contact angle of the PLA film exposed to UV irradiation in 10% v/v acrylamide solution in ethanol without plasma treatment and benzophenone grafting (analogous to experiment 2 above; shown by triangles in Figure 2) decreased only slightly up to a UV exposure time of 5 h but reduced significantly to about 20° for 10 h of UV exposure time (data point not shown in Figure 2). During UV irradiation, PAA and PAAm homopolymers were formed in the ethanol solution. This indicated that both acrylic acid and acrylamide absorbed UV light energy, generated free radicals, and polymerized even in the absence of step 1. In contrast, benzophenone grafting or plasma treatment provided a mechanism by which free radicals were created on the PLA film surface, thereby allowing the growing PAA or PAAm chains to graft from the PLA film surface. It is also possible that the monomers may have migrated into the PLA film bulk and were UV-polymerized, entangling with PLA. This was confirmed by the control experiments for the degradation studies discussed later. ATR−FTIR spectroscopy confirmed the presence of the PAAm chains on the PLA film surface, which were effective at reducing the water contact angle. A similar reduction in water contact angle was not observed for the PAA, most likely because the PAA was not as effective as PAAm in reducing the water contact angle of the PLA films (as shown by results from experiments 3 and 4), and acrylic acid had a lower propensity for adsorption onto the hydrophobic PLA surface.[27]

Experiment 3 used only the plasma activation procedure before the acrylic acid grafting step. The diamonds in Figure 3a show that the water contact angle of the film increased to about 70° from that of the plasma-treated PLA film (∼58°) when that film was irradiated with UV for up to 2 h. This increase could be attributed to the UV exposure and subsequent sonication of the film in ethanol in absence of any PAA grafting. The water contact angle then decreased to about 45°, suggesting that PAA was grafted to the PLA film surface during this time interval. The increase in the water contact angle of the film to about 50° for exposure times greater than 3 h could be attributed to the removal of some of the PAA chains weakly bound to the PLA film surface through the active groups created via the "nonspecific" plasma treatment process.

The squares in Figure 3a show the water contact angle results for PLA films grafted with PAA via the benzophenone grafting step (experiment 4). The results clearly show that the PAA grafting occurred with about 2 h of UV exposure, and no significant decrease in water contact angle was achieved for longer UV exposure times. It should be noted that the water contact angle does not show any increase in the case of experiment 4 for longer UV exposure times as it did in the case of experiment 3, presumably because the nonspecific interactions are eliminated in the benzophenone grafting process (Figure 1). Thus, the "optimum" UV exposure time (i.e., the time above which the surface-property changes are minimal) required for the PAA grafting reaction in the case of plasma activation as step 1 was 3 h while that in the case of benzophenone grafting as step 1 was 2 h.

Similarly, as shown in Figure 3b, the "optimum" UV exposure time required for the PAAm grafting reaction in the case of plasma activation as step 1 was 5 h while that in the case of benzophenone grafting as step 1 was 3 h. The contact angles of the PLA grafted with PAAm films at longer exposure times were about 15°. The specific pattern of the contact angle changes in the case of PLA grafted with PAA when plasma treatment was used as step 1 (diamonds in Figure 3a) was not observed in the case of the corresponding PLA grafted with PAAm films, possibly due to physisorption of PAAm at longer UV exposure times.

It should be noted that these "optimum" times are only for the set of parameters chosen for these grafting reactions. These parameters include energy setting (i.e., power) on the plasma treatment unit (∼18 W used in this study), plasma treatment time (2 min), vessel pressure in the plasma treatment unit (∼0.3−0.5 Torr), concentration of the benzophenone solution used for dip coating (5% w/w in ethanol), UV exposure time for the benzophenone grafting step (10 min), concentration of monomer solution (10% v/v), and solvent for the monomer grafting step (ethanol). Changing any of these parameters may change the "optimum" UV exposure time required for PAA or PAAm grafting and the amount of PAA or PAAm grafted on the PLA film surface. The "optimum" UV exposure time required for PAA or PAAm grafting from the PLA film surface (2−5 h) is significantly longer than that reported in the literature for such grafting on various polymer substrates (on the order of few minutes).[9−12] This was expected as those studies used higher grafting temperatures (>40 °C), used monomers after removing the stabilizers, viz., 200 ppm of MEHQ in the case of the acrylic acid monomer, or, most importantly, used high-power UV lamps (800−2000 W). These particular conditions are not well-suited for PLA surface grafting because of the greater extent of PLA degradation at higher temperatures and under high-power UV irradiation. Therefore, our grafting studies were conducted

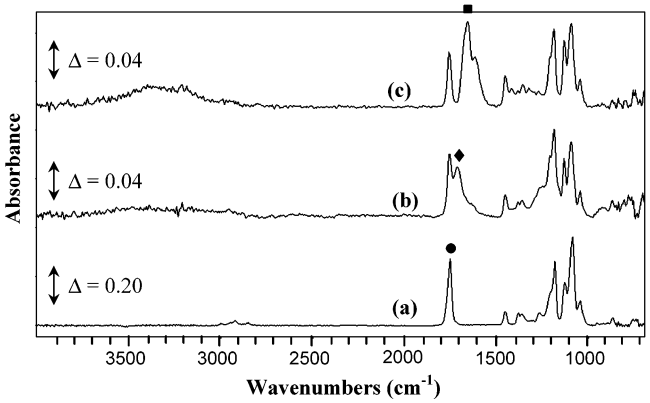

Figure 4. Representative ATR−FTIR spectra for the (a) neat PLA film, (b) PLA film grafted with poly(acrylic acid), and (c) PLA film grafted with polyacrylamide. Spectra a−c all show the "ester peak" at 1756 cm^{-1} (●). Spectrum b shows a shoulder to the ester peak at 1720 cm^{-1} (◆) representing the "acid peak", and spectrum c shows a peak at 1645 cm^{-1} (■) representing the "amide peak".

under relatively mild conditions using a low-power UV lamp (100 W) at room temperature.

Typical ATR−FTIR spectra for neat and surface-modified PLA films are shown in Figure 4. The −C═O peak for the backbone ester in PLA can be observed at wavenumber 1756 cm^{-1} in all of the spectra. The spectrum for PLA grafted with PAA film (spectrum 4b) shows a shoulder to the ester peak at 1720 cm^{-1} representing the grafted acid. Graphical software (ORIGIN) was used to deconvolute peaks at 1720 and 1756 cm^{-1}. The ATR−FTIR peak area ratios, viz., area of the peak at 1720 cm^{-1} divided by the area of the peak at 1756 cm^{-1}, of the PLA film activated with plasma treatment and exposed to UV irradiation in 10% v/v acrylic acid solution in ethanol (experiment 3) are shown by diamonds in Figure 5a. These results showed that the "optimum" PAA grafting reaction time was about 3 h, and no significant increase in the amount of grafted PAA was achieved for longer UV exposure times. A subsequent reduction in the PAR for longer UV exposure times indicated removal of some of the PAA chains weakly bound to the PLA film surface and was consistent with the water contact angle results (diamonds in Figure 3a). Squares in Figure 5a show that significant PAA grafting was achieved in about 2 h using benzophenone grafting as step 1. Here, the PAR remained unchanged for longer UV exposure times and was consistent with water contact angle data (squares in Figure 3a).

Spectrum 4c shows a peak at wavenumber 1661 cm^{-1} corresponding to the −C═O stretches in the amide functionality of PAAm and an amide II peak at 1550 cm^{-1}, which is the combination band of N−H bending and C−N stretching vibrations. The ATR−FTIR peak area ratios, viz., area of the peak at 1661 cm^{-1} divided by the area of the peak at 1756 cm^{-1}, of the PLA film activated with plasma treatment and exposed to UV irradiation in 10% v/v acrylamide solution in ethanol are shown by diamonds in Figure 5b. These results showed that the "optimum" PAA grafting reaction time was about 5 h, and no significant change in amount of grafted PAAm was achieved for longer UV exposure times. The plateau in the PAR values for longer UV exposure times could be because of removal of the PAAm chains weakly bound to the PLA film surface (leading to reduction in PAR) and entanglement of PAAm chains

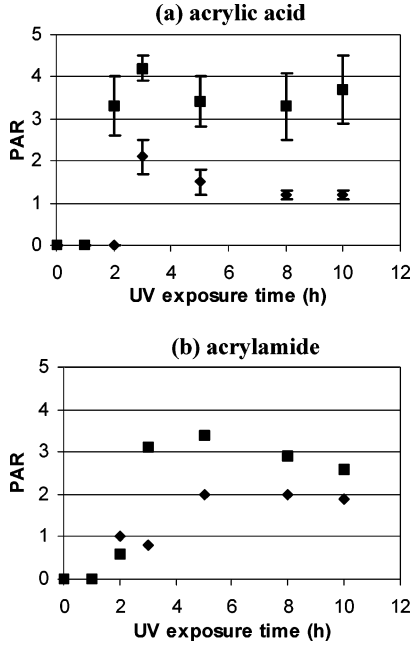

Figure 5. Effect of UV exposure time on the ATR−FTIR peak area ratio (PAR), viz., area of the peak at 1720 cm^{-1} in the case of acrylic acid (or at 1661 cm^{-1} in the case of acrylamide) divided by the area of the peak at 1756 cm^{-1}, of the PLA film activated with plasma treatment (◆) or grafted with benzophenone (■) and exposed to UV irradiation in 10% v/v monomer solution in ethanol. The error bars represent 95% confidence intervals.

(leading to an increase in PAR). These results are consistent with the water contact angle results (diamonds in Figure 3b). Squares in Figure 5b show that the PAAm grafting reaction time was about 3 h with benzophenone grafting as step 1. Here, the PAR changed only slightly for longer UV exposure times and was consistent with water contact angle data (squares in Figure 3b).

As an additional point, hydrogen abstractor initiators like benzophenone can lead to cross-linking of PLA chains if two PLA-bound radicals combine with one another instead of the free radicals from the growing PAA or PAAm chains. A possibility of cross-linking also exists if two free radicals from two different growing PAA or PAAm chains combine, resulting in an insoluble gel. Therefore, the cross-linking possibility during the photografting process was investigated by dissolving the films in respective solvents and filtering the solution through a 0.2 μm Acrodisc filter. The benzophenone-grafted PLA dissolved in chloroform, and the PLA-*g*-PAA film dissolved in 1,4-dioxane (common solvent for PLA and PAA). As noted before, in addition to the surface-grafted layers, both acrylic acid and acrylamide formed a homopolymer in solution when exposed to UV. These homopolymers dissolved in water, confirming that an insoluble PAA or PAAm gel was not formed.

Degradation Studies. Based on the studies described above, the UV irradiation time of 3 h was used for acrylic acid and acrylamide grafting steps. The surface-modified films were then referred to as PLA-*g*-PAA and PLA-*g*-PAAm. Atomic force microscopy images of the neat PLA film surface and the film surfaces resulting after incubating the neat PLA film in buffer solutions with pH = 4, 7, and 10 for 7 days are shown in Figure 6. The neat PLA film had a very smooth surface with an rms roughness 0.26 nm, and the

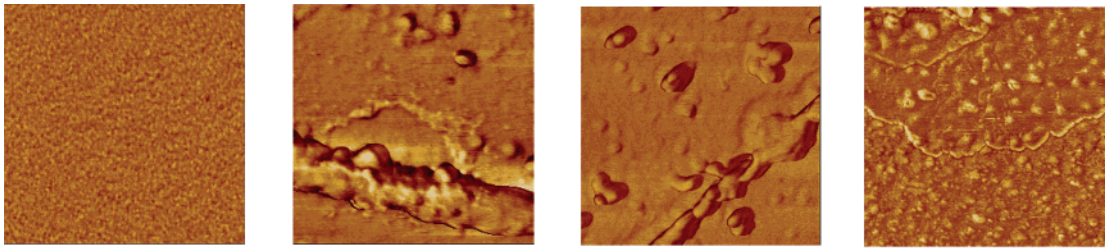

Figure 6. Atomic force microscopy images revealing surfaces of (a) neat PLA film (rms roughness = 0.26 nm) and the PLA film incubated for 7 days in solutions with (b) pH = 4 (rms roughness = 2.0 nm), (c) pH = 7 (rms roughness = 1.6 nm), and (d) pH = 10 (rms roughness = 1.5 nm). All AFM images are phase images of 1 μm × 1 μm area.

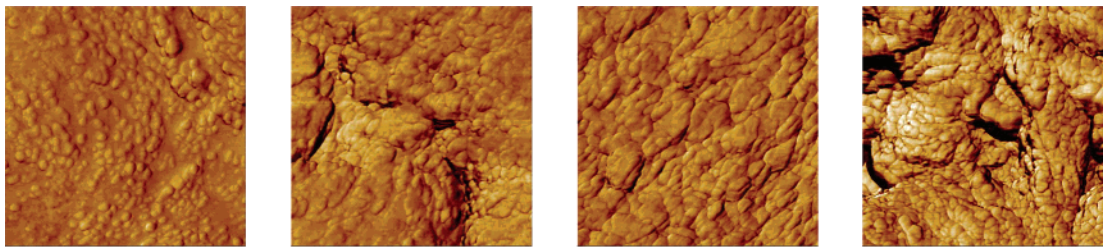

Figure 7. Atomic force microscopy images revealing surfaces of (a) PLA-*g*-PAA film (rms roughness = 15.4 nm) and the PLA-*g*-PAA film incubated for 7 days in solutions with (b) pH = 4 (rms roughness = 32.6 nm), (c) pH = 7 (rms roughness = 17.0 nm), and (d) pH = 10 (rms roughness = 36.4 nm). All AFM images are phase images of 1 μm × 1 μm area.

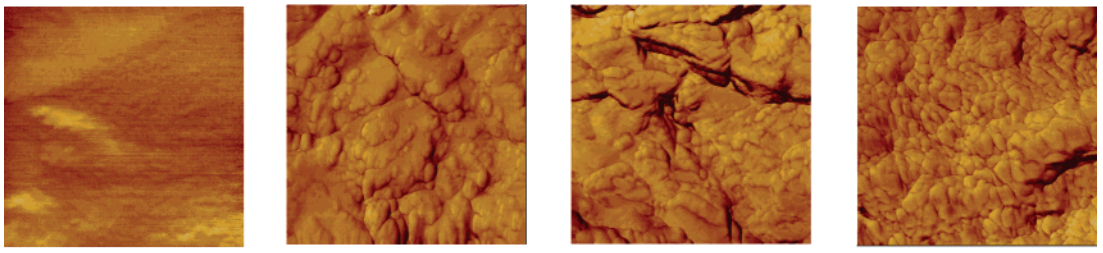

Figure 8. Atomic force microscopy images revealing surfaces of (a) PLA-*g*-PAAm film (rms roughness = 4.4 nm) and the PLA-*g*-PAAm film incubated for 7 days in solutions with (b) pH = 4 (rms roughness = 16.5 nm), (c) pH = 7 (rms roughness = 28.9 nm), and (d) pH = 10 (rms roughness = 20.3 nm). All AFM images are phase images of 1 μm × 1 μm area.

roughness of the neat PLA film marginally increased after it was incubated in the buffer solutions. Figure 7 showed that the PLA-*g*-PAA film had a higher rms roughness (15.4 nm) compared to the neat PLA film surface (0.26 nm). AFM images of the PLA-*g*-PAA film surfaces after incubating the films in buffer solutions with pH = 4, 7, and 10 for 7 days revealed degraded surfaces and generally resulted in higher rms roughness values, e.g., up to 36 nm in the case of the pH = 10 buffer solution. Similar observations were made in the case of PLA-*g*-PAAm film (rms roughness = 4.4 nm) where the incubation in the buffer solutions resulted in higher roughness values, e.g., up to 30 nm in the case of the pH = 7 buffer solution (Figure 8).

The molecular weights of the various neat, surface-modified, and degraded PLA films were measured by chloroform-based GPC. PLA dissolved completely in chloroform. However, PAA and PAAm were insoluble in chloroform. Therefore, when the grafted films were placed in chloroform, the middle (bulk) portion of the film dissolved, but two thin layers of covalently bonded/interdiffused PLA−PAA or PLA−PAAm remained in solution (but not dissolved). The dissolved "bulk" PLA was then characterized using GPC.

Figure 9a shows the effect of incubation time on the molecular weight of neat PLA films. The results indicate that a small degree of degradation occurred over a period of 28 days, and the molecular weights decreased to no less than about 100 000 Da in each of the three buffer solutions. These results are consistent with earlier studies summarized elsewhere.[15] An apparent slight increase in PLA molecular weight observed for early incubation times (1−3 days) might have been due to the leaching of low molecular weight chains into the buffer solutions.[17] The hydrolytic degradation of aliphatic polyesters (e.g., PLA) depends primarily on the kinetics of the chemical cleavage of the ester linkage.[15,16,18−20,22,28,29] After immersion of the PLA films in an aqueous medium, a significant water uptake is necessary to cause the PLA degradation. The penetrating water creates a negative concentration gradient from the surface to the film center, which is expected to drive the diffusion-in process for the water molecules.[18] The neat PLA film is hydrophobic (water contact angle ∼ 82°) and not expected to favor a significant water uptake from the buffer solutions required for PLA degradation through hydrolysis. Additionally, the absorbed water molecules associate or form clusters as they preferentially bind to each other by hydrogen bonding instead of binding to the hydrophobic polymer microvoid surface.[29,30] The absorbed water in this case could be considered as a "free moving"

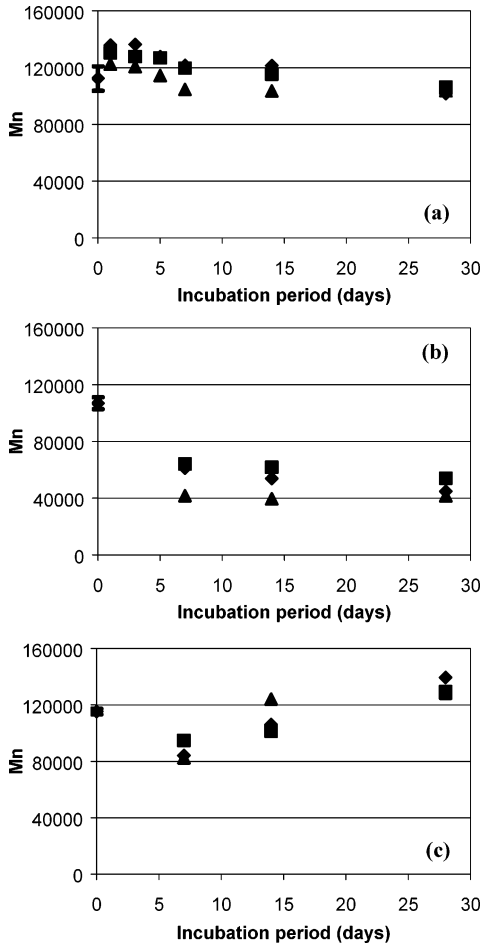

Figure 9. Molecular weights of (a) neat PLA, (b) PLA-*g*-PAA, and (c) PLA-*g*-PAAm films as a function of the incubation time in buffer solutions with (◆) pH = 4, (■) pH = 7, and (▲) pH = 10. The value at incubation time of day 0 in (a) represents the molecular weight of neat PLA pellets and in (b) and (c) represents the molecular weight of the "bulk" PLA of the PLA-*g*-PAA film and the PLA-*g*-PAAm film, respectively, that dissolved in chloroform. A representative 95% confidence interval shows the experimental error.

infiltrant.[20] This phenomenon has been observed predominantly for relatively short incubation times (up to 6 weeks), similar to those used in our study. At longer incubation times (8−32 weeks) several studies reported significant PLA degradation, indicating the absorbed water eventually reacted with the PLA backbone.[15,20]

Subsequently, the PLA molecular weights of the PLA-*g*-PAA and PLA-*g*-PAAm films were measured after incubating the films in the different buffer solutions. The PLA-*g*-PAA films incubated in the pH = 4, 7, and 10 solutions showed a significant decrease in molecular weight, e.g., down to 40 000 Da in the case of the pH = 10 buffer solution (Figure 9b). Results presented in Figure 9c show that an initial decrease and a subsequent increase in the molecular weight were observed in the case of the PLA-*g*-PAAm film. However, the decrease in molecular weight in the case of PLA-*g*-PAAm films was not as significant as that observed in the case of the PLA-*g*-PAA (Figure 9b).

Vert et al. showed that highly crystalline PLA samples degraded more slowly than less crystalline samples.[31] To determine the crystallinity values of the neat and surface-modified PLA films, differential scanning calorimetry (DSC) data were obtained on a MDSC 2920 (TA Instruments) from 30 to 200 °C with a scan rate of 10 °C/min. The degree of crystallinity was calculated from the measured heat of fusion relative to 93 J/g for a 100% crystalline PLA.[32] The neat PLA film showed a very low crystallinity value of about 1%, which was expected for the solvent-casting process with no annealing of the film. The crystallinity values for the PLA-*g*-PAA and PLA-*g*-PAAm films were about 35%. This increase was likely due to solvent-induced crystallization during the photografting process, as neat PLA film soaked in ethanol showed similar behavior. On the basis of the results due to Vert et al.,[31] the surface-modified films could be expected to degrade more slowly compared to the neat PLA. However, the fact that the surface-modified films showed different degradation behavior than neat PLA and the PLA-*g*-PAA degraded faster than the PLA-*g*-PAAm established that the enhancement in the degradation was due to the PAA, although not necessarily due to surface-grafted PAA chains.

Table 2. Control Experiments for Degradation Studies[a]

	step 1	step 2	
expt no.	benzophenone grafting	monomer	UV irradiation
5	yes	no[b]	yes
6	yes	yes	no
7	no	yes	yes

[a] Note that experiment 7 is different than experiment 2 only in the manner that the UV exposure time in experiment 7 was fixed at 3 h. [b] Pure ethanol was used instead of 10% monomer solution in these experiments.

To determine whether the observed degradation of PLA-*g*-PAA was due to the surface-grafted PAA layer, various control experiments were designed to study the degradation behavior of the PLA films (see Table 2). Similar experiments were also performed using acrylamide. Films resulting from these treatments were incubated in pH = 7 solutions for up to 28 days, and the PLA molecular weights were measured using GPC. In experiment 5, PLA film was grafted with benzophenone in step 1 and exposed to UV irradiation for 3 h in the presence of pure ethanol in step 2. These films did not show a significant PLA degradation, confirming that the solvent treatment during the photografting process was not the cause of the observed degradation in the case of PLA-*g*-PAA. In experiment 6, PLA film was grafted with benzophenone in step 1 and placed in 10% monomer solution in ethanol for 3 h without any UV irradiation in step 2. In experiment 7, PLA film, not grafted with benzophenone in step 1, was exposed to UV irradiation for 3 h in the presence of 10% monomer solution in ethanol in step 2. Formation of PAA or PAAm chains in experiment 7 was confirmed by placing the PLA film in chloroform, where insoluble PAA or PAAm chains were observed to be dispersed in the solvent. However, two thin layers of covalently bonded PLA−PAA or PLA−PAAm films were not observed as in experiment 4. Degradation of films from experiments 6 and 7 showed nearly similar molecular weight values compared to those obtained for the degradation of PLA-*g*-PAA seen previously in Figure 9b. Similar behavior was obtained when acrylamide was used instead of acrylic acid, resulting in nearly similar molecular weight values compared to those obtained for the degradation of PLA-*g*-PAAm seen previously in Figure 9c.

These studies established that the major contribution to the observed degradation of PLA-*g*-PAA and PLA-*g*-PAAm was the entangled PAA or PAAm chains (shown by experiment 7) and not necessarily due to the surface-

Table 3. Qualitative Summary of Results for the Experiments Shown in Tables 1 and 2[a]

experiment no.	wettability	degradation rate
4	yes	yes
5	no	no
6	no	yes
7	no	yes

[a] "yes" indicates improvement in the property compared to neat PLA film.

grafted layers. Experiment 6 showed that the acrylic acid or acrylamide monomer that migrated into the film bulk could also contribute to the observed degradation. However, the fraction of the migratory monomer in experiment 7 that was not polymerized could not be determined. The contact angle measurements of films obtained from experiments 5−7 did not show any improvement in PLA surface wettability. These results established that the sonication procedure used after the photografting step removed the unreacted monomers from the PLA film surface but could not necessarily remove the monomers migrated into the film bulk nor the entangled PAA or PAAm chains. Highly vigorous sonication and high-temperature Soxhlet extraction procedures were avoided to minimize the possibility of PLA degradation during the cleaning process itself. The results for experiments 4−7 are qualitatively summarized in Table 3. Clearly, improvement in both the desired properties, viz., surface wettability and degradation rate, was obtained only in experiment 4, where PLA film was grafted with benzophenone in step 1 and exposed to UV irradiation for 3 h in the presence of 10% monomer solution in ethanol in step 2.

The degradation behavior of PLA-*g*-PAA and PLA-*g*-PAAm can then be explained as follows. Copolymerization of poly(ortho esters) with acidic and hydrophilic monomers has shown improved water uptake and enhanced autocatalytic degradation.[28] Therefore, when the PLA film with acrylic acid, acrylamide, PAA, or PAAm was incubated in the buffer solutions, we expect that water from the buffer solutions would cluster near the carboxylic acids or amide functionalities. Such a cluster of water molecules would force a significant water uptake and may accelerate the hydrolysis reaction during the relatively shorter incubation periods considered in our study. However, Zhang et al. noted that the PLA degradation was accelerated by an increase in the protons present in the solutions rather than by an increase in the water concentration over a period of about 20 days.[15] The pK_a of PAA chains is approximately 5, so the acid groups would be ionized at pH = 7 and 10 (and potentially partially ionized at pH = 4).[33] The amide groups of the PAAm would be neutral at all pHs. Therefore, the acrylic acid or PAA provided a large number of localized ionized acid groups, which may explain the significant degradation of the "bulk" PLA achieved in the presence of acrylic acid or PAA compared to neat PLA and PLA-*g*-PAAm. The initial decrease in the PLA molecular weight observed in the case of PLA-*g*-PAAm films (Figure 9c) can be attributed to the degradation due to the increased water uptake. The apparent increase in the molecular weight for an incubation period of 28 days may be due to a delayed leaching of low molecular weight fractions. Such a delay in the leaching process could be caused by the increased resistance to the diffusion-out of the low molecular weight fraction due to the PAAm grafted layer, an effect similar to the heterogeneous degradation process discussed elsewhere.[18,19] A description of PLA degradation vs leaching is provided later.

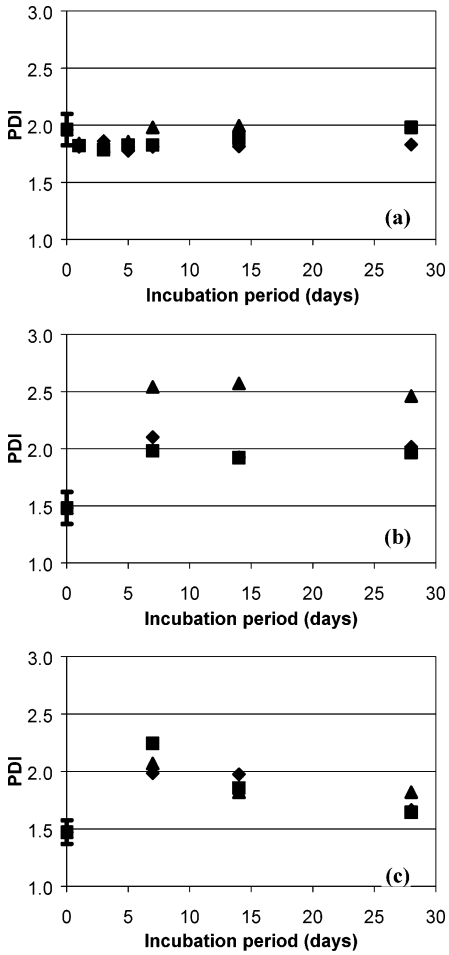

Figure 10. Polydispesity index (PDI) values of (a) neat PLA, (b) PLA-*g*-PAA, and (c) PLA-*g*-PAAm films as a function of the incubation time in buffer solutions with (◆) pH = 4, (■) pH = 7, and (▲) pH = 10. The value at incubation time of day 0 in (a) represents the PDI of neat PLA pellets and in (b) and (c) represents the PDI value of the "bulk" PLA of the PLA-*g*-PAA film and the PLA-*g*-PAAm film, respectively, that dissolved in chloroform. A representative 95% confidence interval shows the experimental error.

For relatively thin films like those used in our research, Siparsky et al. showed that PLA degradation was a reaction-controlled process; i.e., the hydrolysis of the PLA backbone was slower than the water diffusion into the film.[29] Göpferich has discussed that the pH of the incubating media mainly affected the PLA degradation rates through catalysis, reflecting the fastest degradation rate at low and high pH.[19] In view of these observations, it was surprising that our neat and surface-modified films did not yield significantly different molecular weights as a function of pH for a given incubation time. This behavior may be because the degradation was carried out at room temperature and for a shorter duration (<30 days) and requires further study.

To assess the processes of leaching and degradation used to explain the observed molecular weight changes observed in Figure 9, the polydispersity index (PDI) values of the neat, surface-modified, and degraded films were analyzed and are shown in Figure 10. Removal of the low molecular weight fraction material would lead to a reduction in PDI while degradation of the PLA backbone would lead to an increase in PDI.[17,34] The

decrease in PDI observed for early incubation times (1−3 days) confirmed the leaching of low molecular weight fraction material in the case of neat PLA (Figure 10a). An increase in PDI in the case of PLA-*g*-PAA films suggested degradation of the PLA backbone (Figure 10b). In Figure 10c, an initial PDI increase for PLA-*g*-PAAm films supported the degradation due to increased water uptake, while the subsequent PDI decrease for longer incubation times may be due to a delayed leaching of low molecular weight fractions, as stated earlier.

Summary

Poly(acrylic acid) and poly(acrylamide) were photopolymerized from PLA film surfaces using a "nonspecific" plasma treatment or a specific photoinitiator, viz., benzophenone. The grafted films analyzed by ATR−FTIR spectroscopy and contact angle goniometry indicated that the "optimum" UV irradiation time required for the PAA grafting step was 3 h when plasma activation was used as step 1 and was 2 h when benzophenone grafting was used as step 1. The "optimum" time for the PAAm grafting step was 5 h when plasma activation was used as step 1 and was 3 h when benzophenone grafting was used as step 1. These "optimum" times are only for the set of parameters chosen for these grafting reactions, which are reported in the Experimental Section. Based on ATR−FTIR results, the PAA and PAAm grafting density obtained using benzophenone grafting was higher than that obtained using plasma activation. When incubated in various buffer solutions, the PLA-*g*-PAA films showed faster degradation compared to neat, unmodified PLA and PLA-*g*-PAAm films. The faster rate of degradation was attributed to entangled PAA chains resulting from the acrylic acid monomer migrated into the film bulk and not to the surface-grafted layers.

Acknowledgment. This work made use of ERC shared facilities supported by NSF under Award No. EEC-9731680. The authors thank Dr. J. R. Dorgan (Department of Chemical Engineering, Colorado School of Mines), Dr. A. A. Ogale, Dr. S. M. Husson, Dr. A. K. Naskar, Ms. Keisha Walters (Department of Chemical Engineering, Clemson University), Prof. M. J. Drews, Dr. Igor Luzinov, Ms. Kim Ivey, Dr. Swaminathan Iyer (School of Materials Science and Engineering, Clemson University), Dr. D. W. Smith, Mr. Mark Perpall, and Dr. Nilmini Abayasinghe (Department of Chemistry, Clemson University) for their assistance and helpful discussions.

References and Notes

(1) Kimura, Y.; Shirotani, K.; Yamane, H.; Kitao, T. *Macromolecules* **1988**, *21*, 3338−3340.
(2) Schmack, G.; Taendler, B.; Vogel, R.; Beyreuther, R.; Jacobsen, S.; Fritz, H.-G. *J. Appl. Polym. Sci.* **1999**, *73*, 2785−2797.
(3) Schmack, G.; Taendler, B.; Optiz, G.; Vogel, R.; Komber, H.; Haussler, L.; Voigt, D.; Weinmann, S.; Heinemann, M.; Fritz, H.-G. *J. Appl. Polym. Sci.* **2004**, *91*, 800−806.
(4) Hirotsu, T.; Nakayama, K.; Tsujisaka, T.; Mas, A.; Schue, F. *Polym. Eng. Sci.* **2002**, *42*, 299−307.
(5) Incardona, S. D.; Fambri, L.; Migliaresi, C. *J. Mater. Sci.: Mater. Med.* **1996**, *7*, 387−391.
(6) Ouchi, T.; Miyazaki, H.; Arimura, H.; Tasaka, F.; Hamada, A.; Ohya, Y. *J. Polym. Sci., Polym. Chem.* **2002**, *40*, 1218−1225.
(7) Irvine, D. J.; Ruzette, A. G.; Mayes, A. M.; Griffith, L. G. *Biomacromolecules* **2001**, *2*, 545−556.
(8) Cai, K.; Yao, K.; Cui, Y.; Lin, S.; Yang, Z.; Li, X.; Xie, H.; Qing, T.; Luo, J. *J. Biomed. Mater. Res.* **2002**, *60*, 398−404.
(9) Ma, H.; Davis, R. H.; Bowman, C. N. *Macromolecules* **2000**, *33*, 331−335.
(10) Rånby, B. *Int. J. Adhes. Adhes.* **1999**, *19*, 337−343.
(11) Yang, W.; Rånby, B. *Eur. Polym. J.* **1999**, *35*, 1557−1568.
(12) Noh, I.; Hubbell, J. A. *J. Polym. Sci., Polym. Chem.* **1997**, *35*, 3467−3482.
(13) Buchenska, J. *J. Appl. Polym. Sci.* **2002**, *83*, 2295−2299.
(14) Steffens, G. C. M.; Nothdurft, L.; Buse, G.; Thissen, H.; Höcker, H.; Klee, D. *Biomaterials* **2002**, *23*, 3523−3531.
(15) Zhang, X.; Wyss, U. P.; Pichora, D.; Goosen, M. F. A. *J. Bioact. Compat. Polym.* **1994**, *9*, 80−100.
(16) Bergsma, J. E.; Rozema, F. R.; Bos, R. R. M.; Boering, G.; Joziasse, C. A. P.; Pennings, A. J. *J. Mater. Sci.: Mater. Med.* **1995**, *6*, 642−646.
(17) Lam, K. H.; Nieuwenhuis, P.; Molenaar, I.; Esselbrugge, H.; Feijen, J.; Dijkstra, P. J.; Scakenraad, J. M. *J. Mater. Sci.: Mater. Med.* **1994**, *5*, 181−189.
(18) Vert, M.; Li, S.; Garreau, H.; Mauduit, J.; Boustta, M.; Schwach, G.; Engel, R.; Coudane, J. *Angew. Makromol. Chem.* **1997**, *247*, 239−253.
(19) Göpferich, A. *Biomaterials* **1996**, *17*, 103−114.
(20) Burg, K. J. L.; Shalaby, S. W. *J. Mater. Sci.: Appl. Biomater.* **1997**, *38*, 337−341.
(21) Ho, K. G.; Pometto, A. L. *J. Environ. Polym. Degrad.* **1999**, *7*, 93−100.
(22) Agarwal, M.; Koelling, K. W.; Chalmers, J. J. *Biotechnol. Prog.* **1998**, *14*, 517−526.
(23) McDonald, R. T.; McCarthy, S. P.; Gross, R. A. *Macromolecules* **1996**, *29*, 7356−7361.
(24) Torres, A.; Li, S. M.; Roussos, S.; Vert, M. *J. Appl. Polym. Sci.* **1996**, *62*, 2295−2302.
(25) Pranamuda, H.; Tokiwa, Y.; Tanaka, H. *Appl. Environ. Microbiol.* **1997**, *63*, 1637−1640.
(26) Urban, M. W. *Attenuated Total Reflectance Spectroscopy of Polymers: Theory and Practice*; American Chemical Society: Washington, DC, 1996.
(27) Friedsam, C.; Bécares, A. D. C.; Jonas, U.; Seitz, M.; Gaub, H. E. *New J. Phys.* **2004**, *6*, 1−16.
(28) Heller, J.; Penhale, D. W.; Fritzinger, B. K.; Ng, S. Y. *J. Controlled Release* **1987**, *5*, 173−177.
(29) Siparsky, G. L.; Voorhees, K. J.; Dorgan, J. R.; Schilling, K. *J. Environ. Polym. Degrad.* **1997**, *5*, 125−136.
(30) Hsu, W. P.; Li, R. J.; Myerson, A. S.; Kwei, T. K. *Polymer* **1993**, *34*, 597−603.
(31) Vert, M.; Mauduit, J.; Li, S. M. *Biomaterials* **1994**, *15*, 1209−1213.
(32) Barndup, J.; Immergut, E. H. *Polymer Handbook*; Wiley-Interscience: New York, 1988.
(33) Chen, K. M.; Jiang, X.; Kimerling, L. C.; Hammond, P. T. *Langmuir* **2000**, *16*, 7825−7834.
(34) Fischbach, C.; Tessmar, J.; Lucke, A.; Schnell, E.; Schmeer, G.; Blunk, T.; Göpferich, A. *Surf. Sci.* **2001**, *491*, 333−345.

MA049056U