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Elucidating the balance between metal ion complexation and polymer conformation in maleimide vinyl ether polymer multilayer structures

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We have grown layered assemblies of poly[4-(*N*-maleimido)azobenzene-*co*-diisopropyl (2-vinyloxy)-ethylphosphonate], (poly(MAB-VEP)), where interlayer connections are made using zirconium bisphosphonate (ZP) ionic complexation chemistry. The linear optical response of the azobenzene chromophore side group shows constant layer density but a layer-dependent ratio of *trans*-to-*cis* isomers. Optical null ellipsometry data show a constant average layer thickness despite the change in conformer ratio. The change in conformer ratio with the growth of multiple polymer layers results from the steric constraints imposed on the polymer side groups by the formation of the ZP interlayer linkage. The driving force for metal ion complexation is greater than the isomerization barrier of S_0 azobenzene. Once the layers are formed, the side-groups do not exhibit any changes in conformer ratio, even when exposed to UV for a prolonged period.

Introduction

There has been significant recent interest in the design and growth of mono- and multilayer thin films because of their potential utility in chemical sensing,[1] surface modification[2,3] and device applications.[4] From a more fundamental perspective, gaining control over surface chemical identity, structure and thickness is a challenge to the ingenuity of the chemistry community. Many chemical routes to the growth of layered structures at interfaces have been demonstrated, using both crystalline and amorphous substrates. In most of these cases, the dominant growth axis is perpendicular to the substrate surface because individual molecules are used as the fundamental building block for these multilayer interfaces. Intralayer interactions between constituents have, in many cases, been considered to be coincidental and of secondary importance. Recently, several groups have recognized the importance of structural organization within individual layers and they have demonstrated layered growth where the greatest degree of structural integrity resides within the layers.[5–13] Structural integrity parallel to the substrate has been demonstrated for siloxane-based layers,[5–10] electrostatically-bound polymer multilayers[11,12] and polymers containing pendant phosphonate groups, where metal phosphonate interlayer linking chemistry is used.[13] Our interest lies in this latter family of interfaces because of the structural integrity both between and within layers and the chemical versatility of the polymers used in the construction of the layers.

We have reported recently on the photoinduced polymerization of maleimides and vinyl ethers.[14] This family of polymers is thermally stable and, with the appropriate choice of monomer, the properties of the resulting polymer can be adjusted to be suitable for many applications. Among the maleimide vinyl ether (MVE) polymers we have made are those containing pendant protected phosphonate functionalities.[13] Using silane-based deprotection chemistry,[15,16] we have been able to grow multilayers of MVE polymers using Zr phosphonate (ZP) interlayer linking chemistry. For these materials, the adjustment of their properties is achieved by controlling the length of the vinyl ether phosphonate monomer and with the identity of the maleimide N-substituent. For the maleimide monomer substituents, it is synthetically a simple matter to attach chromophores or molecules capable of isomerization and probe the optical properties of these substituents once incorporated into the polymer matrix. In this work we have used 4-(*N*-maleimido)azobenzene (MAB) and diisopropyl (2-vinyloxy)ethylphosphonate (VEP) as monomers in the synthesis of poly(4-(*N*-maleimido)azobenzene-*co*-diisopropyl (2-vinyloxy)ethylphosphonate), (poly(MAB-VEP)). Absorption data on the azobenzene chromophore side group show that the density of each layer is the same but the ratio of conformers ([*trans*]/[*cis*]) decreases with the addition of polymer layers. Optical null ellipsometry data show that the average layer thickness remains constant despite the change in conformer ratio. The change in conformer ratio and constant layer thickness with the addition of polymer layers points to the two different length scales that absorption and ellipsometry sense. The absorption data are the result of local steric limitations imposed on the azobenzene side groups by the formation of $Zr(RPO_3)_2$ linkages. The driving force for metal ion complexation to produce polymer interlayer linkages exceeds the ground state (S_0) isomerization barrier of azobenzene. Once the layers are formed, the side-groups do not exhibit changes in conformer ratio, even after prolonged periods of UV exposure. On a more macroscopic level, the constant ellipsometric thickness per layer points to the disorder inherent in thin films made from polymers.

Experimental

Surface priming chemistry

Fused silica substrates were cleaned by immersion in piranha solution (*Caution! Piranha solution is a potent oxidizer*) for 10 minutes and rinsed with flowing distilled water, followed by hydrolysis in 2 M HCl for 5 minutes, and a final distilled water rinse. Samples were dried with a N_2 stream and were primed

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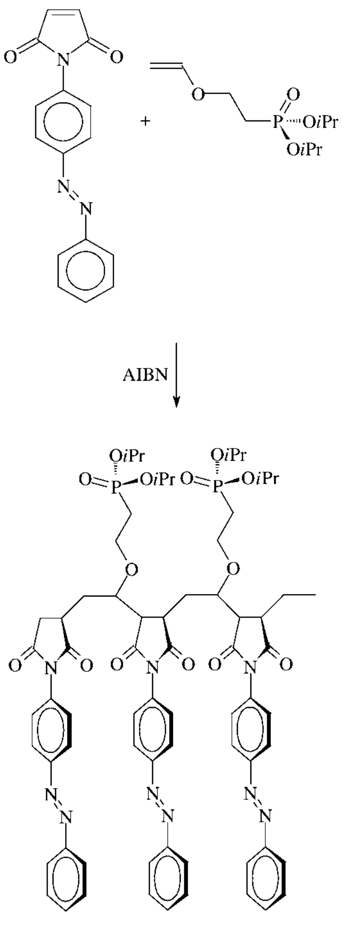
immediately. The substrates were primed with a solution of 0.2 M $POCl_3$ and 0.2 M collidine in anhydrous CH_3CN for 20 minutes at room temperature, followed by rinses with CH_3CN and water. The resulting surface was exposed to Zr^{4+} by immersion in a 5 mM solution of $ZrOCl_2$ in 60% aqueous ethanol for 30 minutes.

Synthesis

The alternating copolymer of 4-(*N*-maleimido)azobenzene (MAB) and diisopropyl (2-vinyloxy)ethylphosphonate (VEP) was prepared by radical copolymerization using azoisobutyronitrile (AIBN) as the initiator.[13] The reaction between MAB and VEP is shown in Scheme 1. We observed no monomer homopolymerization for our reaction conditions. VEP was prepared by the reaction of excess tri(isopropyl) phosphite with 2-chloroethyl vinyl ether at 170 °C for 5 days in an argon atmosphere.[17]

The monomer MAB was prepared by reacting 4-phenylazoaniline (0.1 mol) with maleic anhydride (0.1 mol) in $CHCl_3$ at 25 °C for 12 hours. The resulting amic acid was filtered and dried under vacuum. The amic acid was cyclized to the corresponding maleimide by reaction with acetic anhydride and sodium acetate under N_2 at 70 °C for 4 hours. The crude precipitate was recrystallized twice from absolute ethanol to yield the pure product (70% yield). NMR: (^{1}H, 300 MHz, in DMSO-d_6) $\delta = 7.25$ (s, 2H), 7.6–7.7 (m, 5H), 7.95 (d, 2H), 8.05 (d, 2H).

The copolymer was synthesized by reacting equimolar amounts of MAB and VEP in $CHCl_3$ at 60 °C under a N_2 atmosphere for 18 hours using AIBN (5 mol%) as the initiator. The resulting polymer was dissolved in a minimum amount of $CHCl_3$ and precipitated from ether twice. NMR: (^{1}H, 300 MHz, in DMSO-d_6) 6.9–8.0 (9H), 4.4 (2H), 3.0–4.0 (4H), 2.0–2.6 (2H), 1.4–1.8 (2H), 1.0–1.4 (6H). (^{13}C, 75.48 MHz, in DMSO-d_6) $\delta = 24$, 30–34, 42, 50, 68–74, 78, 120–135, 174–180. We estimate $M_n = 3700$ from end group analysis using ^{1}H NMR data. For our experimental conditions, statistically one of the isopropyl groups terminating each phosphonate oxygen was hydrolyzed to yield a hydroxy group during the course of the polymerization. This displacement is likely due to the presence of HCl formed in $CHCl_3$ solution by AIBN. The reaction of poly(MAB-VEP) with bromotrimethylsilane in anhydrous CH_2Cl_2 at room temperature for ~2 hours yielded a polymer that was partially hydrolyzed, making it capable of forming multilayer assemblies. After deposition, the surface-bound polymer is reacted again with bromotrimethylsilane to deprotect the remaining isopropylphosphonate sites and allow complexation with Zr^{4+}.



Scheme 1 Schematic of alternating copolymerization of MAB and VEP.

Optical null ellipsometry

The thicknesses of the polymer films we report here were measured using optical null ellipsometry. The commercial system (Rudolph Auto-EL II) operated at a 70° incidence angle (with respect to the substrate normal) using a He-Ne laser light source (632.8 nm). Ellipsometric thicknesses reported here are the average of at least six measurements at different points on the substrate of interest. The laser beam is ~1 mm diameter, giving rise to significant spatial averaging in each measurement. Because the films under study are thin, it is not possible to solve the Fresnel equations simultaneously for both adlayer thickness and refractive index. We use the value of $n = 1.45 + 0i$ for the refractive index in all cases. Small changes in the real part of the refractive index have little effect on the calculated thicknesses.

NMR measurements

To characterize the polymeric materials we use both ^{13}C (75.48 MHz) and ^{1}H (299.9 MHz) liquid phase NMR spectroscopies. The instrument is a Varian Innova 300 MHz system and DMSO-d_6 is used as the solvent for all NMR measurements. Assignments of NMR resonances are as reported above.

UV-visible absorption spectroscopy

UV-visible absorbance measurements were made using a Unicam model UV-2 absorption spectrometer. For all measurements the spectral resolution was set to 2 nm. Solution phase measurements were made using 1 cm pathlength cuvettes against a reference of the neat solvent. Measurements of the layers were made in transmimssion mode through the SiO_x substrates, with the reference channel being a bare SiO_x substrate.

Results and discussion

We are interested in understanding the nature of the matrix formed by MVE polymers in layers held together using ZP ionic coordination chemistry. With a sufficient understanding of the structural factors that determine the polymer matrix properties, we will be able to control interface characteristics such as porosity, polarity, and extent of crystallization. MVE polymers with pendant azobenzene sidegroups are useful for probing local organization in layered polymer interfaces because of the well understood spectroscopic and isomerization properties of the azobenzene chromophore.[18–26] Using the chemistry we have reported earlier to construct polymer multilayers,[13] we have grown up to four layers of poly(MAB-VEP). The absorption spectroscopy and ellipsometric thickness of the resulting multilayer provides insight into the strength of interlayer interactions and the role of long-range disorder in these materials. Before discussing these data in detail, we need to consider the possibility of any intrinsic structural anisotropy in these polymer films. We note that these films exhibit no measurable birefringence, suggesting that if there is any microcrystalline structure (which we do not believe to be present) then it must persist over lengthscales substantially shorter than 0.5 μm. The absorbance data (*vide infra*) reveal no substrate orientation-dependence and this information, in conjunction with the absence of birefringence, suggests that the films are nominally amorphous in the plane of the substrate. Despite this finding, it is also possible that the azobenzene side groups are oriented preferentially owing to stacking effects during layer growth. Our experimental absorbance data (*vide infra*) that reveal layer-dependent variations in the *cis*/*trans* side group ratio argue against there being a persistent structural anisotropy associated with the ensemble of side groups. With these caveats in mind, we turn to a discussion of the experimental data.

Poly(MAB-VEP) exhibits a constant average layer thickness (21.7 Å layer^{-1}) with increasing number of layers (Fig. 1). This measurement of interface thickness, which provides a spatial average over a ~1 mm diameter spot size, senses the macroscopic disorder in the polymer layers. The absorption data point to the local steric limitations placed on the azobenzene side groups by the formation of ZP linkages. These data together provide a self-consistent picture of polymer layer morphology. In the absence of other information, the ellipsometry measurements do not offer much chemical insight because only the polymer layer thickness is sensed. Any layer-dependent variation in the structure or density of the polymer would not be readily apparent from these measurements. In an attempt to gain more insight into the morphological properties of these polymer layers, we have examined their UV-visible absorption spectra. We show in Fig. 2 the absorbance spectra of the poly(MAB-VEP)-modified interface as a function of number of layers added. The spectra in the 230–400 nm region are dominated by the absorbance of the azobenzene side groups. We note first that there is a general trend toward increasing absorbance with number of layers, in agreement with the ellipsometric data. We can use the absorbance spectra to estimate the layer loading density (Fig. 3). Based on the absence of apparent structural anisotropy in these films, the transition cross-sections of the $S_2 \leftarrow S_0$ azobenzene side group transitions can be used to determine the total amount of polymer present. We relate the density of chromophores to the absorbance data through the *trans* ($\varepsilon_{313} = 25\,000\ \mathrm{M^{-1}\ cm^{-1}}$, $\sigma_{313} = 4.15 \times 10^{-17}\ \mathrm{cm^2}$) and *cis* ($\varepsilon_{250} = 13\,000\ \mathrm{M^{-1}\ cm^{-1}}$, $\sigma_{250} = 2.16 \times 10^{-17}\ \mathrm{cm^2}$) conformer transition cross sections (Fig. 3). These data indicate a constant amount of polymer is being adsorbed per layer. A second significant feature in the data shown in Fig. 2 is that the bands for the first layer appear to be shifted relative to those for subsequent layers. We understand this phenomenon in terms of the local dielectric response sensed by the azobenzene chromophore. The dielectric response of the SiO_x substrate is substantially different than that of a polymer layer and, because there is only one layer of polymer present, the extent of side group confinement will necessarily be different than for the multilayer samples. The spectral shift we see for the first layer is the result of the presence of a gradient in the dielectric response of the system over the length scale of the chromophore.[27–31]

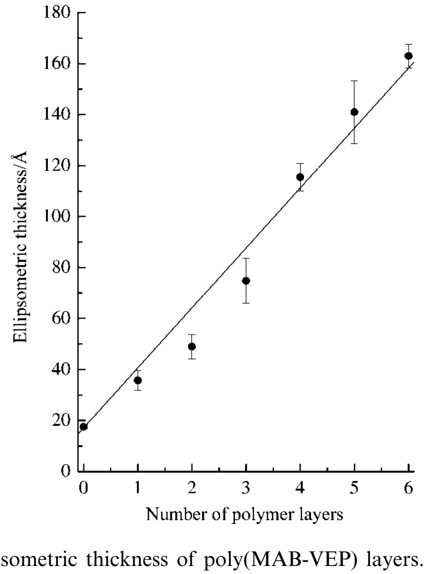


Fig. 1 Ellipsometric thickness of poly(MAB-VEP) layers. The zeroth layer is the primer layer on the oxidized Si substrate, which we measure to be 17.2 Å. The slope of the best-fit line through these data is 21.7 ± 1.1 Å layer^{-1}.

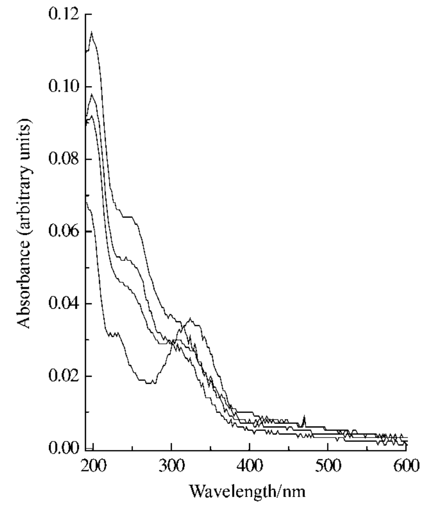


Fig. 2 Plot of absorbance of poly(MAB-VEP) layers as a function of layer deposition. The band positions for the first layer (bottom) are shifted from those for subsequent layers.

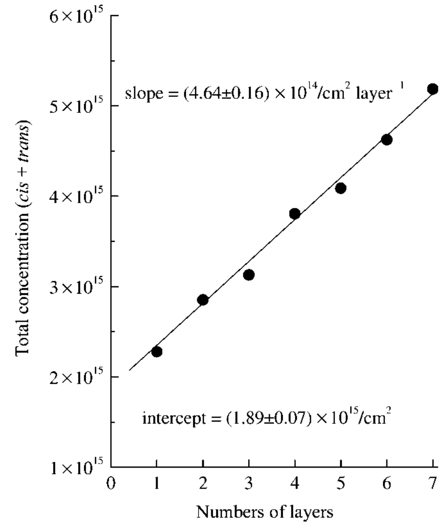


Fig. 3 Total chromophore concentration as a function of number of layers. The data represent the total of the *cis* and *trans* concentrations. The best fit line yields a density of 4.64×10^{14} chromophores cm^{-2} layer^{-1}.

The third point of interest is that the ratio of the absorbance maximum near 313 nm to that near 250 nm depends sensitively on the number of polymer layers present. To understand the significance of this observation, assignments must be made for these two bands. For azobenzene chromophores, it is well known that the $S_2 \leftarrow S_0$ transition for the *trans* form is centered at 313 nm and the $S_2 \leftarrow S_0$ transition for the *cis* conformer occurs at 250 nm.[27–31] The ratio of the two bands is related directly to the relative amount of *cis* and *trans* conformers in the polymer multilayers, as we discussed above. We show in Fig. 4a the maximum absorbances for the *cis* and *trans* isomers and in Fig. 4b we show the ratio of the isomer concentrations as a function of number of layers. The fact that the conformer ratio changes with the number of polymer layers means that the azobenzene side groups are confined significantly by their local environment and the driving force for the formation of the multilayer assembly must be greater than the energetic cost associated with isomerization of the chromophore in its ground state. We note that this situation is true even for the first layer, where [*trans*]/[*cis*] = 0.59. For solution phase azobenzene, essentially no *cis* conformer is present.

It is important to provide some frame of reference to understand the linear optical response of this polymer more fully. We show the absorption spectra of the polymer in solution (Fig. 5a), where the azobenzene side groups are expected to be predominantly all-*trans*, and in a spin-cast film of the polymer (Fig. 5b), where we expect a significant amount of *trans* conformer. For both of these spectra, the *trans* band is centered at ~315 nm, with the *cis* band near 250 nm. The band near 200 nm seen in all spectra is intrinsic to the polymer, either as a higher excited electronic state of the azobenzene chromophore or as an electronic transition associated with another constituent of the polymer. Irradiation of the polymer solution at 315 nm produces azobenzene *cis* conformers, resulting in a change in the absorption intensity of both 250 nm and 315 nm bands (Fig. 5a, dashed spectrum). For the spin-cast film there is a larger contribution from the *trans* conformer than is seen for the ZP layers. This is an expected result based on the local structural restrictions imposed in the layered polymers by the formation of ZP linkages.

We consider next why we observe the change in the azobenzene side group conformation distribution upon polymer layer deposition. In solution, the *trans* form of the azobenzene side group is the thermodynamically stable conformer (Fig. 5a). It is thus unexpected that only 60% of the sidegroups are *trans* in the first polymer layer. The reason for this finding must be that the driving force for the formation of the ZP ionic linkage is greater than the ground state isomerization barrier of the size group, and some of the side groups are converted to the *cis* isomer to accommodate ZP association. We note that, for the spin-cast film, we recover a primarily *trans* conformation since there is no opportunity for sterically restrictive complexation to proceed in the spin-cast matrix. Our data on polymer layer formation imply that we are forming a kinetic product with the ZP-bound polymer layers because there is sufficient structural freedom in the polymer backbone to allow rotation of the maleimide unit about its bond to the pendant ether moiety. We ascribe the formation of this kinetic product to the fast ionic bonding kinetics of the ZP chemistry.

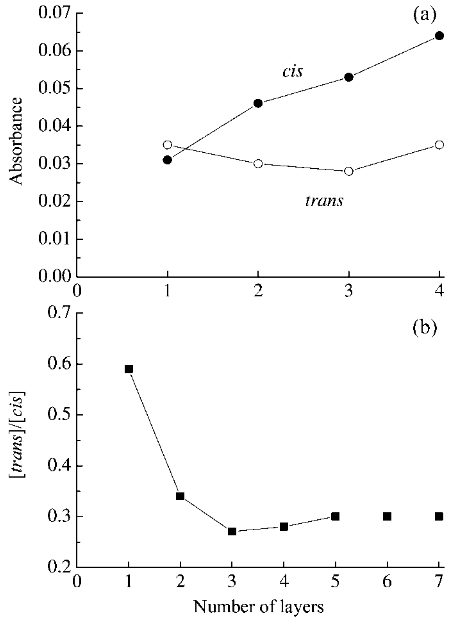


Fig. 4 (a) Absorbance maximum values for *cis* (●) and *trans* (○) conformers as a function of number of poly(MAB-VEP) layers. The *cis* $S_2 \leftarrow S_0$ absorption band is centered near 250 nm and the *trans* $S_2 \leftarrow S_0$ band is at ~313 nm. (b) Ratio of [*trans*] to [*cis*] as a function of number of layers.

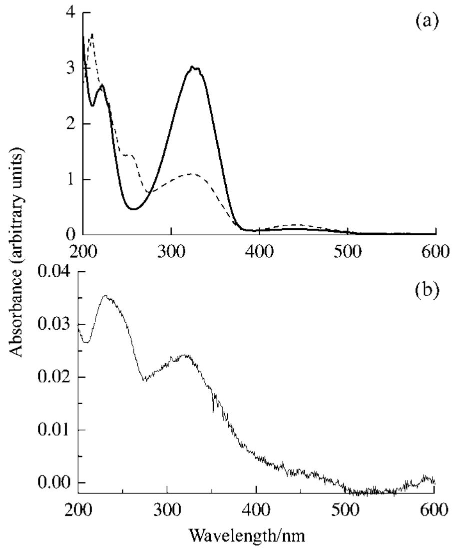


Fig. 5 (a) Absorbance spectra of solution phase poly(MAB-VEP) in CH_3CN. For the native form of the polymer (solid line), the dominant band is at 315 nm. Irradiation of the polymer solution with broadband UV light produces an enhanced concentration of *cis* conformers, as indicated in the dashed spectrum. (b) Absorbance spectrum of a spin-cast film of poly(MAB-VEP).

The ground state barrier for the isomerization of azobenzene is thought to be of the order of 200 kJ mol^{-1} based on semi-empirical calculations, although an accurate experimental determination of this quantity remains to be reported. We can only estimate the strength of RPO_3-Zr-O_3PR group formation because the literature on the solubility of zirconium phosphates and phosphonates is so sparse. We are aware of a reported value of $K_{sp} = 10^{-132}$ for $Zr_3(PO_4)_4$,[32]

$$3Zr^{4+} + 4PO_4^{3-} \rightleftarrows Zr_3(PO_4)_4$$

but we consider this value to be suspect because of the difficulties associated with determining such a small quantity. If we do assume that this value is correct and apply it to the formation of RPO_3-Zr-O_3PR, where the metal to ligand ratio is different, we can estimate the equilibrium constant for RPO_3-Zr-O_3PR formation based on the concentration of free Zr^{4+}. We infer from the K_{sp} value for $Zr_3(PO_4)_4$ that $K_{eq} = 10^{44}$ for the reaction

$$Zr^{4+} + 2RPO_3^{2-} \rightleftarrows Zr(RPO_3)_2$$

and based on this estimate, we calculate $\Delta G = -250$ kJ mol^{-1}. This is admittedly a qualitative estimate, and the ratio of the ZP complexation energy to the side group isomerization energy is consistent with a [*trans*]/[*cis*] = 0.43. From the experimental ratio of [*trans*]/[*cis*] = 0.59, if we assume 200 kJ mol^{-1} is correct for the azobenzene S_0 isomerization barrier, $\Delta G \approx -400$ kJ mol^{-1} for ZP linkage formation. There is thus considerable uncertainty in the free energy of formation for a ZP linkage but, regardless of the exact value, it exceeds the isomerization barrier for S_0 azobenzene.

One potential complication to the above explanation is that the ZP complexation process is itself mediated by the photoinduced isomerization behavior of the side groups. In other words, the ZP complex formation proceeds only when ambient light "toggles" a side group to the *cis* conformation and the complex cannot form if the side group remains *trans*. In order to evaluate this possibility, we have synthesized poly(MAB-VEP) multilayers in the dark, where photoisomerization of the azobenzene side groups by exposure to room light cannot proceed. We find from ellipsometric measurements (632.8 nm) that the polymer layers form equally well under either dark or light lab conditions. The formation of the ZP interlayer complex is thus not dependent on side group photoisomerization.

It is useful to consider the values of the [*trans*]/[*cis*] ratio and how they correspond to fractional concentrations of each isomer. For the first layer, where [*trans*]/[*cis*] = 0.59, the surface is comprised of 63% *cis* isomers and 37% *trans* isomers. As discussed above, even for the first layer there is considerable steric restriction placed on the azobenzene side group. For the second layer, [*trans*]/[*cis*] = 0.43, corresponding to a surface that is, overall 70% *cis* and 30% *trans*. Since the loading density is constant for each layer (Fig. 3), it is tempting to speculate that the second layer is 77% *cis* and 23% *trans*. This ratio holds relatively constant for subsequent layers. Unfortunately, it is not possible to extract the layer-by-layer fractional concentrations of *cis* and *trans* isomers in this manner because of interlayer cooperative effects. The fact that the *trans* absorbance *decreases* with the addition of a second layer demonstrates that the treatment of these polymers as discrete and non-interacting is not valid. In other words, the addition of a polymer layer reduces the amount of *trans* conformer in the layer to which it is adsorbed.

One prediction of these findings is that, once the polymer matrix is formed, interconversion between isomers is not facile. The very forces that cause the isomerization to proceed in the first place act to prevent back-isomerization. To test this hypothesis, we have irradiated a four-layer poly(MAB-VEP) assembly with UV light from a Hg lamp (primary output at 254 nm) for an extended period of time. Excitation of the $S_2 \leftarrow S_0$ transition of either *cis* or *trans* azobenzene gives rise to efficient isomerization in the solution phase.[24,25] Our irradiation of the $S_2 \leftarrow S_0$ transition for the *cis* side group conformer at 254 nm was intended to produce the more stable *trans* conformer. We observed no change in the spectral profile of the four-layer assembly as a function of UV irradiation (Fig. 6a). As a check on the spectroscopic data, we measured the thickness of the 4-layer stack ellipsometrically (Fig. 6b). We found no change in layer thickness over the irradiation time. These data demonstrate that the azobenzene conformers are locked in place, once deposition has occurred, and the rigidity and steric restriction imposed on the side groups is sufficient to prevent isomerization in the formed polymer matrix.

Conclusion

We have found that the conformation of the pendant side group of a polymer multilayer assembly depends sensitively on the details of polymer interlayer linking chemistry and on the steric restrictions imposed by the resulting polymer matrix. Using maleimide vinyl ether polymers with pendant azobenzene side groups, we determined that the ratio of *cis* to *trans* isomers varies in a regular manner with the number of polymer layers. Our linear absorption data demonstrate the change in conformer ratio with increasing layers, and the polymer adsorption density is constant for each layer. The ellipsometric data point to the macroscopic disorder inherent to the deposition of an amorphous polymer film. The driving force for ZP interlayer linking chemistry is greater than the energetic penalty associated with conformational change in the (ground state) side group. From our data we estimate the free energy of formation for the ZP interlayer linkage to be $-250\ \mathrm{kJ\,mol^{-1}} \leqslant \Delta G \leqslant -400\ \mathrm{kJ\,mol^{-1}}$. We anticipate that the use of longer chain vinyl ether monomers will provide a less restrictive environment for the maleimide substituents and this control over polymer structure provides a direct means of controlling the optical response of this family of materials.

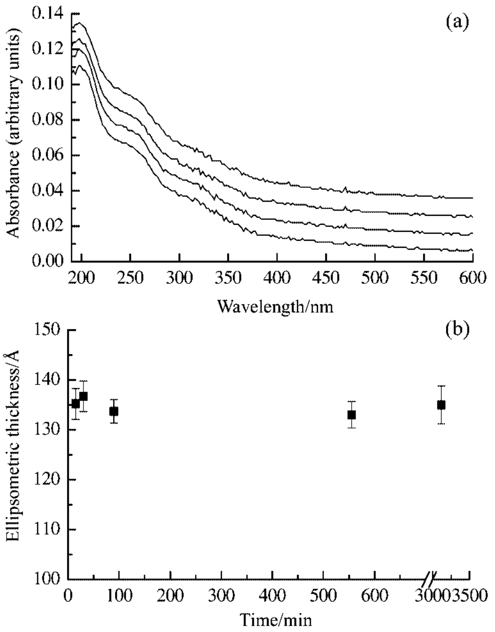


Fig. 6 (a) Absorbance spectra for a four layer stack of poly(MAB-VEP) irradiated with 254 nm light between 1 hour and 50 hours. The spectra are offset from one another for clarity of presentation. (b) Ellipsometric thickness of the same four layer stack as a function of UV irradiation.

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