Photohydrolysis of Substituted Benzyl Esters in Multilayered Polyelectrolyte Films

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Received September 5, 2003; Revised Manuscript Received January 7, 2004

ABSTRACT: Poly(acrylic acid) (PAA) is partially esterified with various benzyl (i.e., benzyl, 3-methoxybenzyl, 3,5-dimethoxybenzyl, and 2-nitrobenzyl) groups, and the resulting benzyl acrylate copolymers are then incorporated into multilayered polyelectrolyte films. Upon exposure to UV light, the benzyl groups are photohydrolyzed. The hydrolysis is monitored by reflectance FTIR spectroscopy, ellipsometry, and advancing water contact angle measurements. The nature of the substituents on the aromatic rings affects the photoreactivity and thermal stability of the films. For example, 3,5-dimethoxybenzyl and 2-nitrobenzyl esters are photohydrolyzed to form primarily acid groups in the film matrix. On the other hand, when benzyl and 3-methoxybenzyl ester films are irradiated, fewer acid groups are formed. Films made with 3,5-dimethoxybenzyl groups appear to be the most thermally stable during the cross-linking of the polymeric film layers.

Introduction

Multilayered polyelectrolyte films have been used as controlled chemical release agents,[1a] nanoreactors,[1b] ion exchange membranes,[1c] and sensors or for separation purposes.[1d,2] These films are prepared by first dipping a material with a charged surface into a solution containing a complementary polyelectrolyte that forms ionic bonds with the surface. Subsequent layers of polyanions/polycations are added by layer-by-layer deposition until a desired thickness is achieved.

Poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH) are useful materials for preparing multilayered polyelectrolyte films.[1,2] Both PAA and PAH are commercially available and soluble in water and can be readily derivatized (PAA through esterification and PAH through amidation). Additionally, PAA/PAH films may be thermally cross-linked after assembly by forming amide bonds between layers. Cross-linking of the layers enhances the overall thermal stability of the films and thus broadens their useful application temperature range.[3]

The objective of this study is to prepare multilayered polyelectrolyte membranes[4] with tunable permeability on a porous alumina substrate. Previously, layer-by-layer deposition was used to form films on nonporous gold surfaces.[2] Tunable permeability was achieved by incorporating a series of partially esterified poly(acrylic acids) (ethyl, *n*-propyl, *n*-butyl, and benzyl esters) into the films.[2] Because of the high degree of hydrophobicity, these films were found to be impermeable to certain ions. However, upon basic hydrolysis of the ester groups, the permeability of the resulting films increased dramatically, and a certain degree of ion selectivity could be achieved.

Unfortunately, the strongly basic conditions required for the aforementioned hydrolysis are incompatible with methods used by us to tether the initial layer of the film to porous alumina. This necessitated the use of alternative mild photohydrolysis techniques.[5]

Recently, first-generation photohydrolyzable films on alumina were prepared by partially derivatizing both PAA and PAH with the photolabile *o*-nitrobenzyl group.[5] These derivatized polyelectrolytes were then coated onto alumina and photohydrolyzed to form films with enhanced ion transport selectivity. However, when thermal cross-linking of the layers was attempted prior to irradiation, most of the *o*-nitrobenzyl groups underwent thermal degradation. This led us to identify a thermally stable photohydrolyzable group that can also form more robust cross-linked membranes.

This study compares (1) the photohydrolyses of films with a variety of aromatic esters (vide infra) and (2) their thermal stability during cross-linking reactions. This would allow one to identify a polyelectrolyte with readily photohydrolyzable groups in addition to enhanced thermal stability.

A wide variety of substituted benzyl esters undergo photohydrolysis.[6] Interestingly, the nature of the substituent on the aromatic ring affects the photohydrolysis products. Certain substituents lead to typical hydrolysis products (acids and alcohols) while others form varying amounts of radical hydrolysis products. The amount of each product type depends on the position and nature of the aromatic substituent.[6] For example, irradiation of 3,5-dimethoxy benzyl esters forms only carboxylic acids upon hydrolysis of the aromatic group, while benzyl and 3-methoxy benzyl esters yield some radical hydrolysis products (including alkanes formed by decarboxylation of intermediate carboxy radicals).[6] This effect is commonly referred to as the “meta effect”.[6]

Experimental Section

Materials. Poly(acrylic acid) (PAA) (M_v = 450 000), poly(allylamine hydrochloride) (PAH) (M_w = 70 000), 3-mercaptopropionic acid (MPA), 1,4-dioxane, dimethyl sulfoxide (DMSO), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 3-methoxybenzyl bromide, and 3,5-dimethoxybenzyl bromide were obtained from Aldrich. Diethyl ether (anhydrous) and sulfuric acid (certified ACS) were obtained from Fischer Scientific. Ethanol was from Pharmco (200 proof), and benzyl alcohol was distilled over magnesium and iodine.

General Polyelectrolyte Synthesis. Poly(acrylic acid) was partially esterified with four different benzyl groups to

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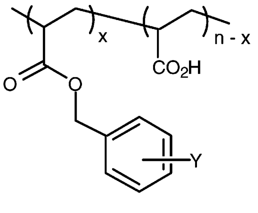
10.1021/ma035321k CCC: $27.50

form derivatized PAA (dPAA, see structures below). The dPAA with an unsubstituted benzyl group (BPAA) was synthesized via Fischer esterification.[2] Partially 2-nitrobenzylated poly(acrylic acid) (2NPAA) was prepared by a nucleophilic substitution method using 1,8-diazabicyclo-[5,4,0]-7-undecene (DBU) catalyst, a nonnucleophilic base, and the corresponding benzyl halide.[5,7] PAA is deprotonated, and the desired alkyl halide is added to the mixture. The extent of polymer derivatization is controlled by the amounts of base and alkyl halide used. Both partially 3-methoxybenzylated poly(acrylic acid) (3MBPAA) and partially 3,5-dimethoxybenzylated poly(acrylic acid) (3,5MBPAA) were prepared by using the DBU method.



Y =	Abbrev. =
H	BPAA
3-OCH$_3$	3MBPAA
3,5-diOCH$_3$	3,5MBPAA
2-NO$_2$	2NPAA

Poly(acrylic acid-*co*-3-methoxybenzyl acrylate) (3MBPAA). The reaction vessel consisted of a three-necked, round-bottomed, 250 mL flask fitted with a magnetic stir bar, a nitrogen inlet, and a condenser. PAA (2.48 g, 40 mmol) was dissolved in DMSO (60 mL) with stirring. After complete dissolution, 6.0 mL of DBU (40 mmol) in 12 mL of DMSO was added, followed by 3.94 mL (28.1 mmol) of 3-methoxybenzylbromide in 12 mL of DMSO. The reaction was allowed to continue for 3.5 h at 45 °C. The progress of the reaction was regularly monitored by IR and ^{1}H NMR. After the desired conversion (between 50 and 75% esterification of acid units) was achieved, the reaction mixture was poured into 2000 mL of acidified (acetic acid) water and precipitated polymer was collected by filtration. Residual DMSO was removed by Soxhlet extraction using acetone. The product was then dried at room temperature under reduced pressure for 24 h. The ^{1}H NMR spectrum in DMSO-d_6 was interpreted as follows: 1.0−2.0 ppm (broad, 4H, backbone CH$_2$); 2−2.48 ppm (broad, 2H, backbone CH peaks); 3.5−3.7 ppm (broad, 3H at 50% ester conversion, OCH$_3$); 5.0 ppm (broad singlet, 2H at 50% ester conversion, benzyl OCH$_2$); 6.5−7 ppm (broad, 3H at 50% ester conversion, aromatic); 7−7.5 ppm (broad, 1H at 50% ester conversion, aromatic). The ^{13}C NMR spectrum (DMSO-d_6) was as follows: 33.55 and 33.85 ppm (methylene backbone); 40.99 ppm (methine CH); 55.99 and 65.00 ppm (OCH$_2$ and OCH$_3$); 114.5, 120.50, 129.50, 137.50, and 159.50 ppm (aromatic); 175.63 and 175.44 ppm (carbonyl).

Poly(acrylic acid-*co*-3,5-dimethoxybenzyl acrylate) (3,5MBPAA). The reaction vessel consisted of a three-necked, round-bottomed, 250 mL flask fitted with a magnetic stir bar, a nitrogen inlet, and a condenser. PAA (1.418 g, 20 mmol) was dissolved in DMSO (30 mL) with stirring. After complete dissolution, 3.0 mL of DBU (20 mmol) in 6 mL of DMSO was added, followed by 3.245 g (14.0 mmol) of 3,5-dimethoxybenzyl bromide in 6 mL of DMSO. The reaction mixture was heated to 45 °C, and the progress of the reaction was monitored on a regular basis by IR and ^{1}H NMR. After the desired percent conversion to ester was achieved (11 h), the product was collected by precipitation by pouring the reaction mixture into 2000 mL of water. The white gelatinous precipitate was washed again with water and then stirred in a solution of water with a few drops of acetic acid for 24 h. The product was then dried under high vacuum for 24 h. The ^{1}H NMR spectrum in DMSO-d_6 was interpreted as follows: 1.0−2.0 ppm (broad, 4H, backbone CH$_2$), 2−2.48 ppm (broad, 2H, backbone CH peaks), 3.5−3.7 ppm (broad, 6H at 50% ester conversion, 2 × OCH$_3$), 5.0 ppm (broad singlet, 2H at 50% ester conversion, benzyl OCH$_2$), 6.3−6.8 ppm (broad, 3H at 50% ester conversion, aromatic). The ^{13}C NMR spectrum (DMSO-d_6) was as follows: 34.50 and 34.80 ppm (methylene backbone); 40.90 ppm (methine CH); 56.50 and 66.00 ppm (OCH$_3$ and OCH$_2$); 100.50, 106.50, 138.50, and 160.50 ppm (aromatic), 174.00 and 176.00 ppm (carbonyl).

General Conditions for Film Formation and Cross-Linking. Each gold-coated silicon slide (2.4 × 1.2 cm piece of a Si 100 wafer that was sputter-coated with 20 nm of Cr followed by 200 nm of Au) was cleaned for 15 min with a Boekel UV/ozone cleaner.

Films were prepared by first forming an anionic monolayer on a gold surface. The surface was dipped into 2 mM mercaptopropionic acid (MPA) in ethanol for 45 min, rinsed with ethanol for 1 min, dried under nitrogen, and then dipped into a 0.02 M solution of poly(allylamine hydrochloride) (PAH) (molarity of polymers is given with respect to the repeating unit).[2] The films were removed from the PAH solution after 5 min, rinsed with water for 1 min, dried under N$_2$, and dipped in a 0.02 M solution of derivatized PAA (dPAA). The film was then removed from the PAA solution after 5 min, rinsed with water for 1 min, and then dried under N$_2$. This completed the formation of the first bilayer of PAH/dPAA. Subsequent bilayers were deposited similarly. Cross-linking of films was carried out by heating at 180 °C (as measured inside the heating vessel) for 2 h under a stream of N$_2$. Since the solubility varied greatly for the four polyelectrolytes, the solvent and pH of the polyelectrolyte solutions had to be carefully modified (vide infra).

Preparation of PAH Solutions. PAH (374 mg) was dissolved in 200 mL of H$_2$O (0.02 M) in a 500 mL beaker with stirring. The pH was adjusted to 5.5 with 0.1 M NaOH (for the solution used for the films containing BPAA). For the films containing the 3MBPAA, 3,5MBPAA and NPAA, a pH of 7−8 was reached with dropwise addition of 0.1 M NaOH.

Preparation of dPAA Solutions. BPAA (0.257 g) was dissolved in 90 mL of THF, after which 60 μL of *N*-methylmorpholine and 10 mL of H$_2$O were added to yield a 0.017 M BPAA solution. A solution of 3MPAA (0.015 M) was made by dissolving 0.264 g of 3MBPAA in 20 mL of DMSO, and then (after dissolution) 76 mL of glacial acetic acid was added dropwise followed by 4 mL of 0.1 M KOH in methanol. The solution had a pH of 1.55. 3,5MBPAA (0.295 g) was dissolved in 20 mL of DMSO, followed by dropwise addition of 76 mL of glacial acetic acid and 4 mL of 0.1 M KOH in methanol to make 0.014 M solution of 3,5MBPAA. A 0.02 M solution of 2NPAA was used (prepared as in ref 5 except twice as concentrated).

Film Characterization. To investigate the photohydrolysis of cross-linked films, each film type was cross-linked (by heating to 180 °C), photoirradiated (for 10 min), and then treated with dilute sodium hydroxide.[5] Films were analyzed by reflectance FTIR spectroscopy, ellipsometry (thickness), and water contact angle measurements (hydrophobicity) after each step. Because the acid and ester carbonyl stretches overlap somewhat, it was also helpful to treat irradiated films with dilute sodium hydroxide solutions to convert acids to carboxylates.[5] This ensures that the residual carbonyl peak is primarily due to the ester groups and allows for more accurate determination of the degree of hydrolysis. By using dilute aqueous sodium hydroxide as the base, hydrolysis of ester groups is avoided.[2,5]

A Nicolet Magna-560 FTIR spectrometer with a Pike grazing angle attachment (80° angle of incidence) was used for external reflection FTIR spectroscopy. An MCT detector was used in the spectrometer. The contact angle measurements were carried out with a FT 200 (first 10 Å) contact angle analyzer. A rotating analyzer ellipsometer (J.A. Woollam model M-44) was used to measure film thickness, assuming a film refractive index of 1.5.

Photohydrolyses. The photohydrolyses of the cross-linked (six bilayer) films were carried out by placing the film in a quartz test tube filled with a 50:50 v:v dioxane/water mixture.[6] A Hanovia 450 W medium-pressure Hg arc lamp cooled with a quartz jacket was used as the light source. The solution containing the film was first bubbled with nitrogen gas for 0.5 h to displace oxygen. The distance between the lamp and the quartz test tube (containing the films) was maintained at about 2.5 cm. The films were positioned in the test tubes so that the coated surface faced the lamp. The cross-linked films were irradiated for 10, 30, and 60 min. After irradiation, the films were rinsed with water and dried under nitrogen. Additionally,

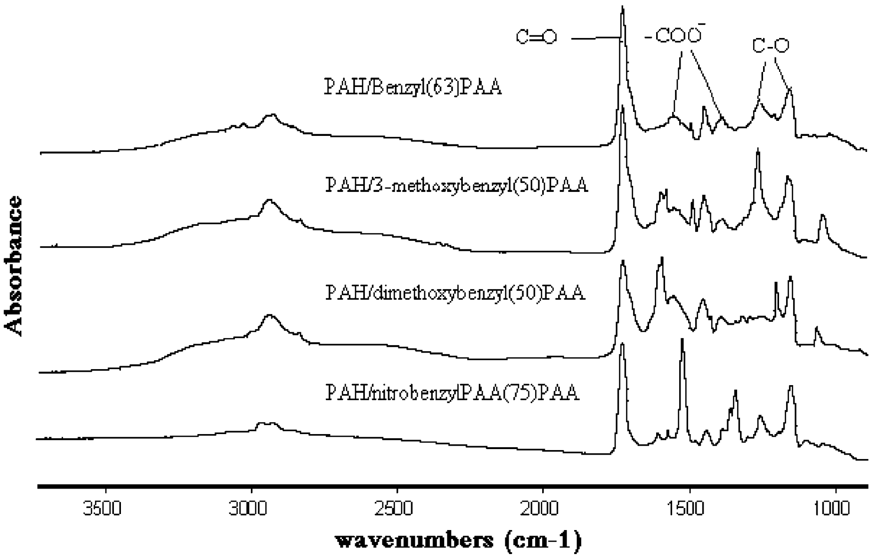


Figure 1. External reflection FTIR spectra of six bilayer PAH/dPAA films on Au (percent derivatization of each copolymer is shown in parentheses).

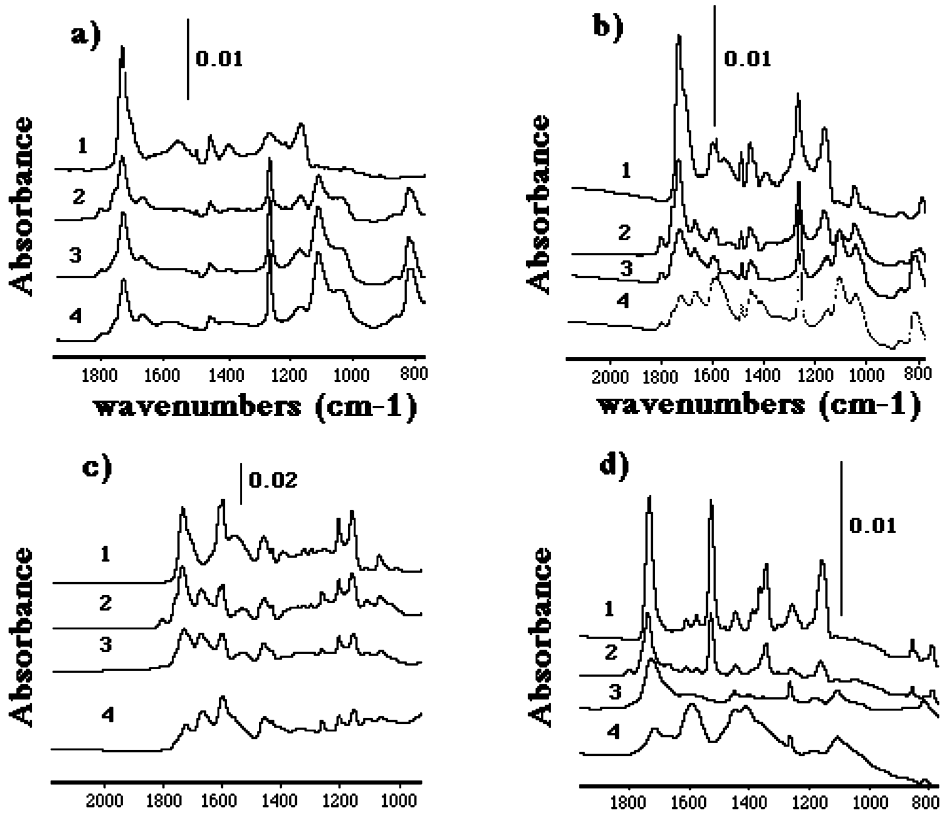


Figure 2. External reflectance FTIR spectra of six bilayer PAH/dPAA films on Au: (a) = BPAA, (b) = 3MBPAA, (c) = 3,5MBPAA, (d) = 2NPAA, 1 = initial film, 2 = cross-linked film, 3 = irradiated film (10 min), and 4 = base-treated film.

the cross-linked films were treated with dilute sodium hydroxide for 5 min and dried again under nitrogen.

Results and Discussion

Figure 1 shows the reflectance FTIR spectra of the four different six-bilayer PAH/dPAA films. The most prominent features in the spectra are the ester carbonyl peaks in the vicinity of 1735 cm^{-1}. The carbonyl stretch of underivatized, un-ionized acid groups overlaps with the ester carbonyl stretch and appears as a shoulder at about 1720 cm^{-1} in some cases. Carboxylate groups exhibit an asymmetric stretch at around 1535 cm^{-1} and a symmetric stretch at around 1400 cm^{-1}. The symmetric and asymmetric C−O−C stretches also appear between 1050 and 1270 cm^{-1} for all the films.

The surface IR spectra of each film are shown in Figure 2 prior to and after cross-linking, after irradiation for 10 min, and after treatment with dilute base. An examination of these spectra indicate that cross-linking of each film leads to a decrease or complete loss of the absorbance due to the carboxylate groups and the appearance of amide (at around 1675 cm^{-1}) and anhy-

Table 1. Loss of Ester Carbonyl Intensity (in %) after Cross-Linking and Photohydrolysis

	film type			
when measurement was taken	BPAA film	3MBPAA film	3,5MBPAA film	2NPAA film
after cross-linking[a]	50	38	16	56
after 10 min irradiation[b]	<5	62	61	56

[a] Percentage decrease in intensity from un-cross-linked films to cross-linked films. [b] Percentage decrease in intensity from cross-linked unirradiated films to films irradiated and treated with base.

Table 2. Thicknesses and Advancing Water Contact Angles for Films

	thickness (Å)			contact angle (deg)		
dPAA	un-cross-linked	cross-linked	irradiated after cross-linking[a]	un-cross-linked	cross-linked	irradiated after cross-linking[a]
BPAA	121 ± 0.3	109 ± 1	90 ± 5 (−17%)[b]	87 ± 0.2	74 ± 1	84 ± 1
3MBPAA	182 ± 4	168 ± 2	159 ± 3 (−5%)[b]	69 ± 1	70 ± 0.1	87 ± 1
3,5MBPAA	544 ± 3	429 ± 21	443 ± 9 (+3%)[b]	62 ± 0.3	74 ± 2	74 ± 1
2NPAA	141 ± 6	105 ± 5	89 ± 1 (−15%)[b]	87 ± 3	74 ± 1	51 ± 0.4

[a] Value after 10 min of irradiation and treatment with weak base. [b] Number in parentheses is percent of thickness lost (or gained) from cross-linking to irradiation/base treatment.

dride bands (between 1750 and 1810 cm^{-1}). The amide cross-link sites are most likely formed via thermal reactions between carboxylate−ammonium ion pairs.[2] The anhydride linkages presumably form by the reactions of ester and acid (or carboxylate) groups.

During both cross-linking and irradiation followed by base treatment, the intensity of the ester carbonyl peak decreases (Table 1). During cross-linking the 2NPAA film loses the most carbonyl intensity (−56%) followed by BPAA (−50%), 3MBPAA (−38%), and finally 3,5MBPAA (−16%). This is a significant indication that the 3,5MBPAA film is the most thermally stable film and retains its dimensions during cross-linking reactions. The loss of ester carbonyl intensity after irradiation/base treatment is an important measure of the degree to which ester groups are photohydrolyzed from the films. Also noteworthy is the observation that in all cases except the 2NPAA film, the intensity of the peaks due to the amide groups remains unaltered during irradiation and base treatment. This indicates that in most cases the cross-links are stable upon exposure to light. Once cross-linked, all films except those made with BPAA show significant photohydrolysis after 10 min.

Characterization of Layered Films by Ellipsometry and Water Contact Angle. The measured thicknesses and water contact angles for each film are displayed in Table 2. The two thickest films (from 3,5MBPAA and 3MBPAA) were both prepared from strongly acidic solutions due to their limited solubility at higher pH. As the pH of PAA solutions decreases, so does the charge density. As charge density decreases, the segmental population of polymer loops and tails increases, leading to thicker bilayers.[8] The physical properties (steric bulk, solubility, etc.) and the extent of derivatization of the initial polymers (BPAA = 63%; 3MBPAA = 50%; 3,5MBPAA = 50%; 2NPAA = 75%) are also likely to contribute to thickness variations. However, aside from increased steric bulk, our understanding as to why the 3,5MBPAA film exhibits significantly higher thickness than the films prepared from 3MBPAA is meager.

Cross-linking tends to decrease film thickness presumably because the ionic bonds (ammonium−carboxylate) are replaced with shorter covalent bonds (amide bonds).[2] The BPAA and 3MBPAA films lose less than 10%, the 3,5MBPAA film loses 21%, and the 2NPAA film loses about 26% of its thickness.

In the case of BPAA and 2NPAA films, the water contact angle decreases upon cross-linking, while the other two either increased or remained constant. This can be attributed partly to the nature of cross-linking reactions. First, amide bonds are formed from salts, which contribute to an increase in the contact angle due to a decrease in hydrogen bonding and film charge density. Second, ester groups are lost, which could contribute to the decrease in the overall contact angle due to the loss of hydrophobic aromatic groups. Thus, depending on which of these competing processes predominate, films of different water compatibilities are formed. This is further augmented from the measured contact angle data. For example, films prepared from 3MBPAA and 3,5MBPAA exhibited a higher degree of hydrophobicity upon cross-linking, consistent with IR data obtained for these films; insignificant loss of ester carbonyl is accompanied by significant amide bond formation. Similarly, a large loss of ester carbonyl (observed from surface IR data) for films derived from 2NPAA and BPAA is consistent with the observed decrease in the water contact angles of these films upon cross-linking.

After irradiation and base treatment, due to enhanced hydrophobicity, the water contact angles of BPAA and 3MBPAA increase. This is consistent with the formation of more radical hydrolysis type products, including cleavage of the ester linkage followed by loss of carbon dioxide from the polymer backbone.[6] The 2NPAA films become more hydrophilic upon irradiation, indicative of a typical ester hydrolysis to form an acid group.[5,6]

The water contact angle for the 3,5MBPAA does not change upon irradiation. Although carboxylate groups are formed during hydrolysis of this group (increasing hydrophilicity), two methoxy groups (also capable of hydrogen bonding) are lost. Furthermore, we have reported that cross-linked films made with underivatized PAA and PAH exhibit water contact angles of about 68°,[2] and this value is close to the value for the 3,5MBPAA films which have been cross-linked and photoirradiated for 10 min (74°). Indeed, as the 3,5MBPAA films are irradiated for longer periods (up to 1 h), their contact angles eventually reach a limiting value of 66°. Cross-linked PAA/PAH films which are hydrolyzed with strong base exhibit contact angle values lower than 10°.[2] Thus, in contrast to the films hydrolyzed by strong base, the photohydrolyzed 3,5MBPAA films exhibit contact angles closer to the model films containing underivatized PAA and PAH. These data suggest that photolysis, in addition to removing esters groups, alters the nature of the films to a lesser extent than hydrolysis with a strong base; hydrolysis by heating with a strong aqueous base results in swollen films with a higher degree of hydrophilicity.

Conclusions

We have shown that various PAA derivatives can be prepared from high molecular weight PAA by both Fischer esterification and a method utilizing DBU. These derivatized polymers form multilayered polyelectrolyte films by layer-by-layer deposition, and the substituted benzyl groups can be photocleaved from the films.

All of the films undergo cross-linking reactions upon heating. The cross-linking process converts the ammonium−carboxylate ionic bonds into covalent amide bonds. Some of the benzyl esters are not as stable as others when exposed to the high temperatures necessary for cross-linking. The relative stability of the ester groups of the films under cross-linking conditions is as follows: 3,5MBPAA > 3MBPAA > BPAA > 2NPAA.

All of the cross-linked films undergo ester photohydrolysis. The least photolabile ester appears to be BPAA. The esters of 3,5MBPAA and 2NPAA films undergo mostly heterolytic cleavage to form films containing acid groups. Alternatively, esters of BPAA and 3MBPAA film photohydrolyze to form films with fewer acid groups, presumably because more radical cleavage occurs. These results are consistent with the “meta effect”.

Acknowledgment. We thank Professor Merlin L. Bruening at Michigan State University for allowing us to use several of his instruments and for helpful discussions in the preparation of this manuscript. We also thank the ACS Petroleum Research Fund and the Centers for Fundamental Materials Research and Sensor Materials at MSU for partial support of this work. A.W.J. and D.K.M. also acknowledge support from the Faculty Research and Creative Endeavors committee, The President’s Research Investment Fund (PRIF), and the Research Excellence Fund at CMU. We thank Jinhua Dai for the preparation of 2NPAA.

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MA035321K