

Ultrathin Film Self-Assembly of Hybrid Organic–Inorganic Metal Coordination Polymers

Houston Byrd,^{*,†} Charles E. Holloway,[†] Jessica Pogue,[†] Sandy Kircus,[†]
Rigoberto C. Advincula,^{*,‡} and Wolfgang Knoll[§]

Department of Biology & Chemistry, University of Montevallo, Montevallo, Alabama 35115,
and Department of Chemistry, University of Alabama at Birmingham,
Birmingham, Alabama 35294-1240, and Max Planck Institute for Polymer Research,
Mainz, Germany D-55021

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We have investigated the self-assembly of ultrathin zirconium coordination monomer and polymer films using a layer-by-layer approach. These materials are of great interest for incorporating metal ion (inorganic) moieties in organic (polymer) films with applications ranging from conductors to catalytic materials. The differences between the polymer and monomer assembly from solution are described. These differences were investigated using UV–vis spectroscopy, AFM, and surface plasmon spectroscopy. The differences in orientation, morphology, roughness, and linearity of deposition reflect the conformational limitations of the polymer toward self-assembly. On the other hand, the sequential assembly of the monomer and Zr metal ion indicates the strong coordination between the metal and the organic ligands, resulting in robust homogeneous films.

Introduction

The promise of directing the properties of materials by controlling the architecture, orientation, and density of molecules within organized organic assemblies has been an important driving force in many aspects of chemical research. One area of investigation has focused on spontaneous “self-assembly” (SA) of organic molecules from solution.^{1–5} Although most of the initial work focused on monolayer formation, Sagiv et al.^{6–8} developed techniques to produce multilayered films of organic moieties. However, attempts to make films greater than a few layers thick resulted in defects within the film. To overcome this problem, Mallouk and co-workers^{9,10} developed a deposition technique to produce multilayered organic–inorganic assemblies using Zr⁴⁺ ions to link α,ω -diphosphonic acid molecules one layer at a time. This SA method produces well-organized films with a high degree of order and thermal stability, which are qualities necessary for optical,^{11,12} electronic,^{13,14} and photocatalytic¹⁵ applications.

Recently, there has been much interest in the fabrication of functional ultrathin films prepared using the alternate

polyelectrolyte deposition (APD), also known as the layered multicomposites by sequential adsorption (LAMSA) technique.¹⁶ In 1991, Decher and co-workers used LAMSA methods to construct well-organized polymer thin films based on electrostatic interactions between cationic and anionic polymers.^{16,17} Since those publications, others have adopted this technique to study polymer thin films that possess conductive or electroluminescence properties.^{18–22}

The goal of much of the SA activities was to prepare surfaces that can mimic physical properties of known materials; however, most of the research focused only on electrical and/or optical properties of the organic components of the films. Our approach is to prepare thin films, which possess both inorganic and organic properties of interest, by utilizing inorganic SA methods to produce metal coordination polymer thin films. A metal coordination polymer is defined as a macromolecule that uses a metal ion as an essential part of the backbone, where the removal of the metal ion would result in severing the polymer chain. Some current areas of applications of bulk metal coordination polymers include synthetic-metal

* To whom correspondence should be addressed.

[†] University of Montevallo.

[‡] University of Alabama at Birmingham.

[§] Max Planck Institute for Polymer Research.

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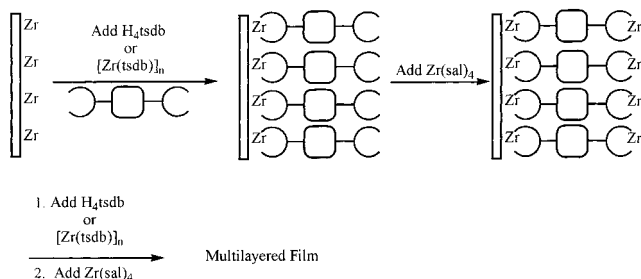
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Scheme 1. Self-Assembly Scheme for the Metal Coordination Polymer Films via Alternate Deposition with $\text{Zr}(\text{sal})_4$ ^a



^a The layers are deposited from solutions of either the H_4tsdb ligand or the bulk $[\text{Zr}(\text{tsdb})]_n$ polymer.

conductors,²³ biologically active materials,²⁴ and catalytic materials.²⁵ The assembly of metal coordination polymers has a potential advantage in that simple changes in the metal center and/or the organic backbone of the SA polymer film will change the physical and chemical properties of the films. The ability to study either the inorganic or organic components is one important difference in metal coordination polymers over classical SA organic polymers and films. Self-assembly deposition techniques will also allow for control of the architecture and morphology of films. For example, the polymer chains will deposit perpendicularly from the surface, unlike the electrostatic organic polymers, which lie flat on a surface. This orientation can lend itself to directional properties of the organic component necessary in nonlinear optics,¹² photovoltaics,¹³ or light-emitting diodes.^{26–28} Another advantage of using metal coordination polymers is that the morphology of the films can be changed depending on the deposition procedures. Constructing the polymer one layer at a time (Scheme 1) should produce a uniform film, whereas constructing the film by depositing from a solution of pre-made bulk polymer should produce a rough film because the repeating units of the bulk polymer vary.

In this paper, we demonstrate that the assembly of metal coordination polymer films is possible and that the orientation and morphology can be controlled. The films were prepared from a series of zirconium coordination polymers and monomers previously developed by Archer et al.^{29–33} as shown in Figure 1. This material was chosen for several reasons. First, the synthesis and characterizations of the polymers are well documented. Second, the monomers and polymers absorb strongly in the UV region

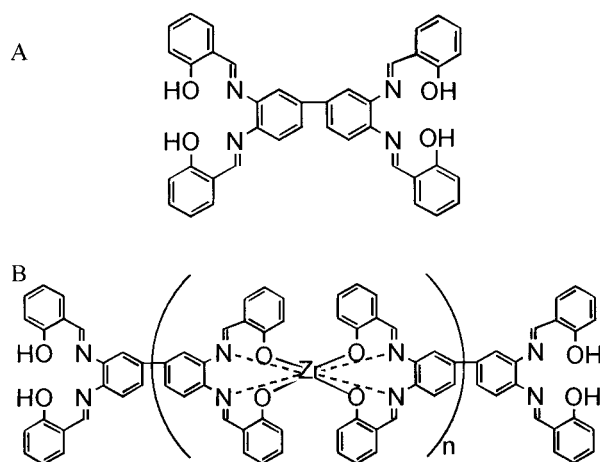


Figure 1. Idealized structures of (A) the H_4tsdb monomer and (B) the $[\text{Zr}(\text{tsdb})]_n$ polymer.

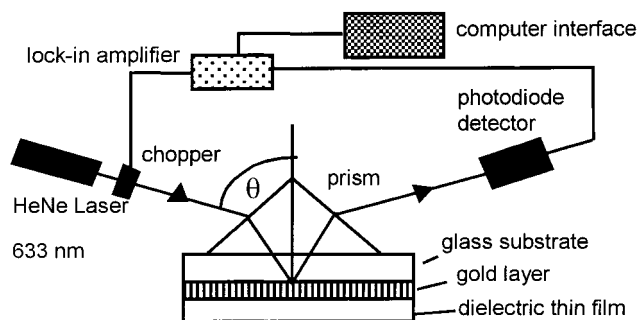


Figure 2. Kretschmann configuration setup for SPS on hybrid inorganic–organic films fabricated using LAMSA.

of the spectrum, and therefore the deposition can be easily followed by UV–vis spectrometry. Finally, the linkage between organic molecules in these polymers is a Zr center, which is similar to Mallouk's method for alkylphosphonates and thus broadens the material basis for these types of films.

Experimental Section

Materials. The following chemicals were obtained from Aldrich: salicylaldehyde, zirconium(IV) acetylacetonate, 3,3'-diaminobenzidine, and the solvents dimethyl sulfoxide (DMSO) and methanol. Tetrakis(salicylaldehyde) zirconium(IV) ($\text{Zr}(\text{sal})_4$) was previously prepared by a standard procedure. All chemicals were used directly without further purification.

Instrumentation. The UV–vis data using quartz slide substrates was collected on a Hewlett-Packard UV–vis spectrophotometer. The surface plasmon resonance spectroscopy (SPS) setup is based on the Kretschmann configuration. The details of the setup have been previously described.³⁴ The surface plasmon is a bound, nonradiative evanescent wave. The maximum of the field amplitude is at the metal/dielectric interface and decays exponentially into the dielectric medium and into the metal. The penetration depth into the dielectric medium depends on the wavelength of the incident light and the dielectric functions of the involved materials. Excitation of surface plasmons in the Kretschmann configuration is achieved with the evanescent waves produced on ATR (attenuated total reflection) at the prism/metal interface (Figure 2). In summary, p-polarized light from a He–Ne laser, $\lambda = 632.8$ nm, is mechanically chopped and illuminates the sample at the base of the prism. The reflected light is recorded by a phase sensitive photodiode detector in conjunction with a lock-in amplifier. Its dc output signal is then converted (ac/dc) and fed into a computer to produce reflectivity versus angle of incidence scans. The data were fitted using an algorithm based on Fresnel theory by assuming an idealized

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layer model; that is, the refractive index of the layers is isotropic and their thickness is uniform and constant. These fits then yield the film thickness. All fittings of the plasmon curves assume a refractive index value of 1.5.³⁵ Measuring in air and water and evaluating the refractive Fresnel fit validated this assumption.³⁴ Curve fitting and thickness data extraction were done using the SPALL 5 software. Sample substrates for the SPS measurements were prepared by evaporating gold (43 nm) on glass, preceded by 2 nm of Cr to promote gold adhesion. Atomic force microscopy (AFM) analysis of the sample surfaces was obtained using a Metris-2000-NC atomic force microscope system from Burleigh Instruments. The images were taken in air with a 5 μ m scanner. All samples imaged were prepared on quartz substrates.

Preparation of H₄tsdb(N,N',N'',N'''-tetrasalicylidene-3,3'-diaminobenzidine). 3,3'-Diaminobenzidine (1.200 g) was dissolved in DMSO (30 mL) in a 100 mL round-bottom flask. To this solution, 3 mL of salicylaldehyde was added. This entire solution was then heated under nitrogen at $\sim 70^\circ\text{C}$ for 1 h. A brown slurry was observed within 20 min, and after 45 min an orange solid began precipitating out of solution. The solid was washed with acetone and dried under vacuum at 100°C for 1 h. The product was purified by dissolving it in the smallest amount of DMSO while heating and stirring. The mixture was placed on an ice bath until crystals formed. These crystals were then washed with acetone and dried using an aspirator. CHN obs(exp): %C, 75.84 (76.17); %H, 4.76 (4.79); %N, 8.80 (8.88). IR (cm^{-1}): 3440, 3050, 1650, 1280.

Preparation of [Zr(tsdb)]_n (catena-poly[zirconium(IV)-(μ -tetrasalicylidene-3,3'-diaminobenzinato-*O,N,N',O'*; *O'',N'',N''',O''''*)). For a typical reaction, DMSO (30 mL) was added to a 100 mL three-neck round-bottom flask that had been heated to 80°C under a N₂ blanket. To this system, Zr(sal)₄ (0.50 g) and 3,3'-diaminobenzidine (0.21 g) were added and dissolved. This solution was stirred and refluxed at 80°C . A yellow-orange precipitate was observed, so the flask was warmed to 135°C until a solution again appeared (within 1 h), and then the reaction was cooled to 70°C and kept at this temperature. A solution of 8.67×10^{-3} M of (H₄tsdb) in DMSO was added five times in 1 mL portions at intervals as close to 12 h as possible. After the fifth addition of H₄tsdb, the polymer precipitated out of solution. The product was filtered and washed with acetone. IR (cm^{-1}): 3050, 1608, 1318.

Deposition. For UV-vis measurements, quartz slides were cleaned in a 1:3 solution of 30% H₂O₂ and concentrated H₂SO₄ (caution: mixture reacts violently with organics). A phosphonic acid surface was deposited using the procedure developed by Katz et al.¹⁴ A cleaned quartz slide was refluxed under nitrogen in a 5 mM aminopropylsilane solution in octane overnight. The slide containing the amine layer was then rinsed with octane followed by acetonitrile. This amine-coated slide was placed in a 5 mM solution of POCl₃ and 2,6-lutidine in dry acetonitrile overnight. The slide was then rinsed with acetonitrile followed by water to prepare the phosphonic acid surface. After the phosphonic acid surface was prepared, the slides were placed in a 5 mM solution of zirconium salicylaldehyde in DMSO for 1 h at 80°C . The Zr slides were then rinsed with DMSO followed by distilled water and dried in a N₂ stream. The Zr slides were then placed in a 5 mM solution of H₄tsdb in DMSO for 1 h at 80°C and then rinsed. Repeating the depositions in the Zr/H₄tsdb solutions produced multilayered films. For the gold-coated slides, a self-assembled monolayer (SAM) of 6-mercapto-1-hexanol was first prepared from ethanol solution. The slide was placed in a solution of 5 mM POCl₃ and 5 mM 2,6-lutidine in dry acetonitrile overnight. The slide was then rinsed with acetonitrile followed by water to prepare the phosphonic acid surface. The deposition procedure then followed is similar to that for the quartz slides.

Results and Discussion

Layer-by-Layer Films from the H₄tsdb Monomer.

The deposition technique for the polymer film adapts Mallouk's one-layer-at-a-time self-assembly approach to prepare the zirconium coordination polymer from the assembly of the H₄tsdb monomer. Briefly, a phosphonic

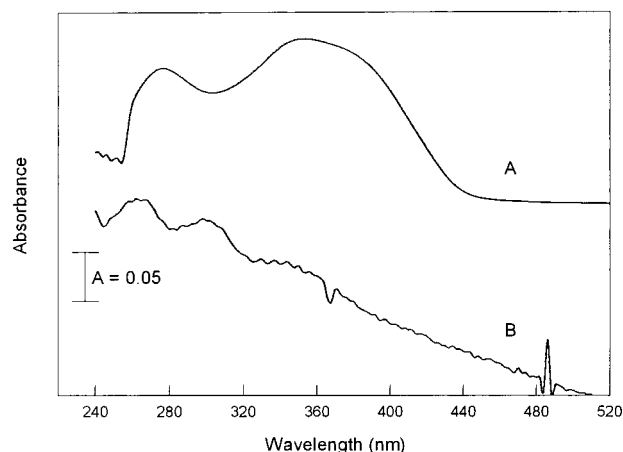


Figure 3. UV-vis absorbance data for a solution of the H₄tsdb monomer in DMSO (A) and for a H₄tsdb monolayer assembled onto a quartz slide (B). The solution spectrum has been scaled to fit with the monolayer spectrum.

acid surface is first prepared on a quartz substrate by standard literature procedures¹⁴ (see Experimental Section). This phosphonic acid layer is the anchoring layer upon which the H₄tsdb monomer will be assembled. The phosphonic acid containing substrate is then placed into a solution containing a Zr species. Various types of Zr species were used in this procedure, such as ZrOCl₂, Zr-acac, and zirconium salicylaldehyde (Zr(sal)₄). The Zr(sal)₄ produced the most consistent growth in the films, based on UV-vis absorbance data, and therefore was used throughout the process. The Zr species bind strongly to the phosphonic acid groups creating a Zr-rich surface. The Zr-rich slide is then placed in a solution containing the H₄tsdb monomer. One end of the monomer (Figure 1a) can "grab" a Zr on the surface, thereby attaching one layer of the monomer to the surface (Scheme 1). This process leaves the other end of monomer available to bind additional Zr species. The film is placed in a second solution containing a source of zirconium, and by alternation of the solutions of the H₄tsdb and the Zr multilayered films are produced, which should mimic the zirconium polymer as shown in Figure 1b.

The deposition process was followed by UV-vis spectroscopy because the H₄tsdb monomer strongly absorbs in the UV region from 250 to 500 nm ($\epsilon \approx 4.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Figure 3 shows a solution spectrum of the H₄tsdb monomer along with that of a monolayer of the H₄tsdb ligand assembled on the surface. Multiple washings of the quartz slide produced no change in the UV-vis spectrum. The absorption maxima for the monolayers, however, are blue-shifted compared to the solution spectra. It is reasonable that this shift occurs as a result of possible π -stacking between the monomers because their orientation is fixed on the quartz surface, whereas the molecules in solution are randomly organized.^{36,37} The monomer spectrum (Figure 3B) is not identical to the solution spectrum (Figure 3A); for example, a prominent band occurs at 308 nm in the monomer spectrum but is absent in the solution spectrum. Although Archer et al.²⁹⁻³³ did not assign any specific transitions to these bands, the band at ~ 300 nm appears in the UV-vis solution spectrum (Figure 7A) of the zirconium polymer ([Zr(tsdb)]_n). This indicates that the band at ~ 300 nm is associated with some interaction between the Zr center and the ligand.

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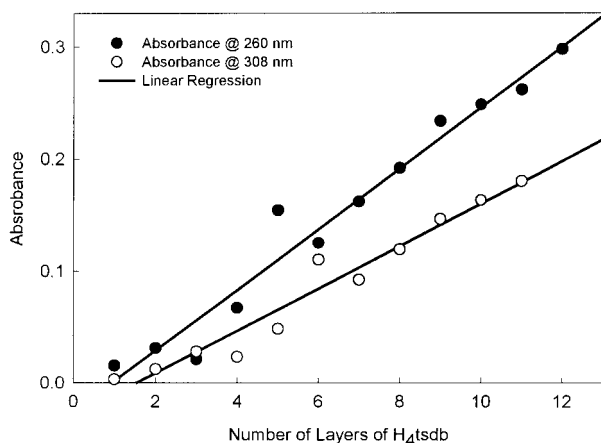


Figure 4. A plot of UV absorbance versus the number of H_4tsdb monomer layers assembled. The solid lines are linear regressions for the data. The linear increase in the data indicates that the same amount of material is being added with each deposition cycle.

Therefore, the presence of this band is expected in the monomer film.³⁸ The absorption band maxima at 262 and 308 nm were monitored as a function of monomer layers deposited onto the quartz slide. It should be noted that the λ_{max} for both bands remained constant throughout the deposition. Figure 4 shows a plot of absorbance versus the number of H_4tsdb layers assembled onto the quartz surface. The linear increase in absorbance demonstrates that the same amount of material was added to the slide with each deposition cycle. However, the data indicate that depositions are erratic in the beginning but become more regular as the number of layers increases. This is possibly due to reorganization of the film during the deposition process, which has also been observed in the electrostatic deposition of organic polymers.¹⁶ UV–vis analysis of these films, as mentioned previously, indicates only that the same numbers of molecules are deposited. Therefore, we investigated the uniformity and surface of the films using SPS and AFM.

We have utilized the SPS technique primarily to investigate the self-assembly, adsorption properties, and film homogeneity of these layers.³⁴ The surface plasmon resonance curve is determined by measuring the reflected intensity as a function of the incident angle and determining the resonance corresponding to a minimum in the measured reflectivity. The shape and position of the plasmon resonance curve are extremely sensitive to the structure and composition of the metal/dielectric interface. As such, deposition of a thin film on the metal induces a significant shift in the resonance minimum to larger angles. Analysis of the curve displacement yields the optical thickness of the adsorbed film. Unique determination of the geometric thickness is not possible but relies upon an assumed value for the film refractive index. We are therefore interested in using SPS to differentiate properties of the metal coordination polymers compared to other LAMSA methods.

SPS data (Figure 5A) of the multilayers prepared from the monomers shows an increase in optical thickness with increasing pair-layers. A plot of thickness versus the number of layers of the H_4tsdb monomer obtained from the Frensel fit of the data shown in Figure 5B indicates that a uniform film is deposited and that the average thickness per H_4tsdb layer is 2.05 nm. This would

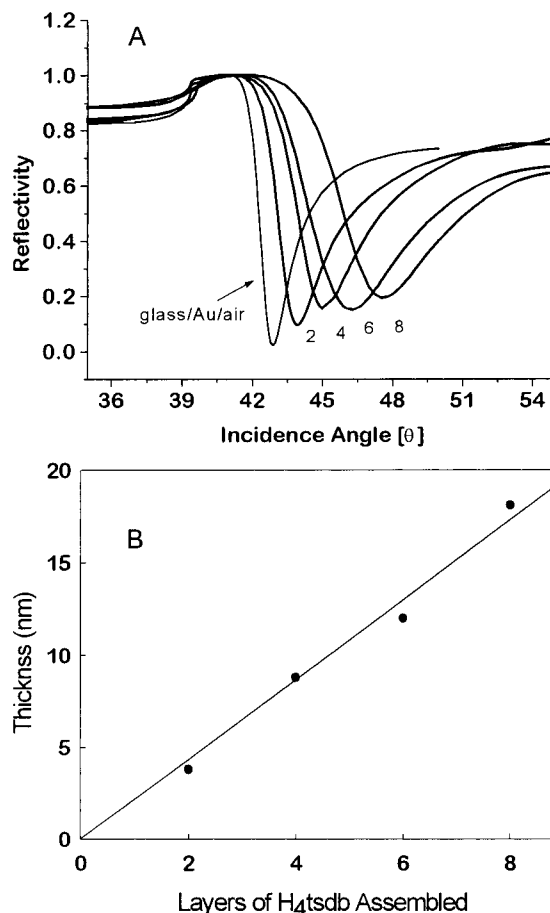


Figure 5. (A) SPS data (633 nm) of multilayer formation by alternate deposition. The numbers indicate the number of H_4tsdb ligands assembled. (B) A plot of thickness as determined by SPS for the layer-by-layer assembly of the H_4tsdb monomer onto a quartz slide. The line is a linear regression of the data and indicates an average thickness of 2.05 nm per H_4tsdb ligand assembled. This would correspond to a thickness of 4.1 nm per pair-layer, which is in excellent agreement with the SPS data.

correspond to a thickness of 4.1 nm per pair-layer (Figure 1B). On the basis of the molecular structure, the thickness increase is consistent with a nearly orthogonal orientation (ca. 1.9–2.2 nm) for the H_4tsdb monomer unit. These data indicate that uniform growth leads to multilayers representing repeat units of the polymer growing orthogonally from the surface. Previous SPS measurements by Corn et al.³⁵ on zirconium phosphonate monolayers indicate that variable refractive indices are also possible based on packing and orientation behavior. It is possible to verify these assumptions by correlating with density measurements using a quartz crystal microbalance (QCM) and X-ray reflection techniques, and further studies are being made.

The surface coverage and roughness of the assembled thin film were also investigated using AFM. A $2 \times 2 \mu m$ AFM analysis of the phosphonic acid surface was obtained as a reference. The phosphonic acid surface is the template layer for the zirconium, upon which the H_4tsdb molecules are assembled. The overall surface area was smooth with a root-mean-square (rms) roughness value of 0.66 nm. The rms value for a seven-layer H_4tsdb film was found to be 2.5 nm for the AFM image shown in Figure 6. As a comparison, AFM studies of known well-organized, close-packed, self-assembled organic-chain films show a roughness of 0.2–0.3 nm.³⁹ The H_4tsdb assembled film is rougher than the organic-chain films and even the initial phos-

(38) We wish to acknowledge helpful reviewers' comments on this point.

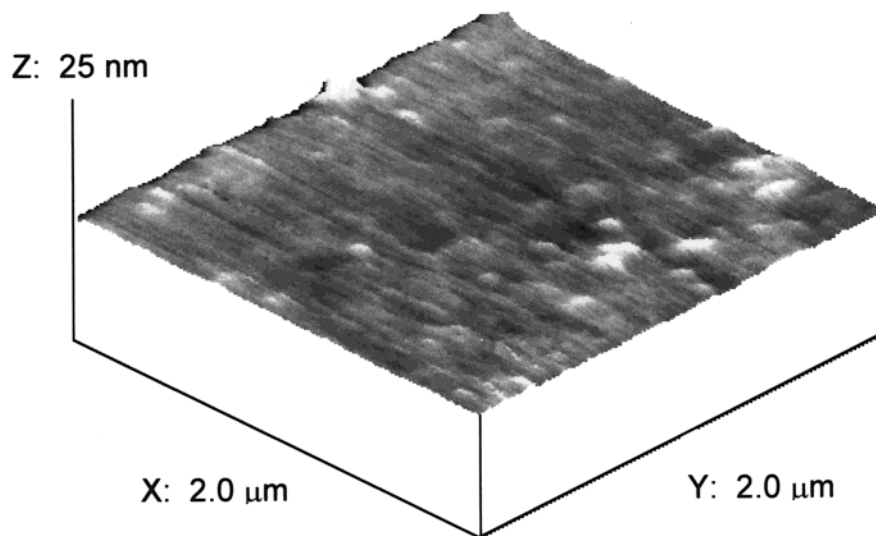


Figure 6. A $2 \times 2 \mu\text{m}$ contact AFM image of a seven-layer H_4tsdb assembled film. The average roughness for the surface of the film is 2.5 nm.

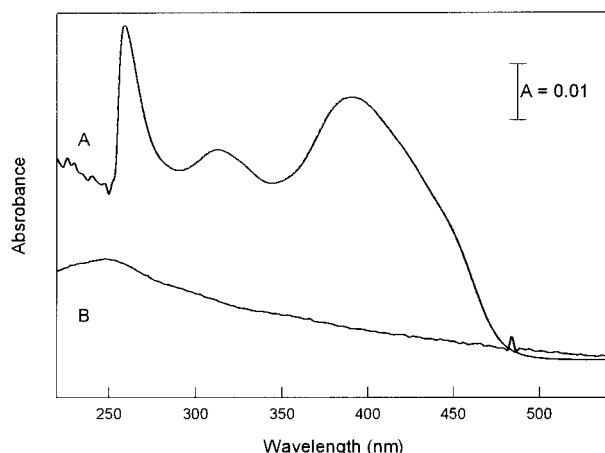


Figure 7. UV-vis absorbance data for (A) a solution of the $[\text{Zr}(\text{tsdb})]_n$ polymer in DMSO and (B) a monolayer assembled onto a quartz slide. The solution spectrum has been scaled to fit with the monolayer spectrum.

phonic acid surface; however, this is expected. The H_4tsdb molecules are bulky and rigid and therefore may not orient themselves tightly with neighboring molecules. The film ideally should possess the same structure as the bulk $[\text{Zr}(\text{tsdb})]_n$ polymer (Figure 1). The polymer itself is not a perfect linear chain but is twisted.^{29,31,33} The fact that the roughness is less than a monolayer's thickness indicates that the film's coverage is uniform. Although the films discussed here are not being studied as optical or electronic devices, the fact that the orientation is perpendicular is important. This indicates that metal coordination polymers can be assembled with directional control. Also, the data indicate that uniform films are achieved by this mode of deposition. A second area we wanted to investigate was the ability to control the morphology of the films by changing the deposition procedure from using a solution of monomer to using a solution of bulk polymer.

Layer-by-Layer Films from the $[\text{Zr}(\text{tsdb})]_n$ Polymer. Because the H_4tsdb monomer has a fixed length, the surface is expected to be relatively smooth. However, assembly of the $[\text{Zr}(\text{tsdb})]_n$ polymer should produce a

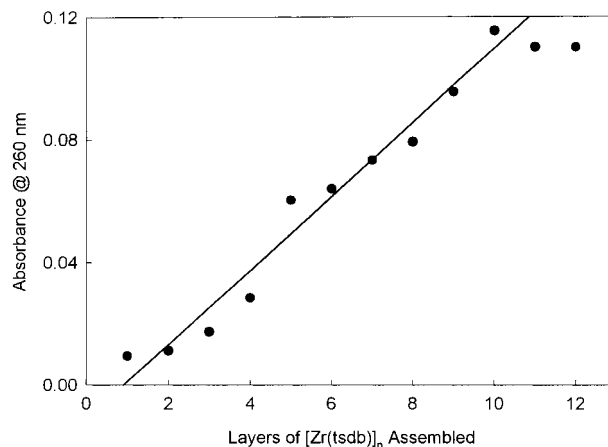


Figure 8. A plot of UV absorbance at 260 nm versus the number of $[\text{Zr}(\text{tsdb})]_n$ polymer layers assembled. The solid lines are linear regressions for the first 10 data points. However, after 10 deposition cycles the increase in absorbance becomes constant.

rougher surface because the number of repeating units, n , varies from 30 to 50, depending on the length of polymerization.³³ Archer also reported that the $[\text{Zr}(\text{tsdb})]_n$ polymer would adhere to bare quartz surfaces.^{31,32} However, when a blank quartz slide was placed into the $[\text{Zr}(\text{tsdb})]_n$ polymer solution and then rinsed, as in the deposition procedure, there was no UV-vis absorbance. The same was true if the phosphonic acid coated slide (without Zr) was placed in the $[\text{Zr}(\text{tsdb})]_n$ polymer solution. Therefore, we investigated the assembly of the $[\text{Zr}(\text{tsdb})]_n$ polymer from solution following the same procedure described previously and outlined in Scheme 1, with the exception that a solution of the $[\text{Zr}(\text{tsdb})]_n$ polymer was used instead of the H_4tsdb monomer. Figure 7 shows the UV-vis absorbance of the $[\text{Zr}(\text{tsdb})]_n$ polymer solution along with one monolayer of the $[\text{Zr}(\text{tsdb})]_n$ polymer assembled on the surface. All of the absorption bands are present in the monolayer film, although only the maximum at 260 nm was intense enough to monitor as a function of polymer layers deposited. The decrease in the intensity of these bands is most likely due to a preferred orientation in the way the molecules align on the surface with respect to the electric field vector from the UV source.^{36,37} Figure 8 shows a plot of absorbance versus the number of $[\text{Zr}(\text{tsdb})]_n$ polymer layers. These data are quite different

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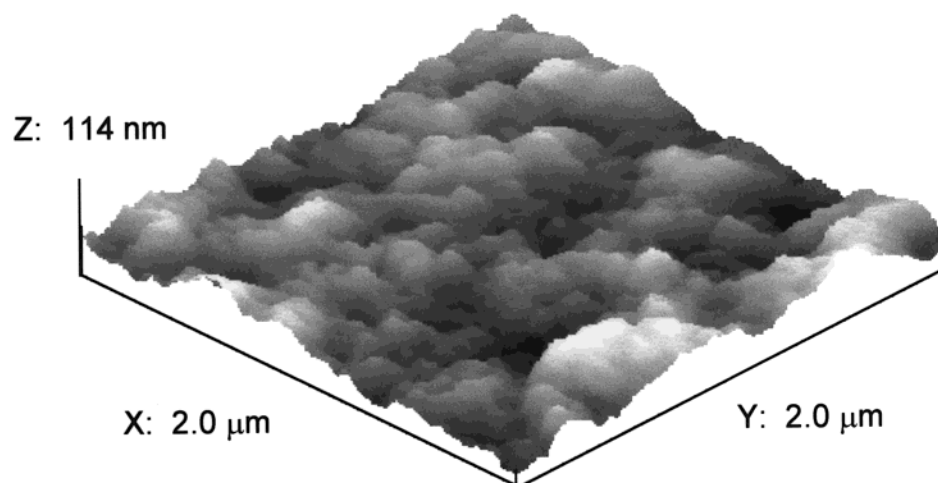


Figure 9. A $2 \times 2 \mu\text{m}$ contact AFM image of a six-layer $[\text{Zr}(\text{tsdb})]_n$ assembled film. The average roughness for the surface of the film is 25 nm.

from those for the assembly of the monomer and indicate that the deposition of the $[\text{Zr}(\text{tsdb})]_n$ polymer is irregular. First, the increase in absorbance versus the number of $[\text{Zr}(\text{tsdb})]_n$ polymer layers indicates that some amount of material was added to the slide with each deposition cycle. After 10 deposition cycles, the absorbance became constant even after further depositions. This leveling off could be attributed to the twist^{29,31,33} of the $[\text{Zr}(\text{tsdb})]_n$ polymer. X-ray results from a model compound show that the two quadridentate ligands around the zirconium center are distorted from a linear geometry.⁴⁰ The nonlinearity minimizes intermolecular stacking and provides a random organic sheath around the metal center.^{31,40} Therefore, it is reasonable that this twist eventually causes fewer and fewer Zr sites to be available to bind further $[\text{Zr}(\text{tsdb})]_n$ polymer molecules until the deposition stops completely. Second, the absolute absorbance value per deposition cycle is lower than the value observed from the H_4tsdb monomer deposition, indicating a lower concentration of absorbing species. This would indicate that fewer molecules are deposited from the $[\text{Zr}(\text{tsdb})]_n$ polymer solution. This is also consistent with a minimization in the intermolecular stacking. Thompson et al. studied the assembly of organophosphonates via AFM analysis and showed that molecules deposited as aggregates from solution.⁴¹ Because the $[\text{Zr}(\text{tsdb})]_n$ polymer molecules' interactions are minimized, it is expected that fewer molecules possess the proper orientation to assemble onto the surface. These differences in UV data, as compared to data for the monomer depositions, suggest that the assembly of the polymer film is not as straightforward and that this may not be a preferred mode of deposition.

SPS data for the polymer deposition supports the UV–vis data because an irregular deposition pattern was revealed; that is, the thickness data did not show a linear increase compared to data for the monomer deposition. The observed spectra were broader and did not consistently shift to higher incidence angles as observed with the monomers. In fact, as the number of layers deposited increased the thickness changes became smaller, which is consistent with the leveling of the absorbance data. This suggests that the polymer does not deposit well and that there may be incomplete coordination (between the metal and the ligand of the end groups) during the

deposition process. This correlates well with the observed differences in the UV–vis absorbance compared with that of the monomer and is more evident with the AFM data. It is possible that the polymers can be described as merely being physically adsorbed on each cycle, which results in desorption during the washing steps in some cycles. However, UV analysis of the films after multiple washings showed no decrease in absorbance once the films were deposited.

The surface coverage and roughness of the $[\text{Zr}(\text{tsdb})]_n$ assembled thin film was also investigated using AFM. The overall film was rough, and a root-mean-square roughness value of 25 nm was obtained for a six-layer $[\text{Zr}(\text{tsdb})]_n$ polymer film (Figure 9). The surface of this film is 10 times rougher than those of the films prepared from the H_4tsdb solution. The surface roughness clearly demonstrates that a uniform film is not produced, which supports the SPS data. There are two possible explanations for the roughness observed. The first is simply that varying polymer chain links are deposited, which would give rise to the uneven surface. However, we would expect to observe continued growth in UV absorbance. The second possibility is that not all $[\text{Zr}(\text{tsdb})]_n$ polymer molecules assemble with the correct orientation for binding further molecules. This would create regions where growth essentially stops. We believe there is some combination of the previous explanations given that fact that an increase in the UV–vis absorbance versus deposition number is observed, but after a few cycles the increase stops. If the variation in chain links alone caused the roughness, we would expect the deposition to continue. However, if none of the molecules assemble with the correct orientation then we would expect no increase in absorbance. What is clear from the data is that depositing the bulk polymer from solution does not produce consistent, homogeneous films.

Conclusions

We have investigated the formation of metal coordination polymer ultrathin films by solution self-assembly techniques using monomer and polymer solutions. The morphology of the surface changes depending on the deposition process of metal coordination polymers. The monomer and the Zr metal coordinated in a linear fashion (polymerized) during deposition, based on UV–vis, SPS, and AFM measurements. Furthermore, the orientation of the growing polymer is determined to be nearly orthogonal from the substrate, based on the dimensions

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of the monomeric units and the layer thickness. The solution-synthesized polymer, on the other hand, did not have well-behaved deposition properties, which resulted in rough films as determined by AFM and SPS measurements.

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