Acid-Enhanced Interfacial Polymer Layer Growth

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We report on the growth of interfacial multilayer structures formed from maleimide−vinyl ether alternating copolymers. The thickness and density of these polymer layers can be controlled by adding acid to the interlayer cross-linking reaction. We have demonstrated this control for several different interlayer cross-linking strategies, where amide, ester, urea, and urethane interlayer covalent bonds are formed. For all reactions, the addition of concentrated acid during polymer layer deposition resulted in a 2- to 4-fold increase in the loading density of the polymer relative to the acid-free reaction, depending on the acid used and its concentration. These findings are consistent with acid catalysis (HCl) and/or dehydration (H_2SO_4).

Introduction

Designing and constructing polymeric materials where there is explicit control over the identity of each molecular layer, in conjunction with covalent interlayer linking chemistry, is an emerging effort in interface science. The field of layered growth started with the work of Langmuir and Blodgett,[1,2] resulting in physisorbed L−B films, advanced through the discovery of self-assembling alkanethiol/gold monolayer structures[3−13] to covalent,[14−17] ionic,[18−34] polymeric,[35−52] and polyelectrolyte multilayers.[53−64] Such materials have found use in chemical sensing,[65−69] surface second-harmonic generation,[22,70,71] and electronics and electro-optics.[72] A

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common concern in all of these application areas is the extent of order and the uniformity of coverage of the layered assembly. We have developed a means to deposit maleimide−vinyl ether (MVE) alternating copolymer[73] multilayers, one layer at a time, with covalent interlayer linking chemistry[74,75] and are interested in achieving control over the density of individual polymer layers. We observe an increase in layer thickness and, in some cases, density when HCl or H_2SO_4 are added to the cross-linking reactions used in the polymer layer growth process. This work demonstrates that we have three distinct types of control over the construction of these materials. First, we can control the identity of the functional constituents incorporated into the polymer adlayer by substitution of the polymer side group(s).[75] Second, we have control over the covalent chemistry used to form the interlayer linkage for assembly of multilayer structures.[74] Third, the work we report here demonstrates that we can control the loading density of the polymer at each layer through the addition of HCl or H_2SO_4 to the cross-linking reaction.

The ability to design well-behaved thin film systems where there is some level of control over the density of specific functionalities within the adlayer matrix could prove beneficial in areas such as the design of sensor materials, for example, where each functional group behaves as an individual sensing element. Controlling the density of functional constituents within a layer could also provide a means to mediate conductivity or

diffusion. Our interest in the design of covalently bound polymer multilayer assemblies is based on the ability of these materials to mediate interfacial adsorption and desorption phenomena. We have reported recently on design schemes and deposition strategies for a variety of alternating copolymers using covalent interlayer attachment chemistry.[74,75] We observed that the addition of a small amount of concentrated sulfuric acid during ether cross-linking between polymer adlayers led to a marked increase in adlayer absorbance compared to the results for adlayers where no H_2SO_4 was added.[74] We have undertaken a study to understand this effect more fully and report our findings here. In addition to the acid-mediated enhancement in the ellipsometric thickness of the polymer adlayers, we observe a significant increase in absorbance per layer when interlayer linking chemistry is performed in the presence of H_2SO_4. The thickness measurements taken by themselves could be indicative of either an increase in the amount of material adsorbed or simply an increase in the extent of structural disorder within the layers. When these findings are viewed in light of the absorbance data, it is clear that the change we observe is an increase in adlayer density, and not simply disorder.

The enhancement of adlayer deposition with the addition of acid is not the same for all cross-linking reactions. To address the comparative importance of acid catalysis and dehydration in these reactions, we have studied adlayer deposition and cross-linking using H_2SO_4 and HCl. HCl enhances acid-catalyzed reactions, but cannot play a role in dehydration. The presence of H_2SO_4 in these systems could drive these reactions toward product formation according to LeChatelier's principle. In the ester and amide formation reactions, adipoyl chloride is used as the cross-linking agent. In these cases, it is likely that the reaction proceeds via the elimination of HCl, calling our assertion of adlayer thickness enhancement by dehydration into question. To better understand this reaction, we have prepared a separate substrate in a manner consistent with experimental conditions used in polymer adlayer deposition, except we omitted the polymer layer. We found that the surface acid chloride groups were converted to the corresponding carboxylic acid almost exclusively, indicating that the amide and ester formation reactions were between the amine or alcohol and a carboxylic acid, consistent with the explanations we offer for the enhanced deposition. The urea and urethane formation reactions proceed with the formation of a carbamic acid intermediate. The presence of water in the system would lead to decomposition to an amine and CO_2. In this case, the presence of H_2SO_4 leads to the removal of adventitious water in the reaction medium. In all cases, we observed measurably greater deposition of polymer with the addition of sulfuric acid than with the addition of hydrochloric acid, suggesting that, for these reactions, dehydration and protonation are both important, but dehydration plays a dominant role in mediating the reaction efficiency.

We have also examined polymer adlayer deposition as a function of acid concentration. We assembled ester-linked multilayers of poly(NPM−VOB) using adipoyl chloride as the cross-linker and varied the concentration of acid added to the reaction. The adlayer deposition

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Scheme 1. (Top Panel, Left to Right) Structures of Poly(3CPM−APVE), Poly(NPM−VOB), and Poly(4BPM−APVE); (Bottom Panel) Reaction Schemes for the Several Cross-linking Strategies Employed in This Work
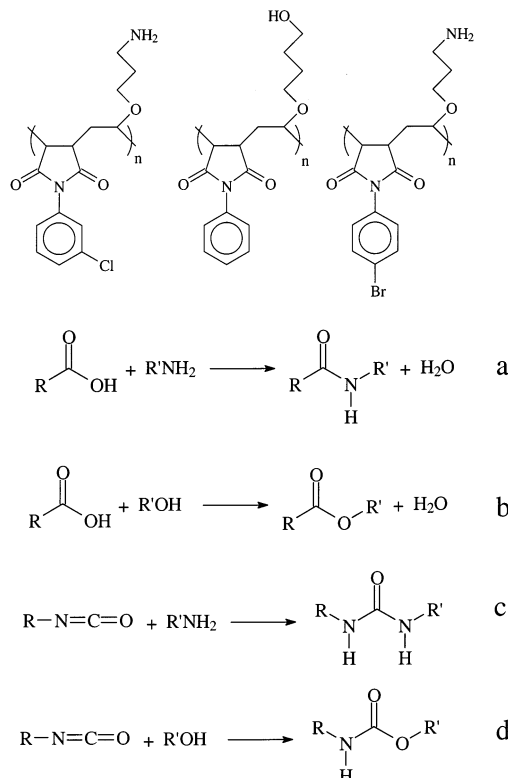
process depends linearly on acid concentration to a point, with the growth appearing to saturate at high acid concentrations. We also note that there is a marked difference between the deposition of the initial polymer layer for the reactions performed with HCl compared to those done with H_2SO_4. We consider the similarities and differences found for the addition of the two acids during the adlayer deposition reaction and interpret these effects in terms of the reactions responsible for adlayer cross-linking.

Experimental Section

Synthesis. We use the alternating copolymers poly(*N*-phenylmaleimide-*co*-1-vinyloxy-4-butanol), poly(NPM−VOB), poly(3-chlorophenylmaleimide-*co*-3-aminopropyl-1-vinyl ether), poly(3CPM−APVE), and poly(4-bromophenylmaleimide-*co*-3-aminopropyl-1-vinyl ether), poly(4BPM−APVE) (Scheme 1 top panel) in this study. The synthesis and layered interfacial assembly of these polymers has been detailed elsewhere.[74,75] These polymers are capable of participating in ester, urethane, ether (poly(NPM−VOB)). and amide and urea (poly(3CPM−APVE) and poly(4BPM−APVE)) interlayer linkages.

Substrate Preparation. Gold-coated substrates and silicon and quartz wafers were cleaned using piranha solution (3:1 $H_2SO_4:H_2O_2$) for ~15 min. (*Caution! Piranha solution is a strong oxidizer!*) These substrates were then removed and rinsed with ethanol and then water and dried under a stream of nitrogen. Silicon and quartz substrates were used in subsequent adlayer deposition reactions without further modification. For these substrates, the surface silanol groups are used directly in adlayer deposition reactions. Prior to adlayer deposition, gold substrates were exposed to 0.01 M 6-mercapto-1-hexanol in 60:40 ethanol:H_2O solution at 40 °C for ~30 min. Following activation of the surface with 6-mercapto-1-hexanol,

the terminal hydroxyl groups were used in adlayer deposition reactions. The substrates used for the formation of ester and amide linkages were first reacted with adipoyl chloride in the presence of 4-methylmorpholine for 30 min at 35 °C. The substrates used for the formation of urea and urethane linkages were reacted with 1,6-diisocyanatohexane in the presence of 4-methylmorpholine. Following surface modification, the substrates were exposed to ≈5 mL of the appropriate polymer solution at a concentration of 10 mM in reagent-grade dimethyl sulfoxide. For reactions where acids were added, the concentration range examined was between 0.073 and 0.290 M for HCl and between 0.108 and 0.432 M for H_2SO_4. It should be noted that these are the final concentrations after the addition of the acid to the polymer solutions. The concentrations of HCl and H_2SO_4 are not the same in these experiments because the concentrated reagents were measured and added by volume, not concentration.

Optical Ellipsometry. Ellipsometric thickness data on the deposited polymer multilayer assemblies were acquired using a Rudolph Auto-EL II optical ellipsometer operating at 632.8 nm. The software used for data collection and processing was acquired from the manufacturer (Rudolph DAFIBM). The refractive index of the polymer adlayers was taken to be $n = 1.54 + 0i$ in all cases. The thickness of the polymer multilayer assembly was measured after each deposition cycle. Regression of the ellipsometric data was performed using Microcal Origin V.6.0 software.

UV−Visible Spectroscopy. Absorption spectra of the polymer adlayers were acquired using a Cary 300 UV−visible spectrophotometer. For these measurements, the adlayers were deposited on quartz substrates and absorption spectra acquired after each deposition cycle. Data were collected at 190 and 500 nm at a scan rate of 600 nm/min with 1-nm spectral resolution.

Infrared Spectroscopy. FTIR spectra of the polymer adlayers on gold substrates were collected using a Nicolet Magna 750 FTIR spectrometer. Spectral resolution was 4 cm^{-1} for all measurements. An external reflectance sample mount set at an incidence angle of 80° was used for data collection. Spectra of samples assembled on silicon were acquired using a Nicolet Magna-IR 550 setup to acquire data in transmission mode at Brewster's angle.

Results and Discussion

We report here on the role(s) of HCl and H_2SO_4 in mediating the cross-linking reactions used in the deposition of covalently linked maleimide−vinyl ether alternating copolymer multilayers.[74,75] The addition of a small amount of acid to the reaction vessel mediates the deposition of polymer adlayers. We have investigated the role of acid in the mediation of amide, ester, urea, and urethane bond formation, and we observe adlayer deposition enhancement in each case. Both spectroscopic and ellipsometric data point to the acid enhancement of adlayer thickness, by a factor of between 2 and 3, depending on the functionality being formed. The chemistry we use for adlayer growth is deliberately self-terminating at each layer,[15,16,20,74,75] and the addition of subsequent layers requires an activation step. For the cases where the thickness and absorbance both increase as a result of adding acid to the interlayer linking reaction, the data are the result of an increase in the density of the polymer adlayers. We consider the results for specific systems next. The UV−visible and ellipsometric data for each system are summarized in Tables 1 and 2.

Amide Cross-Linked Polymer Multilayers. Poly-(3CPM−APVE) is bound to the substrates we use here by first reacting the surface functionality with adipoyl

Table 1. Dependence of Ellipsometric Thickness on Acid Addition for Amide, Ester, Urea and Urethane Crosslinked Adlayers

cross-link functionality	without acid (Å/layer)	with 0.145 M HCl (Å/layer)	with 0.216 M H_2SO_4 (Å/layer)
amide	19		30
ester	22	34	45
urea	10	35	39
urethane	12	20	32

chloride and then reacting the polymer amine functionalities with terminal acid chlorides. Spectroscopic and ellipsometric data for this system are shown in Figure 1. Multilayers of these amine-terminated polymers can be assembled using adipoyl chloride as the cross-linking agent to form amide interlayer bonds (Scheme 1a). This reaction is performed under anhydrous conditions and proceeds with or without the addition of acid, and for both experimental conditions, we obtain reproducible behavior. Ellipsometry shows regular layer growth with a slope of 19 Å/layer, and UV−visible absorbance spectroscopy shows a linear increase in adlayer absorbance with a slope of 0.019 au/layer.

The addition of concentrated H_2SO_4 to the reaction vessel during layer deposition gives rise to a measurable change in the layer growth characteristics. In the presence of 0.216 M H_2SO_4, we recover ellipsometric data showing 30 Å/layer and UV−visible absorbance data showing 0.042 au/layer. As discussed above, the adlayer deposition chemistry we use ensures the deposition of individual polymer layers. Because there is an increase in both ellipsometric thickness and absorbance per layer with the addition of H_2SO_4 to the layer deposition reaction, the data indicate an increase in adlayer density.

In an attempt to resolve whether protonation of a reaction intermediate accounts for our findings, we have repeated these experiments with the addition of HCl
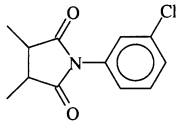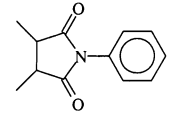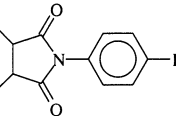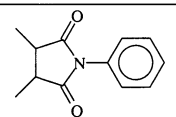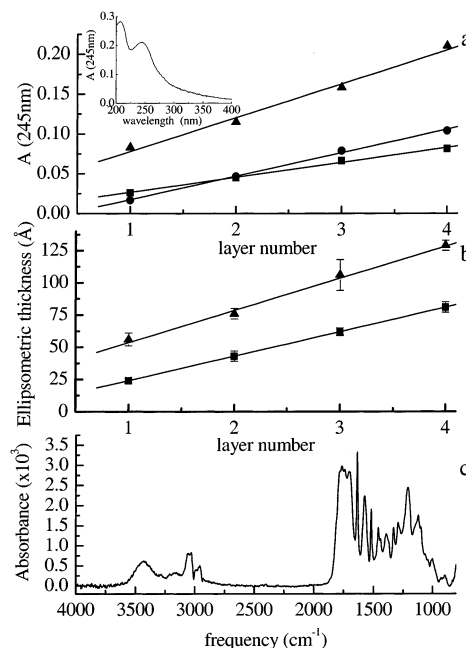

Figure 1. Data for amide-linked poly(3CPM−APVE). (a) Dependence of optical absorption at 245 nm on the number of polymer adlayers. ■ are data points for acid-free growth, ● are data for adlayer growth with 0.145 M HCl, and ▲ are data for adlayer growth with 0.216 M H_2SO_4. Inset: UV−visible absorption spectrum for a four-layer assembly of poly(3CPM−APVE). (b) Ellipsometric thickness of poly(3CPM−APVE) adlayers as a function the number of layers deposited for growth without acid added (■) and with 0.216 M H_2SO_4 added (▲). (c) FTIR spectrum of a two-layer assembly of poly(3CPM−APVE).

instead of H_2SO_4. The presence of 0.145 M HCl during the adlayer cross-linking reaction also gives rise to enhanced adlayer growth, with UV−visible absorbance spectroscopy yielding a slope of 0.0294 au/layer, intermediate between the anhydrous and H_2SO_4-mediated

Table 2. Dependence of Absorbance Data on Acid Addition for Amide, Ester, Urea, and Urethane Cross-linked Polymer Adlayers

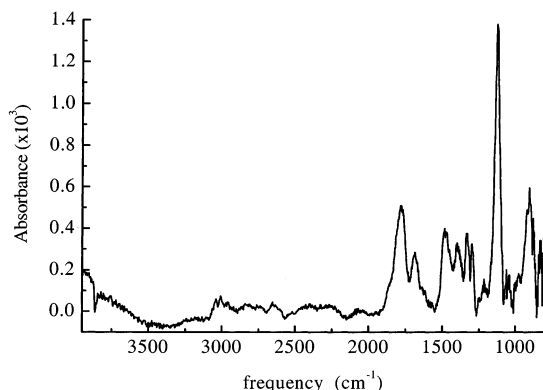| Crosslink functionality	chromophore	Absorbance maximum	Without acid (a.u./layer)	With 0.145 M HCl (a.u./layer)	With 0.216 M H_2SO_4 (a.u./layer)
Amide		245 nm	0.0188	0.0294	0.0424
Ester		231 nm	0.0309	0.0303	0.0603
Urea		255 nm	0.0043	0.0052	0.0102
Urethane		231 nm	0.0093	0.0265	0.0348

Figure 2. FTIR spectrum of a substrate treated with adipoyl chloride showing essentially complete conversion of the terminal acid chlorides to carboxylic acids.

reactions. We were unable to acquire ellipsometry data for the HCl-mediated reaction because HCl damaged the gold substrate surface, likely due to the destruction of the chromium adhesion layer. The FTIR spectrum of the cross-linked adlayers is shown in Figure 1. We observe the stretching resonances characteristic of amides and free NH functionalities at approximately 1655 cm^{-1} (amide I) and 3300 cm^{-1}, respectively, and the bands are identical for adlayers grown without acid and with H_2SO_4 and HCl. In all cases, the reaction products are the same. It appears to be counterintuitive that the addition of HCl (or H_2SO_4 for that matter) would enhance the deposition due to the fact that we use adipoyl chloride as a cross-linking agent, which generates HCl as a cross-linking reaction product. To resolve this issue, we prepared a substrate under similar experimental conditions to those for polymer deposition and observed that the acid chloride groups were almost exclusively converted to the corresponding acid (Figure 2). Thus, the layer deposition reaction is between an amine and a carboxylic acid, and the explanations of dehydration and protonation for acid addition follow logically. We believe the mechanism of the reaction to be simple nucleophilic substitution by addition–elimination, where the reaction proceeds by attack of the acid from the polymer nucleophilic terminal amine, with the elimination of H_2O.

Ester Cross-Linked Polymer Multilayers. The attachment of poly(NPM–VOB) to the substrate and subsequent adlayer deposition proceeds in the same manner as described above for poly(3CPM–APVE), with poly(NPM–VOB) reacting with adipoyl chloride to produce an ester moiety (Scheme 1b). Spectral and ellipsometric data are shown in Figure 3. For ester formation, we observe enhanced adlayer density when either H_2SO_4 or HCl are added to the reaction. For the deposition of the polymer layer in the absence of acid, we recover a growth rate of 22 Å/layer from ellipsometric data, 34 Å/layer for growth when HCl concentration is 0.145 M and 45 Å/layer for growth when the final H_2SO_4 concentration is 0.216 M (Table 1). For adlayers formed either without addition of acid or with H_2SO_4 addition, UV–visible absorbance results are consonant with the ellipsometric data, yielding 0.0309 au/layer at 231 nm for acid-free growth and 0.0603 au/layer for 0.216 M H_2SO_4 mediated growth. The absorbance data for adlayers grown in the presence of 0.145 M HCl yield a slope of 0.0303 au/layer, the same to within the
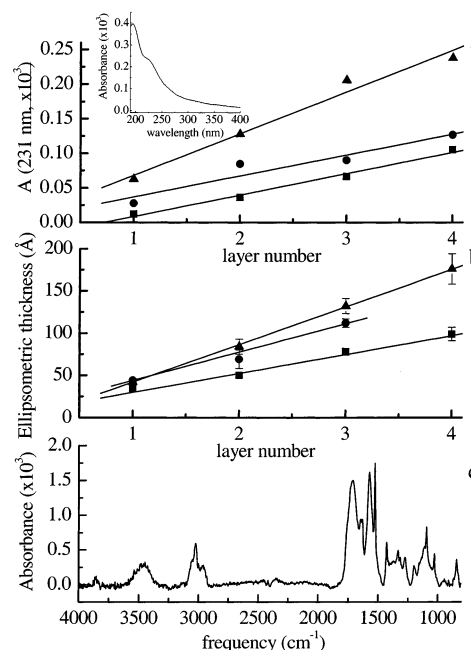

Figure 3. Data for ester-linked poly(NPM–VOB). (a) Dependence of optical absorption at 231 nm on the number of polymer adlayers. ■ are data points for acid-free growth, ● are data for adlayer growth with 0.145 M HCl, and ▲ are data for adlayer growth with 0.216 M H_2SO_4. Inset: UV–visible absorption spectrum for a four-layer assembly of poly(NPM–VOB). (b) Ellipsometric thickness of poly(NPM–VOB) adlayers as a function of the number of layers deposited for growth without acid added (■), with 0.145 M HCl (●), and with 0.216 M H_2SO_4 added (▲). (c) FTIR spectrum of a two-layer assembly of poly(NPM–VOB).

experimental uncertainty as that measured for acid-free growth. This finding, in conjunction with the ellipsometry data, indicates that the adlayer density does not change for ester formation, but the polymer morphology does change upon adlayer exposure to HCl. The experimental data for ester formation suggest that it is not acid catalysis, but rather dehydration that dominates the ester formation reaction. The function of H_2SO_4 here is to sequester H_2O as it is formed during the reaction. We note that this reaction is somewhat more difficult to control than the other reactions presented here. In some instances, it was difficult to deposit more than three molecular layers before large deviations from linearity were noticeable. The FTIR spectrum of the ester-cross-linked polymer layers is shown in Figure 3. Our findings for the growth of ester-cross-linked adlayers with the addition of acid are consistent with dehydration and protonation as discussed above for the amide-cross-linked adlayers. We also examined the growth of ester-cross-linked polymer adlayers without the addition of acid and with the addition of morpholine. We observed no significant enhancement for this reaction, consistent with our assertion that the acid chloride groups are predominantly converted to the corresponding carboxylic acid (Figure 2). Had these groups been acid chlorides, the presence of the base would have led to an enhancement according to LeChatelier's principle.

Urea Cross-Linked Polymer Multilayers. Poly-(4BPM–APVE) adlayers are bound to substrates cross-linked by the formation of a urea functionality (Scheme 1c). Spectral and ellipsometric data for this system are shown in Figure 4. The reaction to form urea linkages
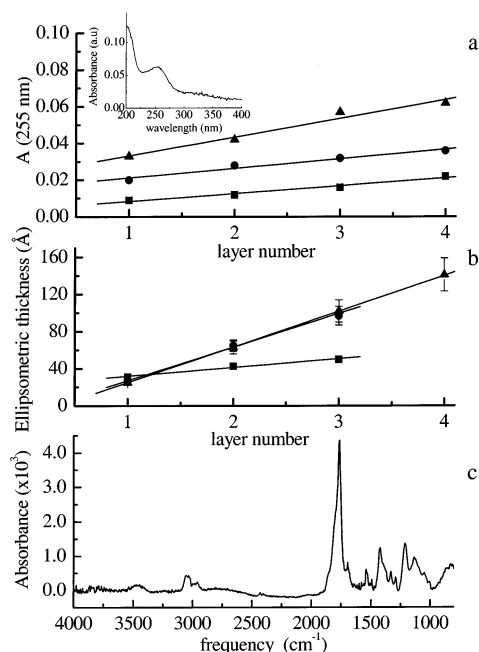
Figure 4. Data for urea-linked poly(4BPM−APVE). (a) Dependence of optical absorption at 255 nm on the number of polymer adlayers. ■ are data points for acid-free growth, ● are data for adlayer growth with 0.145 M HCl, and ▲ are data for adlayer growth with 0.216 M H_2SO_4. Inset: UV−visible absorption spectrum for a four-layer assembly of poly(4BPM−APVE). (b) Ellipsometric thickness of poly(4BPM−APVE) adlayers as a function of the number of layers deposited for growth without acid added (■), with 0.145 M HCl (●), and with 0.216 M H_2SO_4 added (▲). (c) FTIR spectrum of a two-layer assembly of poly(4BPM−APVE).

is between the polymer amine group and an isocyanate functionality, present in the adlayer structure by virtue of our use of 1,6-diisocyantohexane as a cross-linking reagent. The function of 1,6-diisocyanatohexane in the formation of adlayer assemblies is analogous to adipoyl chloride in the reactions described above. When adlayers are grown under anhydrous conditions, we observe modest adlayer growth, with ellipsometry indicating a thickness of 10 Å/layer and UV−visible absorbance at 238 nm yielding a linear dependence on adlayer deposition cycles with 0.0043 au/layer. We note that the thicknesses and absorbance values we recover for this reaction scheme are lower that those recovered for an acid-free ester and amide layer growth, indicating a relatively low polymer adlayer density under these reaction conditions. We observe adlayer density enhancement with the addition of HCl or H_2SO_4 to the cross-linking reaction, with ellipsometry indicating 35 Å/layer for growth with 0.145 M HCl and 39 Å/layer for growth with 0.216 M H_2SO_4. As with the ester formation, the polymer morphology does play some role in the adlayer growth because the UV−visible absorption data yield slopes of 0.0052 au/layer for 0.145 M HCl and 0.0102 au/layer for 0.216 M H_2SO_4. Thus, while the ellipsometric data point to similar adlayer thicknesses, the absorbance data point to substantially different loading densities, even after the difference in acid concentration for the two reactions is taken into account.

We have established that the reaction chemistry used for forming covalent multilayers using isocyanate/amine chemistry depends sensitively on the presence of water.[16] Under anhydrous conditions, single layers can form in a regular manner, and with the addition of water, adlayer growth becomes much less well controlled. The addition of concentrated H_2SO_4 or HCl to the reaction vessel during layer deposition appears to facilitate urea formation. We understand this effect in the context of H_2SO_4 removing adventitious water that would lead to the formation and subsequent degradation of the unstable carbamic acid functionalities, precluding their participation in urea formation. The isocyanate carbon is highly electrophilic, making it susceptible to attack by nucleophiles such as water and amines. Attack at this site by water leads to the formation of the carbamic acid, which is unstable. Reaction of the carbamic acid with an amine leads to the formation of a urea, and in the absence of acid this reaction appears to be inefficient. In these cases, the addition of acid to the reaction likely serves to protonate the isocyanate group, making it more electrophilic and increasing its reactivity toward nucleophiles such as alcohols and amines. The enhancement observed with H_2SO_4 is, again, probably due to its ability to sequester water that would lead to the degradation of the carbamic acid. As noted above, the enhancement in absorbance data is almost a factor of 2 greater for H_2SO_4 addition than for HCl addition, even though the concentration of H_2SO_4 is only 1.5 times greater than that of HCl. In an anhydrous environment, we expect H_2SO_4 to function predominantly as a monoprotic acid.

Urethane Cross-Linked Multilayers. The reaction of poly(NPM−VOB) with 1,6-diisocyanatohexane produces urethane interlayer linkages (Scheme 1d). The substrate, containing terminal −OH functionality, is exposed to 1,6-diisocyanatohexane in the presence of methylmorpholine in anhydrous acetonitrile to produce an isocyanate-terminated surface. When depositing poly(NPM−VOB) on this activated substrate (Figure 5), we observe an enhancement in layer density when the adlayer deposition reaction is performed with the addition of HCl or H_2SO_4. The ellipsometric data yield a slope of 12 Å/layer for acid-free deposition, 20 Å/layer in the presence of 0.145 M HCl, and 32 Å/layer in the presence of 0.216 M H_2SO_4. UV−visible absorbance data of the polymer adlayers show a similar trend, with a slope of 0.0093 au/layer for acid-free growth, 0.0265 au/layer for HCl-mediated adlayer deposition, and 0.0348 au/layer for H_2SO_4-mediated deposition. This reaction is qualitatively similar to that used for urea interlayer formation, save for the formation of a urethane moiety. In contrast to the urea interlayer linking chemistry, both the ellipsometry and absorbance data point to an adlayer density enhancement that is greater for H_2SO_4 than for HCl. Similar to acid-free deposition for the urea cross-linked adlayers, we recover modest adlayer growth, indicating that the surface reactivity of isocyanate functionalities is not as facile as that of acid chlorides. As discussed above, the reaction of isocyanates with nucleophiles such as amines and alcohols is susceptible to competitive reaction with water, resulting in the presence of carbamic acid terminal functionalities, which would likely decompose to amines. However, in the presence of concentrated acid we observe an increase in the ellipsometric thickness. In the case of concentrated H_2SO_4, the fact that this species is an efficient dehydrating agent minimizes the competitive effects of
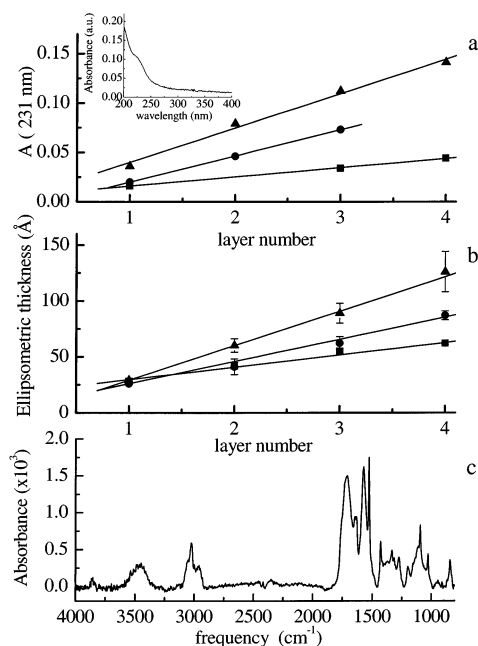
Figure 5. Data for urethane cross-linked poly(NPM–VOB). (a) Dependence of optical absorption at 231 nm on the number of polymer adlayers. ■ are data points for acid-free growth, ● are data for adlayer growth with 0.145 M HCl, and ▲ are data for adlayer growth with 0.216 M H_2SO_4. Inset: UV–visible absorption spectrum for a four-layer assembly of poly(NPM–VOB). (b) Ellipsometric thickness of poly(NPM–VOB) adlayers as a function of the number of layers deposited for growth without acid added (■), with 0.145 M HCl (●), and with 0.216 M H_2SO_4 added (▲). (c) FTIR spectrum of a two-layer assembly of poly(NPM–VOB).

water, allowing for the efficient formation of the urethane moiety. In the case of hydrochloric acid, we would again expect to see an enhancement due to acid catalysis either in protonation of the imine or in stabilization of an alkoxide reaction intermediate.

The effect of adding H_2SO_4 or HCl to the cross-linking reactions used in the formation of several polymer adlayer structures is, in general, to increase either the density or the disorder of the material deposited at the interface. The cross-linking reactions we use are simple addition–elimination reactions that rely on nucleophilic attack. These reactions are typically efficient and in many cases can be catalyzed by the presence of acid or driven to completion by the abstraction of water. Both H_2SO_4 and HCl can serve as a source of protons while H_2SO_4 can also function as a dehydrating agent. Thus, for reactions that are enhanced more by the presence of H_2SO_4 than HCl, such as ester and urea formation, it is reasonable to expect both acid catalysis and dehydration contribute to our experimental findings. Because both amide and ester reactions proceed with the elimination of water, the dehydrating capability of H_2SO_4 plays a major role in these reactions. While the formation of urea and urethane linkages does not proceed by water elimination, it should be noted that the intermediate (carbamic acid) formed in these reactions is susceptible to nucleophilic attack by water, leading to the decomposition of this species. In this case, the ability of H_2SO_4 to remove water would lead to enhancement in the deposition of these polymers. We can view these findings in the context of LeChatelier's principle, where the removal of reaction products (H_2O

Table 3. Slopes of the UV–Visible Absorbance Data for the Addition of HCl and H_2SO_4 as a Function of Concentration for the Cross-linking of Poly(NPM–VOB) with Adipoyl Chloride To Form an Ester Linkage[a]

volume of acid added (mL)	[HCl] (M)	adlayer absorbance (au/layer)	[H_2SO_4] (M)	adlayer absorbance (au/layer)
0.03	0.073	0.0135	0.108	0.0154
0.06	0.145	0.0157	0.216	0.0296
0.12	0.290	0.0097	0.432	0.0273

[a] The data were acquired using lower molecular weight poly(NPM–VOB) than was used for the measurements presented in Table 2.
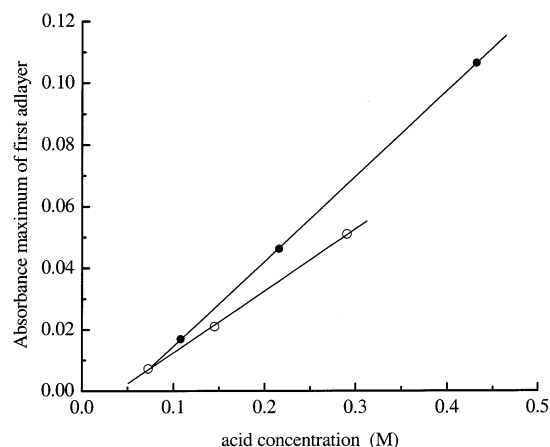

Figure 6. Dependence of ester-bound poly(NPM–VOB) monolayer absorbance at 231 nm on acid concentration for the initial polymer layer. (○) HCl added; (●) H_2SO_4 added. The different concentration dependencies for each acid indicates the importance of both protonation and dehydration in the ester formation reaction.

for these reactions) would tend to drive the cross-linking reactions to completion. These findings thus provide a simple means of controlling the density of covalently linked polymer adlayers at a variety of interfaces.

We have also measured adlayer deposition density as a function of acid concentration. In this work, we have assembled ester-linked multilayer systems of poly-(NPM–VOB) using adipoyl chloride as the cross-linking agent, where we varied the concentration of HCl or H_2SO_4 as a function of deposition cycle. We performed these reactions with HCl concentrations in the range of 0.073–0.290 M and with H_2SO_4 concentrations in the range of 0.108–0.432 M. We find that, for both HCl and H_2SO_4, increasing acid concentration initially yields an increase in the slopes of the absorbance data, and for the highest concentrations of acid used here, we observe a modest *decrease* in the slope of the absorption data (Table 3). These data suggest that there is an optimal pH range for the deposition reactions, indicative of a balance between multiple phenomena that contribute to the adlayer deposition process. For both acids, we observe an enhancement in the thickness of the initial layer that is related linearly to acid concentration, with H_2SO_4 producing thicker initial adlayers than HCl (Figure 6). In each case, the growth of the initial polymer adlayer is enhanced to a greater extent than the growth of subsequent adlayers. We understand this effect in the context of the greater availability of the reactive groups on the substrate surfaces and possibly the reactivity of the surface-bound functionalities being

greater than the functionalities contained in the cross-linking agents. This latter issue remains open to investigation but, from a phenomenological point of view, the experimental acid concentration dependence of adlayer growth demonstrates the ability to control polymer adlayer density by synthetic means.

Conclusions

We have demonstrated the ability to control the density of polymer adlayer deposition at interfaces using a simple modification to the cross-linking reactions used to connect adlayers. This new capability provides three distinct levels of control over interfacial adlayer preparation. We have control over the identity of the functional moieties incorporated into the polymer used in adlayer deposition by synthetic means. This level of control is important in the preparation of materials where specific chemical functionalities are required. We have also demonstrated previously that polymer adlayers can be assembled in discrete layered structures where each layer is of molecular dimension. We can connect individual polymer adlayers to one another by means of either ionic complexation or the formation of covalent cross-links between polymer side groups. The third level of control, which is the focus of the work we have reported here, is the ability to control the density of the polymer adlayers. This new capability bears directly on our ability to control mass transport properties within these ultrathin interfacial materials. The control that we have established over adlayer density is determined by the mechanism(s) of the cross-linking reactions used in multilayer construction. The addition of H_2SO_4 or HCl to the cross-linking reactions gives rise to an enhancement in the extent of reaction because of dehydration and/or acid catalysis, depending on the reaction used. For all of the systems examined here we recover significant enhancement in the absorbance as well as ellipsometric data for the polymer deposition reactions to which sulfuric acid is added, relative to the results for the corresponding acid-free reactions. The addition of HCl gives rise to smaller enhancements in thickness and, sometimes absorbance as well, suggesting that the presence of HCl influences the extent of disorder in the polymer adlayer as well as mediating the cross-linking reaction to adjacent layers. Because these adlayer deposition reactions are self-terminating at each step, the observed enhancements in ellipsometric thickness and absorbance are necessarily the result of control over the density of the polymer adlayer. We anticipate that the addition of H_2SO_4 or HCl to the polymer adlayer cross-linking reactions will play a role in determining the interface morphology, and this is an issue that we intend to address.

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