Strategies for Covalent Multilayer Growth. 2. Interlayer Linking Chemistry

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We report a strategy for the covalent assembly of polymer multilayers at interfaces, where growth is accomplished one layer at a time. The individual layer constituents are maleimide−vinyl ether alternating copolymers with side groups that possess reactive functionalities. The identity of the polymer layer side groups determines the chemistry we employ in interlayer linkage formation. We report on the selective creation of amide, ester, ether, urea, and urethane interlayer linkages. We achieve controlled multilayer growth using each of these covalent bonding schemes. The resulting multilayer structures show linear growth in terms of thickness, measured ellipsometrically, and total mass loading, measured by UV−visible and FTIR spectroscopies.

Introduction

The design of interfacial materials where there is explicit control over the identity and ordering of the constituent layers is an area of intense research effort.[1−8] To date, there have been several means devised to control layered material growth at interfaces, including Langmuir−Blodgett deposition,[9,10] thiol/gold monolayer self-assembly,[11−14] and metal bisphosphonate layer growth.[7,15−35] Each method has its advantages and shortcomings, so there is a continued need to identify novel layer growth chemistry where the resulting materials are relatively well-organized and the chemistry binding the layers together is sufficiently robust to be useful. We describe here the assembly of several polymer multilayer systems where the interlayer linking chemistry involves the formation of covalent bonds. The scheme we report here is, in a sense, the layer-by-layer cross-linking of thin polymer films where the structure of the polymers in a given layer (parallel to the substrate) can be controlled. The polymers we use in the creation of the multilayer structures have been described in detail in the preceding paper.[36] Careful choice of the polymer side groups allows layers to be added to the interface through either ionic or covalent interlayer linking chemistry,[37,38] facilitating the assembly of materials that can function either as ionic conductors or as insulators.

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We are interested in covalently linked polymer multilayers for several reasons. Earlier work on zirconium bisphosphonate (ZP) ionically linked multilayer structures showed that interlayer excitation transport was inefficient by virtue of the polarizable zirconium bisphosphonate sheets that connect the layers in these materials.[35] To control interlayer excitation transport in layered interfaces, a necessary first step is the elimination of these polarizable layers; we replace the ZP functionality with covalent organic functionalities (vide infra). We have chosen to use polymers as the layer constituents in this work because of the combined ease of preparation and the degree of structural versatility available with maleimide−vinyl ether alternating copolymers.[39] Polymers provide structural integrity within individual layers, allowing the opportunity to create relatively porous structures where there is a gradient in some property of the interface (e.g., dipole moment) along the surface normal axis.[40] Such interface properties are likely to be of use in chemical separations and sensing.

The polymers we reported in the preceding paper[36] allow control over the individual layers through synthetic design.[33] The interlayer linking chemistry applied to these polymers that we report in this paper allows for a second level of control; we can choose the means of interconnection between individual layers. In this work we will focus on an array of covalent interlayer linking chemistries that we have applied to layered material growth. The resulting materials are all robust and the strategies we discuss should be applicable to the growth of a variety of other materials in layered structural motifs. We anticipate that this level of interface structural control will find use in the design of materials intended for specific purposes, such as the creation of a chemical potential gradient normal to the substrate plane.

Experimental Section

We describe the procedures for substrate preparation and then present several strategies for covalent linking of polymer layers. We have used gold, quartz, and silicon substrates for this work, with the choice of substrate being determined by the measurement to be performed. We used gold substrates for optical null ellipsometry and FTIR measurements, silica substrates for UV−visible spectroscopy, and oxidized silicon for ellipsometry and Brewster's angle transmission FTIR measurements. We have chosen specific chemical systems to demonstrate the chemistry of interest and have not attempted to report on all of the possible permutations of polymers and interlayer bonding schemes.

Substrate Preparation. Gold, quartz, and silicon wafers were prepared by cleaning in piranha solution (3:1 H_2SO_4:H_2O_2) for ≈15 min, followed by rinses with ethanol and water. The substrates were then dried under a stream of nitrogen gas. The quartz and silicon wafers were then exposed to a 5 M HCl solution for ≈15 min followed by ethanol and water rinsing and drying under nitrogen. After cleaning and preparation, the substrates were exposed to the appropriate solution to give the desired terminal functionality.

To functionalize the gold surfaces with hydroxyl groups, the cleaned substrates were exposed to a 60:40 ethanol:water 10 mM solution of 6-mercaptohexan-1-ol for ≈30 min at ≈40 °C. For the quartz and oxidized silicon surfaces, the surface silanol groups were used directly and without prior treatment for further functionalization.

To produce amine-terminated surfaces, the gold substrates were exposed to a 60:40 ethanol:water 10 mM solution of cystamine dihydrochloride for 30 min at ≈40 °C. Quartz and silicon wafers were exposed to ≈5% solution of 3-aminopropyltrimethoxysilane in toluene at room temperature overnight.

To create a surface terminated with an acid chloride functionality, the substrate is reacted with an (α,ω)-diacid chloride. Hydroxyl-terminated gold substrates were exposed to a solution of 10 mL of anhydrous acetonitrile, 0.3 mL of 4-methylmorpholine, and 0.3 mL of adipoyl chloride under an inert atmosphere of argon at room temperature for 30 min to produce a surface terminated with an acid chloride functionality. Quartz and silicon wafers were treated in the same way, where the surface silanol groups were reacted with adipoyl chloride.

To create an epoxide-terminated surface, gold substrates that had been previously prepared to present a hydroxyl terminal functionality were exposed to a 1% (v/v) solution of 1,4-butanediglycidyl ether in anhydrous acetonitrile. Concentrated sulfuric acid (5 drops) was added dropwise to the reaction vessel to facilitate the epoxide ring opening. The reaction was allowed to proceed at room temperature for ≈5 min before rinsing. Silicon and quartz wafers were reacted directly with 1,4-butanediglycidyl ether in a manner similar to that for the gold substrate. For these substrates, the reaction is directly with the silanol groups present on the surface.

For isocyanate-terminated substrates, the gold substrates treated with 6-mercapto-1-hexanol were immersed in a solution of 10 mL of anhydrous acetonitrile, 0.3 mL of 4-methylmorpholine, and 0.3 mL of 1,6-diisocyanatohexane and heated to ≈40 °C for 30 min. As with the other reactions, the quartz and silicon substrates were treated in a similar manner and their native silanol groups were used as the reactive functionalities.

Optical Null Ellipsometry. Values of ellipsometric thickness of the deposited polymer multilayer assemblies were acquired using a Rudolph Auto-EL II optical null ellipsometer. This instrument is equipped with a HeNe laser operating at 632.8 nm. The Software (Rudolph DAFIBM) used for data collection was acquired from the manufacturer. The refractive index was taken to be $\mathbf{n} = 1.54 + 0i$ for all films. Even though this value may differ by a small amount depending on the identity of the polymer film, changes over a physically realistic range affect the recovered thickness negligibly.

UV−Visible Spectrophotometry. The absorption spectra of the multilayer assemblies were acquired using a Cary 300 UV−visible spectrophotometer. The layers were synthesized on quartz and the data were acquired after the deposition of each individual layer. The scan rate for all measurements was 600 nm/min and the spectral resolution was 1 nm. The data were processed and plotted using Microcal Origin version 6.1 software.

Infrared Spectroscopy. FTIR spectra of the multilayer assemblies on gold substrates were collected using a Nicolet Magna 750 FTIR spectrometer operating with Omnic software. The spectral resolution was set to 4 cm^{-1} for all spectra collected. An external reflectance sample mount set at an incidence angle of 80° was used for data collection. Spectra of samples grown on silicon were acquired using a Nicolet Magna-IR 550 set up to acquire data in the transmission mode using a Brewster's angle attachment.

Results and Discussion

The goal of this work is to demonstrate that careful choice of the functional groups incorporated into alternating copolymers provides accessibility to simple reactions that form amide, ester, ether, urea, and urethane functionalities, allowing the regular growth of multilayer systems. In many cases, there is more than one way to generate a particular covalent interlayer linkage,

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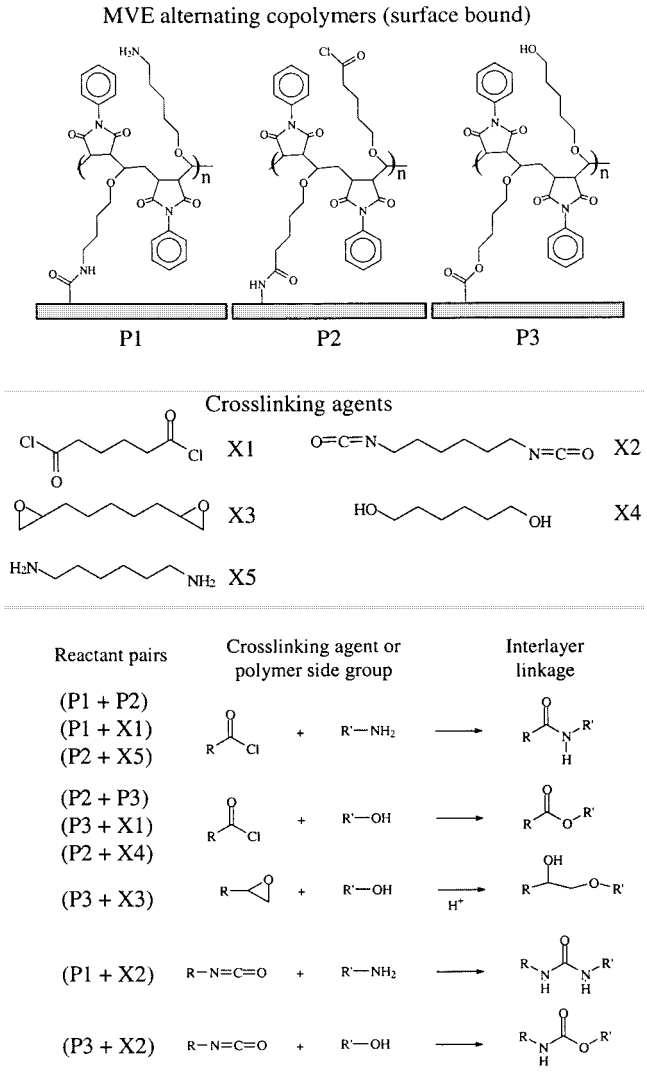
with the order of the chemical functionalities used being determined by the polymer native functionality or initial modification of the substrate.

It is our intent to demonstrate the facile nature of our approach to the controlled growth of multilayer interface structures. We use alternating copolymerization chemistry where the polymerization reaction is templated from the substrate initially. At each step of the growth process, the reactive interface cannot grow another layer until it is presented with the requisite monomer. By presenting the interface with only one type of monomer at a time, controlled growth of individual molecular layers is possible. In cases where the same multilayer is available through multiple routes (save for orientation of the interlayer linking functionality), we report the reaction(s) that we have demonstrated experimentally. Depending on the monomer species used in the MVE polymer synthesis, either the maleimide or vinyl ether side groups can be used for interlayer attachment.

Amide Chemistry. Amide interlayer linkages are created by reaction of an acid chloride with an amine and we report three viable routes. (1) An amine-terminated substrate is exposed to a solution of an MVE alternating copolymer with acid chloride side group functionalities, resulting in the direct formation of an amide bond between the polymer side groups and the substrate. Subsequent layers are added by exposure of the acid chloride containing a polymer (topmost) layer to an (α,*ω*)-diamine, followed by reaction of the aminated surface with the MVE alternating copolymer (P2 + X5 in Scheme 1). (2) An (acid chloride)-terminated substrate is exposed to a solution of an MVE alternating copolymer with amine-terminated side groups. Controlled multilayer growth is achieved by reacting the polymer amine side group with an (α,*ω*)-diacid chloride (adipoyl chloride) followed by exposure to the MVE polymer (P1 + X1 in Scheme 1). This layer growth scheme is identical to the first save for the orientation of the resulting amide interlayer linkage. (3) An amine-terminated substrate is exposed to a MVE alternating copolymer containing acid chloride side groups, followed by exposure to a MVE alternating copolymer with amine-terminated side groups (P1 + P2 in Scheme 1). In this scheme, no interlayer linker is necessary. The choice of initial polymer layer in this scheme is determined by the reactive functionality presented by the substrate.

Copolymerization of 3-chlorophenylmaleimide and 3-aminopropyl-1-vinyl ether produces poly(3-CPM−APVE),[36] a polymer that is capable of participating in amide interlayer linkage formation. Reacting poly(3-CPM−APVE) with adipoyl chloride leads to the formation of amide interlayer linkages. The IR spectrum of the amide-linked multilayer assembly (Figure 1b) reveal amide I, II, and III bands, where the amide I band corresponds to the carbonyl stretching mode centered at ≈1655 cm^{-1}. Amide II and III bands correspond to N−H bending vibrations and C−N stretching modes occurring at approximately 1595 and 1421 cm^{-1}, respectively. In addition, the band centered at ≈3330 cm^{-1} corresponds to the stretching modes of the free −NH groups. UV−visible spectroscopy is used to monitor layer deposition, by observing the aromatic absorbance band centered at 248 nm. The observed spectral red shift relative to the *N*-phenylmaleimide copolymer is the result of the chloro functionality at the 3-position. We observe a loading density for the amide-linked assembly that is constant with the number of MVE polymer layers (Figure 1c). From the ellipsometric data (Figure 1a) we recover a slope of 19 Å/layer for the amide-linked multilayer, consistent with that seen for several other interlayer linking strategies.

Scheme 1. (Top) Idealized Schematics of Surface-Bound MVE Alternating Copolymers (P1 = Amine-Terminated MVE Copolymer, P2 = (Acid Chloride)-Terminated MVE Copolymer, and P3 = Hydroxyl-Terminated MVE Copolymer; (Center) (α,*ω*)-Difunctional Cross-linking Agents Used in This Work; (Bottom) Various Reactions between Polymer (P) and Cross-linking Agent (X) or Different Polymer (P)



Ester Chemistry. Ester interlayer linkages are achieved by the reaction of an acid chloride with an alcohol. There are three routes to multilayer formation using this chemistry. (1) A MVE alternating copolymer with hydroxyl-terminated side groups is reacted with an (acid chloride)-terminated substrate. Multilayer assembly is achieved by reacting the polymer hydroxyl side groups with a diacid chloride followed by exposure to the MVE polymer (P3 + X1 in Scheme 1). (2) The complement of the first route can be used, where the

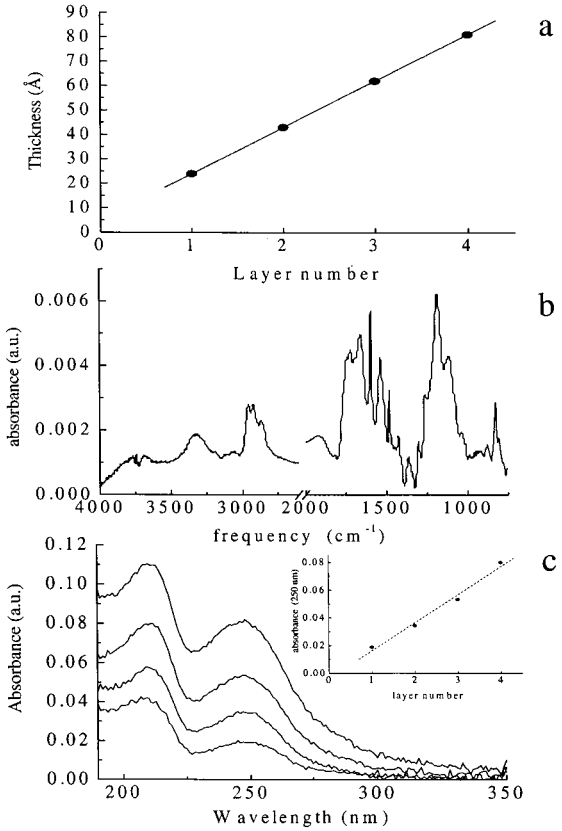


Figure 1. Poly(3CPM−AVPE) with amide interlayer linkage. (a) Dependence of ellipsometric thickness on the number of layers; (b) IR spectrum; (c) UV−visible spectra as a function of the number of layers. Inset: Dependence of absorption maximum on the number of layers.

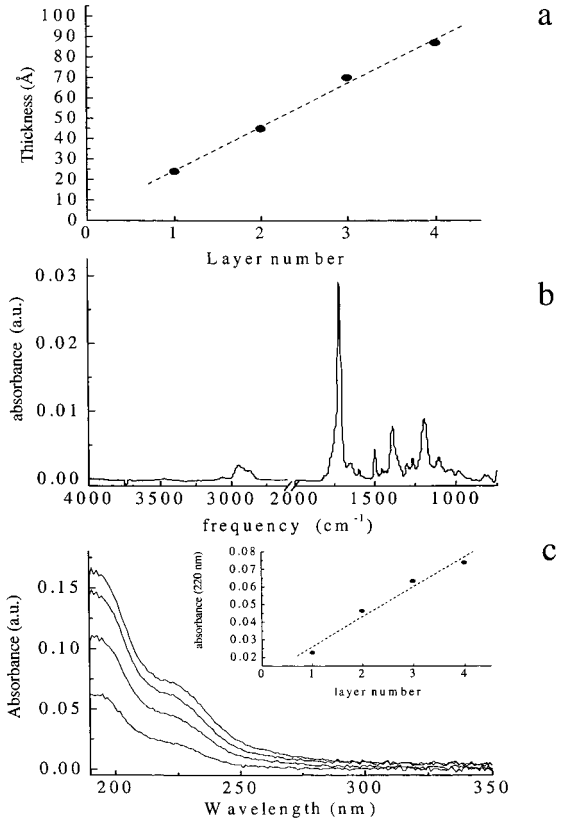


Figure 2. Poly(NPM−VOB) with ester interlayer linkage. (a) Dependence of ellipsometric thickness on the number of layers; (b) IR spectrum; (c) UV−visible spectra as a function of the number of layers. Inset: Dependence of absorption maximum on the number of layers.

MVE polymer contains (acid chloride)-terminated side groups and the interlayer linking moiety is an (α,ω)-diol (P2 + X4 in Scheme 1).

To realize this chemistry, we used the alternating copolymer of *N*-phenylmaleimide (NPM) and 1-vinyloxy-4-butanol (VOB), poly(NPM−VOB) (Figure 1a). The reaction of poly(NPM−VOB) with adipoyl chloride results in an ester-linked multilayer assembly. Linear growth was seen in the ellipsometric data (Figure 2a), with a slope of 21 Å/layer. As discussed in earlier work, it is not a straightforward matter to evaluate the thickness of a layer relative to a molecular structure calculation (e.g., molecular mechanics) because the loading density of the interface is not known quantitatively. The thickness we recover experimentally is consistent with other multilayer structures we report here (vide infra) and have reported elsewhere. The absorbance data indicate a linear growth as well (Figure 2c, inset), although it is not possible to determine the absolute loading density from these data because the extinction coefficient at 220 nm for poly(NPM−VOB) is not known.

A slight modification of this reaction scheme has been reported previously.[41] In that work, the reactive polymer side group is attached to the maleimide monomer and the vinyl ether monomer is terminated with a diisopropylphosphonate functionality; the interlayer linking chemistry can proceed through the maleimide monomers. In this reaction scheme, the monomers are 4-hydroxyphenylmaleimide (HPM) and ethyl vinyl ether diisopropyl phosphonate (VEP), and the interlayer linking moiety is adipoyl chloride. We note that phosphoester formation is precluded in this layer growth scheme because of the presence of the diisopropyl protecting groups on the phosphonate functionality.[41] The MVE polymer is capable of participating in ionic and/or covalent interlayer linkages. For ionic multilayer formation, the phosphonate groups are deprotected by reaction with bromotrimethylsilane,[41] resulting in the efficient hydrolysis of these groups to the corresponding phosphonic acid. Sequential exposure of the interface to M^{4+} (M = Zr, Hf) and the MVE polymer, with deprotection chemistry used as required, results in ionic multilayer formation. Figure 3a shows the infrared spectrum of a multilayer of poly(HPM−VEP), linked by the formation of zirconium bisphosphonate moieties. For covalent interlayer linkage, the terminal hydroxyl group of the poly(HPM−VEP) polymer is capable of participating in ester, ether, or urethane interlayer linkages. Figure 3b shows the IR spectrum of a four-layer stack of poly(HPM−VEP) assembled using ester-linking chemistry. The ester carbonyl stretching is centered at ≈1720 cm^{-1} (superimposed on the maleimide asymmetric C=O stretch). The broad band centered around 3200 cm^{-1} is an indication of residual water or hydrogen-bonded phosphonic acid functionalities within the multilayer. The ellipsometric and UV−visible spectroscopic data for this multilayer indicate linear growth. We recover a slope of 16 Å/layer for the ellipsometric data (Figure 3c). Regression of the UV−visible absorbance data was

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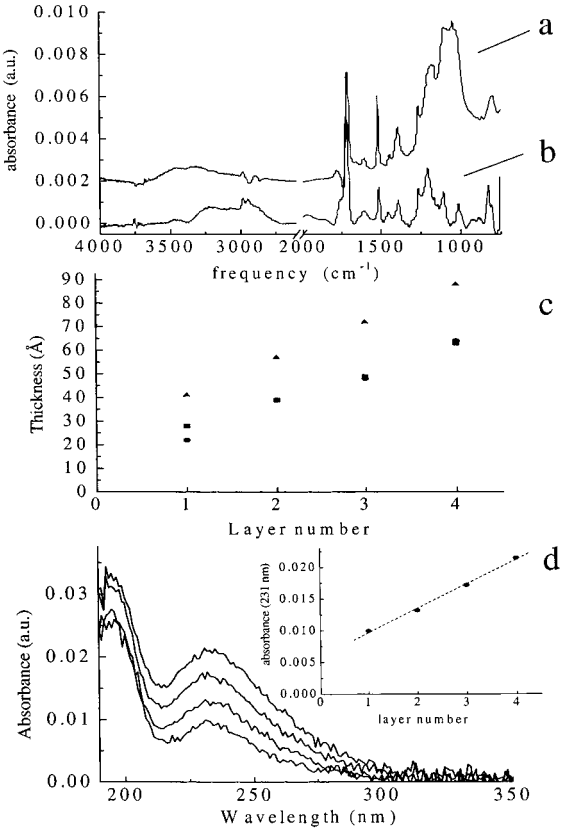

Figure 3. Poly(HPM−VEP) with ionic and covalent interlayer linkages. Top panel: (a) Infrared spectrum of ionically bound multilayers and (b) IR spectrum of covalently bound multilayers. The spectra have been offset for clarity. (c) Dependence of ellipsometric thickness on the number of layers. (d) UV−visible spectra as a function of the number of layers. Inset: Dependence of absorption maximum on the number of layers.

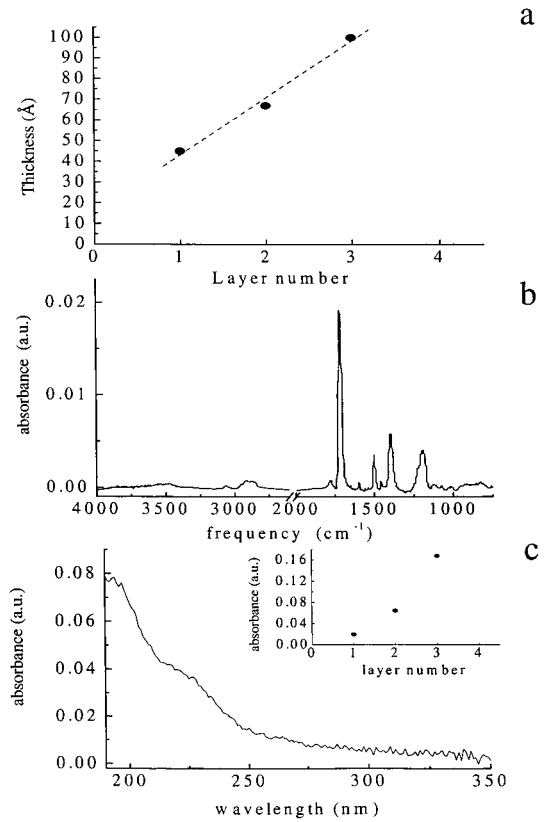

Figure 4. Poly(NPM−VOB) with ether interlayer linkage. (a) Dependence of ellipsometric thickness on the number of layers; (b) IR spectrum; (c) UV−visible spectra as a function of the number of layers. Inset: Dependence of absorption maximum on the number of layers.

made possible by monitoring the aromatic absorbance band centered at 231 nm (Figure 3d).

Ether Chemistry. We have demonstrated ether connections between MVE polymer layers using a ring-opening reaction of an epoxide with a hydroxyl group. The reaction of an MVE polymer with hydroxyl-terminated side groups with an epoxide-functionalized substrate in the presence of a strong acid leads to ether-linked multilayer assemblies. Subsequent exposure of the MVE polymer surface to an (α,ω)-diepoxide yields an epoxide-terminated surface ready for further reaction (P3 + X3 in Scheme 1).

The reaction of an adlayer of poly(NPM−VOB) with 1,4-butane diglycidyl ether leads to ether linkages. Multilayer assembly was monitored using ellipsometry and FTIR and UV−visible spectroscopies. A linear response was observed for the regression of the ellipsometric data (Figure 4a), and we recover a slope of 29 Å/layer. This thickness is substantially greater than that which we observe for the other multilayer assemblies, suggesting either greater loading density or greater conformational disorder within the MVE polymer layer. We note that the formation of ether interlayer linkages appears to be limited to the deposition of two or three layers before terminating. There are several interesting features contained in the data for this system. First, the UV−visible spectroscopy suggests that there is a much higher loading density of the chromophore when compared to the deposition of the same polymer system using either ester or urethane interlayer linkage (Figure 4b), and this finding is consistent with the ellipsometric data. The anomalously high layer density may be the result of the way we performed the reaction. We used concentrated sulfuric acid to facilitate the epoxide ring-opening reaction and to promote ether formation. There is no analogous reaction step in the formation of ester or urethane interlayer bonds. Repeating the epoxide ring-opening reaction with HCl instead of H_2SO_4 yielded lower density layers. We observe a similar pattern when the reactions for the ester-, amide-, and urethane-linked system are performed in the presence of H_2SO_4 versus HCl, suggesting the importance of dehydration by the H_2SO_4 in these reactions. We will explore this issue more fully in a subsequent study. We also note that there is an unexpectedly large IR resonance near 1700 cm^{-1} for the ether-linked assembly (Figure 4c). This is not an expected result because the ring-opening reaction should yield a secondary alcohol and an ether (Scheme 1). One possible explanation for this observation is the oxidation of the alcohol to a ketone, and this result is consistent with the absence of a strong OH stretching resonance (Figure 4c). To test for the possibility of this reaction, we reacted an oxidized silicon substrate with 1,4-butane diglycidyl ether. The IR spectrum of the ether-modified substrate is dominated by resonances associated with the asymmetric C−O−C stretch centered about 1100 cm^{-1} (Figure 5a). The substrate was then immersed in anhydrous acetonitrile and a few drops of concentrated sulfuric acid were added to

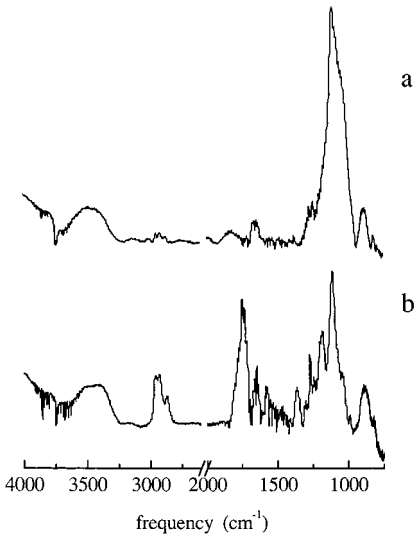

Figure 5. Ether chemistry for modified substrate. (a) FTIR showing C−O−C stretch of epoxide prior to reaction; (b) FTIR of ring-opened system after reaction, indicating ketone and acid functionalities.

facilitate the ring-opening hydrolysis reaction. The substrate was then heated to ≈40° for 30 min. The IR spectrum of the reacted substrate showed a marked decrease in the C−O−C stretch, consistent with the ring-opening reaction, and the presence of C═O stretching bands of almost equal intensity (Figure 5b). The carbonyl resonance appears as a doublet, with one peak centered at ≈1726 cm^{-1} and the other at about 1745 cm^{-1}. These two resonances are consistent with the formation of an aldehyde and a carboxylic acid, respectively.[42] This chemistry is difficult to control beyond the deposition of about two to three molecular layers, after which we observe no further growth. If the epoxide groups are being opened and subsequently oxidized, as the IR data suggest, then they are rendered capable of participating in interlayer bonding. It is also possible that the epoxide reaction proceeds to the intralayer, which would also preclude the formation of interlayer ether linkages. It may be possible to minimize such side reactions by running these reactions at room temperature, using strictly anhydrous solvents, and minimizing atmospheric exposure.

Urea Chemistry. Urea linkages are made by the reaction of an amine with an isocyanate. An isocyanate-functionalized substrate is exposed to an MVE polymer with amine-terminated side groups. The surface layer of a polymer is reacted with a (α,ω)-diisocyanate and then with another layer of the same MVE polymer (P1 + X2 in Scheme 1). The complementary chemistry where an amine-terminated surface is reacted with a MVE polymer containing isocyanate side groups is also possible.

We use poly(3-CPM−APVE)[36] to grow urea-linked multilayer structures. Reacting poly(3-CPM−APVE) with 1,6-diisocyanatohexane leads to urea formation. The IR band assignment for the urea-linked multilayer structure is virtually identical to that for the amide-linked multilayer, save for differences in band intensities, as expected. The IR spectrum of the amide-linked multilayer assembly (Figure 1b) reveals amide I, II, and III bands where the amide I band corresponds to the carbonyl stretching mode centered at ≈1655 cm^{-1}. Amide II and III bands correspond to N−H bending vibrations and C−N stretching modes occurring at approximately 1595 and 1421 cm^{-1}, respectively. In addition, the band centered at ≈3330 cm^{-1} corresponds to the stretching modes of the free NH groups. This band is significantly larger in the urea-linked multilayer than in the amide-linked layers, as expected, because each urea moiety possesses two free NH groups. We also observe larger amide II and III bands for the same reason. As with the amide-linked multilayers, we monitor the 248-nm absorbance band—which corresponds to the 3-chlorophenylmaleimide moiety—using UV−visible spectroscopy. We observe a higher loading density of the polymer for the amide-linked assembly than for the urea-linked multilayer (Figure 6c). One explanation for this finding is that urea formation may be less efficient than amide formation under our reaction conditions (reaction conditions were identical for both deposition schemes). The ellipsometric data for the urea-linked assembly show a slope of 10 Å/layer. This result is smaller by a factor of ≈2 compared to the amide-linked system and is consistent with the UV−visible absorbance data.

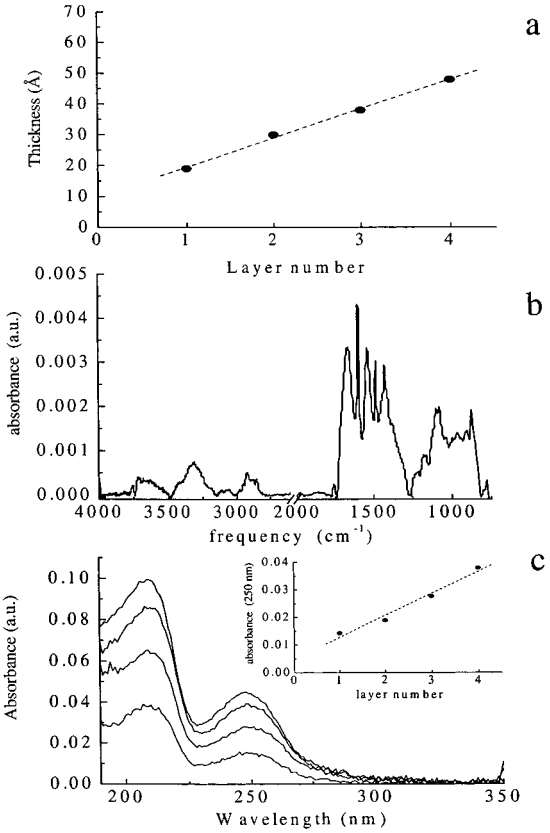

Figure 6. Poly(3CPM−AVPE) with urea interlayer linkage. (a) Dependence of ellipsometric thickness on the number of layers; (b) IR spectrum; (c) UV−visible spectra as a function of the number of layers. Inset: Dependence of absorption maximum on the number of layers.

Urethane Chemistry. The formation of urethane linkages can be accomplished by the reaction of a hydroxyl group with an isocyanate group. We report two such schemes here. (1) A hydroxyl-terminated substrate

(42) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds, 5th ed.*; John Wiley & Sons: New York, 1991.

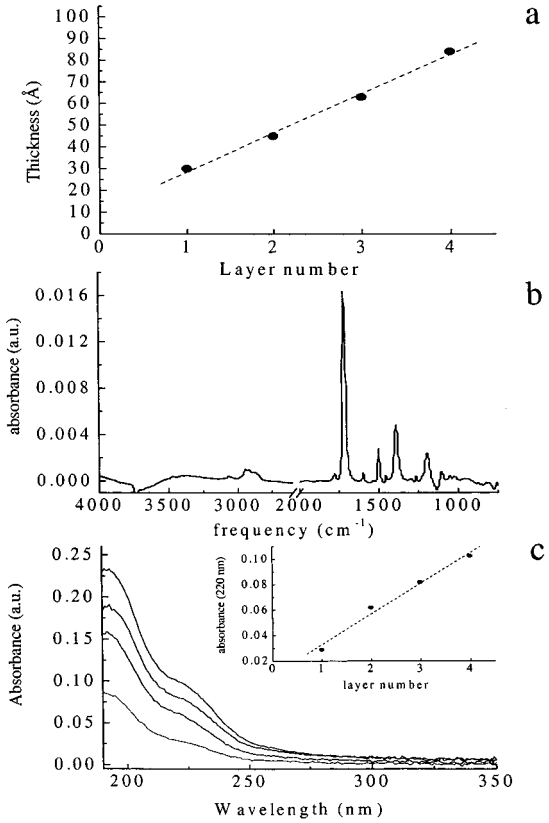

Figure 7. Poly(NPM−VOB) with urethane interlayer linkage. (a) Dependence of ellipsometric thickness on the number of layers; (b) IR spectrum; (c) UV−visible spectra as a function of the number of layers. Inset: Dependence of absorption maximum on the number of layers.

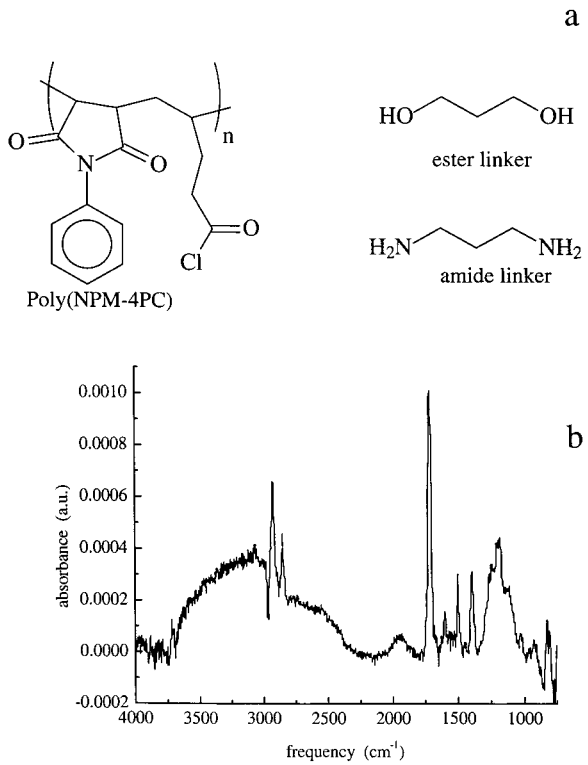

Figure 8. Poly(NPM−4PC). (a) Structures with amide and ester linkers. (b) IR spectrum of a poly(NPM−4PC) layer bound to the substrate by an ester linkage and with remaining acid chloride functionalities hydrolyzed by exposure to air.

is reacted with an (α,ω)-diisocyanate, followed by exposure to an MVE polymer with hydroxyl-terminated side groups. Multilayers are assembled by alternate exposure of the substrate to the diisocyanate and the MVE polymer (P3 + X2 in Scheme 1). (2) An MVE polymer with isocyanate-terminated side groups is exposed to a hydroxyl-terminated substrate. This reaction results in the formation of a urethane linkage. Multilayer assembly is achieved through alternate exposure to a diol and the MVE polymer.

We use poly(NPM−VOB) and 1,6-diisocynatohexane to form urethane-linked multilayer assemblies. The ellipsometric data (Figure 7a) reveal linear growth with a slope of 18 Å/layer, consistent with that seen for the amide-linked layers and larger by a factor of ≈2 than that for the urea-linked multilayers. This finding suggests that the reaction of isocyanates with alcohols is more efficient than that with amines. Growth of the urethane-linked layers was monitored using FTIR and UV−visible spectroscopies, and regular growth was observed with these methods as well (Figure 7b,c).

In addition to the alternating copolymerization of maleimides and vinyl ethers, we can also use alkenes as reactive monomers. The interlayer linking chemistry we describe above is equally applicable to such polymers and in all cases is determined by the terminal functionalities of the resulting polymer side groups. The copolymerization of NPM and 4-pentenoyl chloride, poly(NPM−4PC), is capable of participating in both ester and amide interlayer linkages as shown in Figure 8a. This reaction scheme appears to be less successful than the same interlayer-linking chemistry used for the MVE alternating copolymers. For poly(NPM−4PC) we see layer growth that is limited to one or two molecular layers before terminating. One explanation for this behavior is that the oxidation of the acid chloride groups to the acid followed by intermolecular hydrogen bonding between the acid functionalities render these groups less accessible for subsequent layer deposition. It is also possible for the putative carboxylic acid groups to hydrogen bond with solvent or adventitious water during rinsing and measurement. Examination of the IR data (Figure 8b) is consistent with these explanations. The broad −OH stretch centered at ≈3100 cm^{-1} is characteristic of intermolecular hydrogen bonding. A second piece of evidence in support of this information is the position of the C═O band in these polymer adlayers. Dimerization of carboxylic acids shifts the carbonyl stretch to a lower frequency than that of the free carboxylic acid. For a poly(NPM−4PC) adlayer the C═O stretch is centered at ≈1710 cm^{-1}, whereas for an acid chloride, the C═O stretch is expected to be near 1775 cm^{-1}.

Conclusions

We have demonstrated our ability to design and assemble polymer multilayers with layer-by-layer control of the polymer identity and interlayer linking chemistry. We have presented the design and synthetic schemes for the preparation of these polymers in the preceding paper. In this paper we have presented our strategies for assembling these materials into layered structures where the identity of the polymer side groups allows simple chemical reactions to be used to link the

individual layers. The functionalities formed by this simple chemistry include amide, ester, ether, urea, and urethane. The design and assembly schemes we present here have the distinct advantage of easy preparation of the monomers and polymers, ease of assembly of these materials into multilayers, and relatively short deposition times. We have also shown that, depending on the functional groups of the copolymer, it is sometimes possible to assemble these materials where prior surface preparation is not necessary, as is the case for reactions on silicon and quartz wafers. In these cases, the silanol groups serve as the reactive moiety to which our polymers can be tethered.

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