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MULTILAYER SELF-ASSEMBLIES AS ELECTRONIC AND OPTICAL MATERIALS

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ABSTRACT

The layer-by-layer growth of film structures consisting of sequential depositions of oppositely charged polymers and macrocycles (ring-shaped molecules) have been constructed using molecular self-assembly techniques. These self-assembled thin films were characterized with X-ray reflectometry, which yielded (1) the average electron density, (2) the average thicknesses, and (3) the roughness of the growth surface of the self-assembled multilayer of macrocycles and polymers. These observations suggest that inorganic-organic interactions play an important role during the initial stages of thin-film growth, but less so as the thin film becomes thicker. Optical absorption techniques were also used to characterize the self-assembled multilayers. Phorphyrin and phthalocyanine derivatives were chosen as one of the building blocks of the self-assembled multilayers because of their interesting optical properties.

INTRODUCTION

The sequential deposition of multilayers has attracted recent interest because it allows the fabrication of artificial materials with unusual properties.¹ Here, self-assembly techniques are used to produce material in a layer-by-layer manner, as opposed, for example, bulk crystal growth. However, the growth of so-called engineered or functional multilayers is extremely challenging because many parameters of the multilayer interfaces must be optimized in order to fabricate mechanically and chemically robust structures. For example, strains across components in the multilayer should be minimized, while chemical affinity across these layers should be maximized in order to promote structural integrity and adhesion. These issues are very complex, and often investigations focus on the growth of monolayers rather than multilayers.²

Recently, Decher³ used charge interactions to assemble multilayers of polycations and polyanions. Others⁴ have adopted this method because it is an extremely simple and versatile technique to construct multilayer structures. Unlike covalently bound self-assembled mono- and multilayers,¹ charge interactions are very weak in water. In order to make reasonably robust films using charge interactions, previous work involved the fabrication of multilayer films using polymers containing many charged groups.

An important issue concerning the fabrication of multilayers using charge interactions is: what is the minimum number of charges needed for a molecule to self-assemble into a thin film? If this number, typically ≥ 200 for polymers, can be reduced to a very small number, e.g., less

than six, then multilayers could be grown from a larger material base than presently possible using charged polymers.

In order to form a self-assembled film, the charge interactions which bind the film together must overcome forces that may dissociate the film. For example, the dissociation energy due to thermal motion of molecules is about 0.6 kcal/mole, while a single non-selective (random) secondary interaction in water, such as a charge-charge attraction or hydrogen bonding, are about 5 kcal/mole. Based on this consideration, a molecule with four charges which act in concert to hold the film together, should have enough bonding affinity to overcome non-selective interactions. In this paper, we describe a multilayer molecular self-assembly with alternating macrocycles containing only four charges and positively charged polymers. The macrocycles used are $\alpha,\beta,\gamma,\delta$ -tetrakis(5-sulfothienyl)-porphine (TSTP) and nickel phthalocyanine-tetrasulfonic acid (NiPc), tetrasodium salt; and the polymer is poly(diallyldimethylammonium chloride) (PDDA) (Fig. 1).

Figure 1. Structures of $\alpha,\beta,\gamma,\delta$ -tetrakis(5-sulfothienyl)-porphine (TSTP) and nickel phthalocyanine-tetrasulfonate (NiPc), and their self-assembly of PDDA/NiPc/PDDA/TSTP.

The purpose of this study is to determine whether a macrocycle with four charges can be used as a building block to produce a self-assembled multilayer with optical properties. In order to gauge the success of thin-film formation, small-angle X-ray reflectometry is used to characterize the layered structure of this self-assembled system. In particular, X-ray reflectometry provides information about the electron density of the multilayer, its thickness, and the roughness of the growth interface.^{5,6}

RESULTS AND DISCUSSION

We found that PDDA (polycation) will attract NiPc or TSTP (anions) molecules, which results in the growth of alternating PDDA/NiPc or PDDA/TSTP multilayer. Multilayer growth is impossible with either component alone because polyions can not stack on top of themselves

without multivalent counterions. The multilayer thin films are a result of sequential reactions between PDDA and NiPc or TSTP on the growth surface, which yields alternating layered structures of PDDA and NiPc or TSP. We do not expect that there is ordering or crystalline within each layer because of the nature of organic polymers. Considering long polymeric chains, a mixture formation through interpenetration and diffusion of the macrocycle molecules between layers is unfavorable while compared to layered structures.

Figure 2 shows the optical spectra of multilayer thin-film growth from alternating dipping from negatively charged macrocycles and positively charged polymer PDDA. For PDDA/NiPc system, we observed strong Q bands at 630 nm and 665 nm. For the PDDA/TSTP system, the strong phorphyrin Soret band at ~430 nm was observed. These characteristic bands are ideal for monitoring the growth of multilayer thin films. Complex systems such as PDDA/NiPc/PDDA/TSTP can be obtained while replacing one of the macrocycle with another in every other deposition sequence. This flexibility at nanoscale of thin-film growth will allow incorporation of molecules with unusual properties such as charge transfer and nonlinear optical response.

Figure 3 illustrates the successful growth of the multilayer in a layer-by-layer manner. Optical absorption spectrum shows that the amount of materials deposited is essentially the same for each layer. Moreover, X-ray reflectivity measurements confirm that the amount of materials deposited for each bilayer corresponds a certain increase of the film thickness with a constant density. These prove the layered structure in the PDDA and NiPc system.

In order to obtain information about the structure of the multilayer, e.g., its electron density, ρ_e , thickness, Δ , and surface roughness, σ , reflectivity profiles of simple models were calculated and compared to the observed data. For the uncoated substrate ($n=0$), the model

Figure 2. Optical absorption of PDDA/NiPc (top), PDDA/TSTP (middle), and PDDA/NiPc/PDDA/TSTP (bottom).

consisted of a Si substrate with electron density ρ_{Si} , terminated by an overlayer of SiO_2 with electron density ρ_{SiO_2} and thickness Δ_0 . The roughness of the air- SiO_2 and SiO_2 -Si interfaces were represented as error functions⁷ whose derivatives—Gaussian peaks, have root-mean-square widths of σ_{Si} and σ_{SiO_2} , respectively. The X-ray reflectivity of the electron density depth profile, $\rho(z)$, was calculated using the Parratt formalism.⁵ The structural parameters of the model, i.e., ρ , Δ , and σ , from which $\rho(z)$ is determined, were perturbed (adjusted) so as to minimize χ^2 —the sum of the square differences between the calculated and fitted profiles weighted by the variance of the measurement.⁷ The curvature of χ^2 , as the adjustable parameters were independently perturbed about their optimal values, was used to deduce the degree of certainty (within 1- σ) to which a parameter was known.⁷

The solid curve in the upper profile of Fig. 4 is the profile calculated for the best fitting model. The electron density used for the Si substrate was that in the literature ($0.71 \text{ e}^-/\text{\AA}^3$).⁸ The electron density refined for the SiO_2 overlayer was $0.49 \pm 0.1 \text{ e}^-/\text{\AA}^3$. This value is in good agreement with that obtained from ref. 8. The thickness of the SiO_2 overlayer was determined to be $12 \pm 1 \text{\AA}$, which is also in good agreement with previous work.⁸⁻¹⁰ The roughness of the SiO_2 -Si interface was determined to be $3 \pm 1 \text{\AA}$, while the roughness of the air- SiO_2 interface was somewhat larger— $5 \pm 1 \text{\AA}$. Since the deposition of PDDA onto the substrate is not expected to alter the roughness of the substrate, the electron density profile representing the uncoated substrate served as the foundation for later models used to fit the reflectivity profiles taken of the multilayer.

The model for the coated substrate consisted of a layer with uniform electron density, ρ_N , thickness Δ_N , and air-sample roughness σ_N , on top of the model for the sample substrate discussed earlier. By choosing to represent the multilayer as a material with uniform electron density, variations in the electron density across the PDDA-NiPc bilayer were ignored. This variation, which is expected to be on the order of 10%, occurs over a very small distance—a distance, $2\pi/Q_{\text{max}}$, much smaller than the thinnest film that can be detected when X-ray data are collected to $Q_{\text{max}} \sim 0.27$.¹¹ The parameters, ρ_N , Δ_N , and σ_N , were adjusted to produce calculated profiles (solid curves in Fig. 4) that fitted the data very well.

To the extent the models adequately represent the structure of the multilayer, three conclusions can be drawn from the experiment. First, the electron densities of the bilayers did

Figure 3. Linear growth characteristics of PDDA/NiPc versus the number of bilayers.

not change during the fabrication of the multilayer. In other words, the electron density of the first deposited bilayer was not significantly different than that of any other bilayer. Since the chemical composition of a bilayer is known on the basis of charge neutrality to be one unit NiPc, $\{\text{Ni}[\text{C}_8\text{H}_3\text{N}_2\text{SO}_3]_4\}^{4-}$, to four monomeric units of PDDA, $[\text{C}_8\text{H}_{16}\text{N}]^+$, and using the mean of the electron densities, the mass density of a bilayer is computed to be $1.16 \pm 0.06 \text{ g/cm}^3$.

The second conclusion drawn is that the average thickness of the material deposited during the first two complete dipping cycles was large (about $20 \text{ \AA}$ thick), decreased sharply with subsequent depositions, and finally approached a value of about $8 \text{ \AA}$ after the deposition of about 40 bilayers. The sharp decrease in the mean per layer thickness of multilayer occurring after two dippings suggests that the inorganic substrate may play a role in the initial growth of the multilayer. As the PDDA polymer and NiPc macrocycle were deposited on the silicon substrate, a new inorganic-organic interface was created. The polymer might reorganize at this interface to direct the charged moieties onto the inorganic surface and minimize exposure of the hydrophobic chain segments to the hydrophilic surface. Therefore, the first few layers could contain many polymers that were twisted and turned to produce thicker films. As the film grows thicker, the polymers might have taken on more relaxed and extended structures because of the absence of inorganic hydrophilic interactions with the substrate. This may have led to a dramatic decrease of the relative bilayer-thickness for the first few layers.

Figure 4. Reflectivity profiles (o) of the Si-substrate terminated by SiO_2 ($n=0$) and the multilayer sample after differing numbers of PDDA-NiPc bilayer depositions.

The third conclusion is that the roughness of the air-sample interface or growth surface increased with each dipping. The roughness after the first deposition ($\sigma = 14 \text{ \AA}$) was larger than the roughness of the air- SiO_2 interface ($\sigma = 5 \text{ \AA}$). The roughness of the growth surface generally increased with each deposition. Similar increases in the roughness of polymer-multilayers have been observed previously by Kellogg *et al.*¹² They attribute the increase to an accumulation of defects which may occur during deposition of the polymer film. In the PDDA-NiPc multilayer system, tilting of the NiPc macrocycle might produce defects that can lead to an increase in the

roughness of the sample surface. To some extent, the PDDA polymer may "repair" or form bridges over defects, since the PDDA molecule is a long polymer chain compared to the NiPc macrocycle.

CONCLUSION

The growth of self-assembled multilayers from macrocycles and macromolecules was monitored with X-ray reflectometry and optical absorption. The X-ray measurements, were used to determine the electron density and thickness of the multilayer averaged over its lateral dimensions, and the roughness of the growth surface after different steps in the fabrication process. The electron density of a bilayer was found to be the same regardless of when the bilayer was deposited onto the sample. The average thickness of the first-deposited bilayers was large and decreased quickly to a value that did not change significantly after 40 bilayer-depositions. Furthermore, the roughness of the growth surface was found to increase with each deposition. Optical absorption measurements show that there is an approximately linear relationship between the absorbance (the density of macrocycles) with the number of bilayers.

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