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PHOTOELECTRON SPECTROSCOPY STUDY OF AMMONIA-INDUCED CHANGES IN ELECTROSTATICALLY-ASSEMBLED CONJUGATED POLYMER FILMS

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ABSTRACT

Exposure of electrostatically assembled polyelectrolyte films comprised of the anionic carboxylic conjugated polymer poly[2-(3-thienyl)-ethanolhydroxycarbonylmethyl-urethane], hereafter referred to as H-PURET, and polycations such as poly(diallyldimethylammonium) chloride, hereafter referred to as PDADMAC, to aqueous ammonia vapor leads to dramatic changes in the ultraviolet-visible absorption spectrum. In the case of H-PURET/PDADMAC, a shift from 442 to 494 nm is observed upon overnight ammonia exposure. X-ray photoelectron spectroscopy has been used to investigate the mechanism of the changes in optical properties. The C1s, O1s and S2p core levels exhibit negligible ammonia-induced changes. Two N1s peaks are observed in virgin H-PURET/PDADMAC assemblies, and ammonia exposure causes the nitrogen peak corresponding to the H-PURET side chain to become more intense relative to that of the PDADMAC layer. This selective change in the N1s feature suggests that ammonia interacts with the polythiophene side-chain, presumably by deprotonating the fraction of carboxylic acid groups that remain in the H-PURET layer. This deprotonation apparently leads to

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structural or single chain conformational changes in the conjugated polymer layers that alter the electronic absorption spectrum.

Key Words: Conjugated polymer; Programmed electrostatic assembly; Polythiophene; X-ray photoelectron spectroscopy

INTRODUCTION

Programmed-electrostatic assembly of conjugated polymers has emerged as a convenient means of fabricating well-defined multilayer films with electronic, photonic and sensor applications.[1–5] Briefly, a solid substrate with a charged planar surface is immersed in an oppositely charged polyelectrolyte solution, and the polymeric layer is adsorbed by electrostatic attraction. Depending on the details of the polyelectrolyte solution, ionic groups may remain exposed, effectively reversing the surface charge. After rinsing in water, the substrate is immersed in a solution containing an oppositely charged polyelectrolyte relative to that used in the previous step. Again, a charged polymer layer is adsorbed, but now the original surface charge is restored. By sequentially repeating these steps, alternating multilayer assemblies may be fabricated, with the film thickness determined by the number of repetitions of the cycle.

In previous investigations,[6,7] two anionic conjugated polyelectrolytes, a hydrolyzed urethane-substituted polythiophene, poly[2-(3-thienyl)-ethanolhydroxycarbonylmethyl-urethane], hereafter referred to as H-PURET, and 5,7-dodecadiyn-1,12-bis-(hydroxycarbonylmethylurethane), hereafter referred to as HP4BCMU, were electrostatically assembled in aqueous solutions with different polycations to study how the choices of counterion layer and pH affect the morphology and optical properties of the assemblies. Chitosan and poly(-diallyldimethylammonium) chloride, hereafter referred to as PDADMAC, were used as the polycations. Relevant chemical structures are shown in Fig. 1. These studies showed that while switching polycations did not alter the visible absorption spectra of HP4BCMU assemblies, it dramatically affected the optical properties of H-PURET multilayers. In the latter case, the absorbance maximum was found to range from 435 to 516 nm, depending on the polycation and solution pH during assembly. The lack of sensitivity of the optical properties of HP4BCMU to its counterion layer may be due to its robust conju-gated backbone.

It was also found that exposure of H-PURET films to aqueous ammonia vapor led to significant red shifts in their UV-Vis absorbance spectra, as demonstrated in Fig. 2. This phenomenon occurred regardless of whether the conjugated polyelectrolyte was the outer layer (i.e., as opposed to the case of stopping the assembly sequence with the polycation on top). Possible mechanisms by which ammonia exposure may affect the assemblies include chemically bonding to the conjugated polyelectrolyte layer or affecting its structure by modifying its morphology.

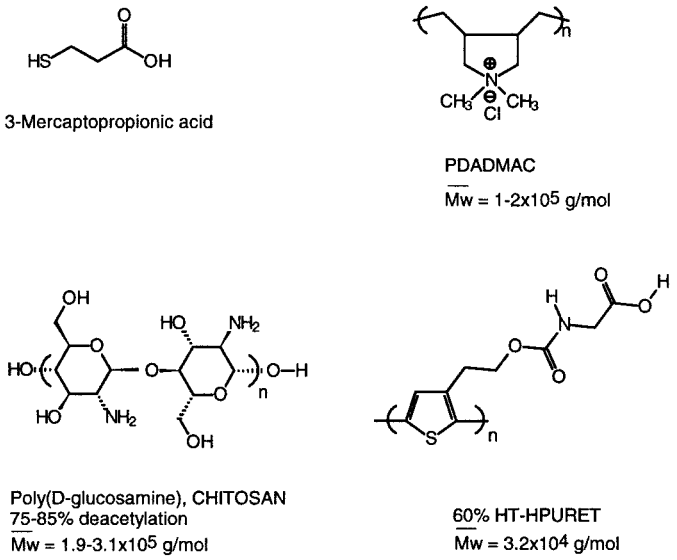

Figure 1. Chemical structures of the polyelectrolytes and the thiol used in this study.

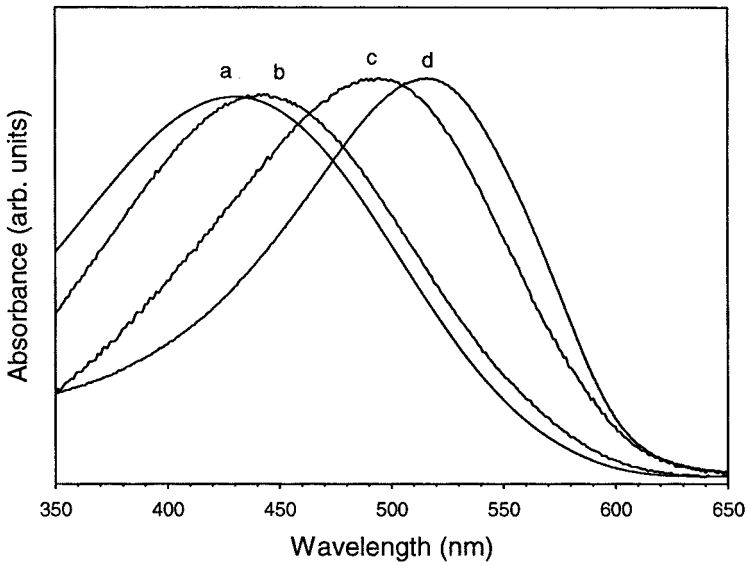

Figure 2. Ultraviolet–visible absorbance spectra of 30 bilayers of HPURET/chitosan deposited each at pH 4.0 (a); 4 bilayers of H-PURET/PDADMAC deposited each at pH 4.5 (b); the ammonia-exposed 4 bilayer sample (c); 30 bilayer HPURET/chitosan deposited, respectively, at pH 12, at pH 4.0 (d).

The present work describes surface science investigations aimed at understanding ammonia-induced changes of H-PURET/PDADMAC assemblies. These include X-ray photoelectron spectroscopy (XPS) before and after ammonia exposure, and the use of a mercaptopropionate priming layer assembled on gold to improve the quality of the polymeric assemblies.

EXPERIMENTAL

Chemicals

H-PURET (60% head-to-tail configuration, $Mw = 3.2 \times 10^4$ g/mol) was prepared according to the literature.[8] PDADMAC ($Mn = 1-2 \times 10^5$ g/mol), 75–85% deacetylated chitosan ($Mw = 1.9-3.1 \times 10^5$ g/mol), and 3-mercaptopropionic acid were purchased from Aldrich Chemical Company. All chemicals were used as received unless otherwise described.

Preparation of Electrostatically-Assembled Films and Ammonia Exposure

For UV-Vis studies, quartz slides that had been ultrasonically cleaned for 3 h with 1% "Chem-Solv" (Aldrich) and rinsed with distilled water were employed as the substrate. Electrically grounded gold substrates were needed for the photoelectron spectroscopy experiments in order to minimize charging that would lead to shifts of the binding energies of the peaks. A gold mirror, purchased from Edmund Scientific (IR grade, 76×102 mm, 6 mm thickness), was cut into ca. 1 cm $\times$ 1 cm pieces that were cleaned in freshly prepared piranha solution (30% H_2O_2:concentrated $H_2SO_4 = 1{:}3$) for 30 seconds, rinsed with distilled water, and dried in a stream of nitrogen. For those experiments in which a thiol on gold assembled monolayer was used as the priming layer, the layer was prepared by dipping freshly cleaned substrates into 10 mM ethanol solutions of the organomercaptan for 24 h. Following deposition, the thiol on gold layers were rinsed in pure solvent and dried under flowing nitrogen. For electrostatic assembly, the first immersion was in a cationic solution consisting of 2×10^{-3}M PDADMAC dissolved in water at pH 4.5 (pH adjusted by addition of HCl). This was followed by adsorption from anionic H-PURET 10^{-4} M solutions at pH 4.5. A dipping time of 10 min was used for each solution, and in between polycation and polyanion dips, it was immersed in a pH 4.5 rinsing solution made by adding HCl to deionized water and then dried in a stream of nitrogen gas. The cycle of alternately dipping in the polycation and polyanion solutions could be repeated any number of times to build up arbitrarily thick films. In the case of electrostatic assembly on the thiol on gold priming layers, the first PDADMAC layer was adsorbed directly onto the thiol, just as it was on either the quartz or bare gold substrates.

Ammonia vapor exposure was performed by filling the bottom of a dessicator with an aqueous 28% ammonium hydroxide solution. The electrostatically assembled film was then placed in the dessicator, but it did not touch the solution. The top was replaced on the dessicator, and the samples were typically exposed overnight.

Photoelectron Spectroscopy

The XPS experiments were performed in an oil diffusion-pumped VG ESCALAB II photoelectron spectrometer having a base pressure of ca. 1.0×10^{-9} mbar. MgKα radiation ($h\nu = 1253.6$ eV) was used as the excitation source, and electron kinetic energies were measured with a concentric hemispherical analyzer operating in constant analyzer energy mode with a pass energy of 20 eV. Silver paint was used to form a conductive path from the edges of the gold substrates to the sample stubs, which were held at electrical ground during the XPS measurements. Photoelectrons were detected approximately normal to the sample surface, and binding energies are reported with respect to the Fermi level.

RESULTS AND DISCUSSION

Figures 3, 4, and 5 show the C1s, S2p and O1 s regions, respectively, for 4 bilayer H-PURET/PDADMAC films before and after exposure to aqueous ammonia vapor. In this case, H-PURET is the outer layer. The bilayer sample was prepared by dipping in pH = 4.5 polycation and polyanion solutions. Spectra are also included for H-PURET and PDADMAC films spin-coated onto gold from 0.01% (in dimethylformamide) and 20 wt% (in water) solutions, respectively. Spin-coating rotation speeds of 500 and 1000–1500 rpm were used for the H-PURET and PDADMAC films, respectively. Profilometry measurements of electrostatically assembled H-PURET/PDADMAC films (adsorbed in acidic solutions) indicate an average bilayer thickness of ca. 88 Å. As shown in Fig. 3, the C1s spectrum for the 4-bilayer assembly is more similar to that of H-PURET than that of PDADMAC, as expected since H-PURET is the outer layer and MgKα XPS detects photoelectrons from depths of only 50–100 Å. As shown in Fig. 4, the S2p region of the assembly is also similar to that of spin-coated H-PURET. Previous work[9] has discussed in detail XPS spectra of spin-coated films of the related urethane-substituted polythiophene, poly[2(3-thienyl)ethanol n-butoxycarbonylmethylurethane].

Comparison of the C1s, S2p and O1s spectra of the assemblies before and after ammonia exposure indicates that only negligible changes occur in these core levels due to ammonia vapor exposure. In contrast, as shown in

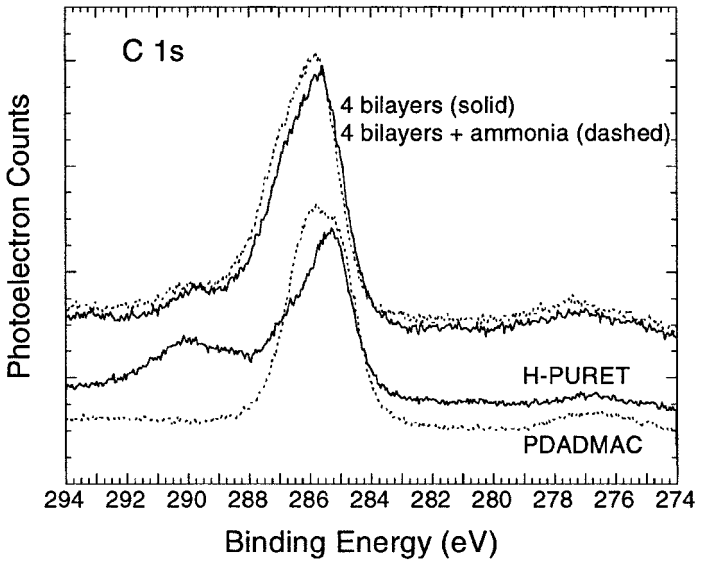

Figure 3. MgKα X-ray photoelectron spectra of the C1s region for spin-coated films of PDADMAC and H-PURET on gold substrates and for assemblies of 4 bilayers of HPURET/PDADMAC before and after ammonia exposure.

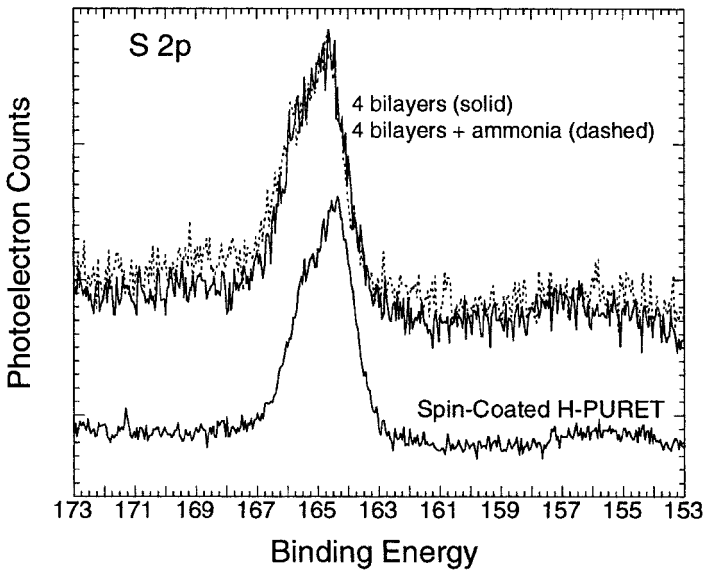

Figure 4. MgKα X-ray photoelectron spectra of the S2p region for a spin-coated film of HPURET on gold and for assemblies of 4 bilayers of HPURET/PDADMAC before and after ammonia exposure. The spin-coated H-PURET spectrum is offset for easy viewing.

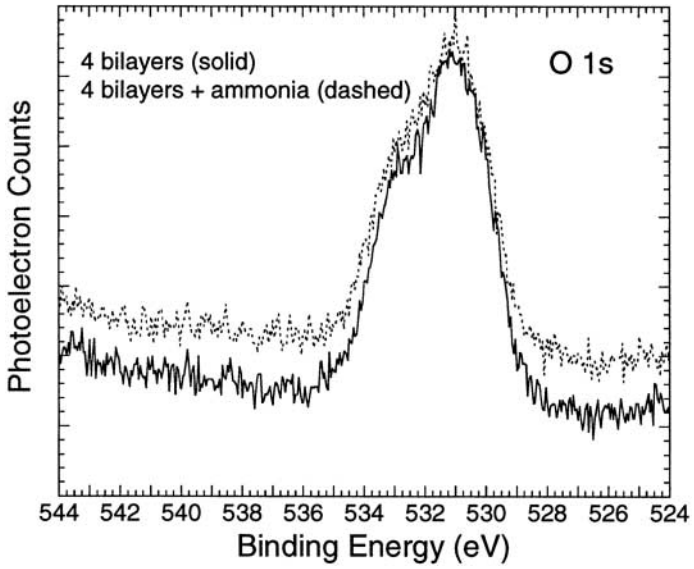

Figure 5. MgKα X-ray photoelectron spectra of the O1s region for assemblies of 4 bilayers of HPURET/PDADMAC before and after ammonia exposure.

Fig. 6, distinct changes occur in the relative intensities of the N1s peaks at 403.35 and 400.60 eV due to PDADMAC and H-PURET, respectively. Before exposure, the intensities are comparable; ammonia exposure leads to an increase in the height of the N1s feature originating from the H-PURET layers. Similar results have been observed for samples having a larger number of bilayers and for ones with PDADMAC as the outer layer.

In the process of fabricating these types of assemblies on gold substrates, the films were often found to be of variable quality with respect to uniformity and often patchy. This is in contrast to their preparation on quartz. The stability of thiol-functionalized molecules self-assembled on gold substrates[10] has led us to explore the possibilities of using a mercaptopropionate priming layer. The electrostatic assembly procedure was identical except that the additional step of first adsorbing the thiol layer on the gold surface was performed. This led to dramatic improvements in the quality of the films. Fig. 7 displays the N1s spectra for virgin and NH_3-exposed 4.5 bilayer H-PURET/PDADMAC samples assembled on a mercaptopropionate-primed gold surface. As in the case of the unprimed assemblies, the intensity of the N1s H-PURET peak is enhanced. The other core level spectra remain unchanged.

These results show that exposure to aqueous ammonia vapor selectively alter the N1s XPS feature and suggest that the H-PURET side-chain is primerily affected either by chemically reacting with NH_3 or by undergoing

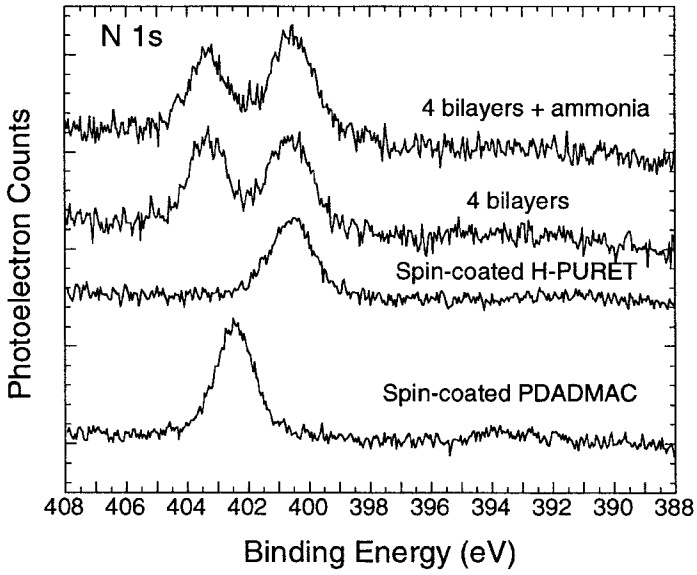

Figure 6. MgKα X-ray photoelectron spectra of the N1s region corresponding to the same samples in Fig. 3. The spectra are offset for ease of viewing.

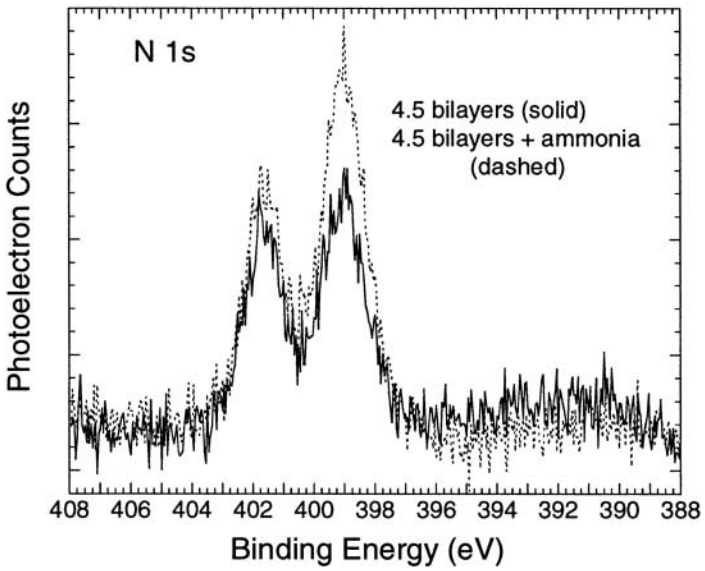

Figure 7. MgKα X-ray photoelectron spectra of the N1s region for assemblies of 4.5 bilayers of HPURET/PDADMAC before and after ammonia exposure. In this case, the assembly was carried out on a self-assembled mercaptopropionate layer, and the PDADMAC layer is on top.

morphological changes that affect its electronic spectrum. While the extra intensity in the lower binding energy N1s peak of the assembled films could result from complexed ammonia, it seems more likely that the major effect is a morphological change caused by deprotonation of the H-PURET carboxylic acid group in the side-chain. Nabok et al.[11] have observed ammonia and n-butylamine vapor-induced changes in the UV-Vis absorbance spectra of electrostatically assembled cyclo-tetrachromotropylene films and attributed those changes to a deprotonation mechanism, although no spectroscopic evidence to support this was presented. In the present case of the H-PURET films, the lack of changes in the O1s spectrum indicates that only a small fraction of the carboxylic acid groups are affected, consistent with the fact that a majority of these groups exist in the carboxylate form and are engaged in electrostatically bonding to the PDADMAC layer. Interestingly, it was found that exposure of the films to gaseous ammonia did not change the optical properties of the assemblies. It appears that aqueous ammonia is needed.

Attempts were made to perform He I ultraviolet photoelectron spectroscopy (UPS) to directly monitor changes in the electronic structure of the H-PURET assemblies. Unfortunately, valence spectrum features typically observed for polythiophenes,[12,13] including the localized thiophene ring features typically observed ca. 4.0 eV below the Fermi level and delocalized features tailing toward the Fermi level, could not be observed. Recent work by Herrera and Whitten[14] has shown that for spin-coated films of the related polythiophene, poly[2(3-thienyl)ethanol n-butoxycarbonylmethylurethane], these UPS features can only be observed upon thermal decomposition of the side-chain.

CONCLUSION

The dramatic red shift in the UV-Vis absorption spectra induced by exposure of H-PURET/PDADMAC assemblies to aqueous ammonia vapor corresponds to an enhancement of the N1s core level feature in the XPS spectrum due to the H-PURET layer. The lack of changes in the other XPS core levels suggests that ammonia exposure alters the polythiophene side-chain, presumably by deprotonation of the remaining carboxylic acid groups. This deprotonation then leads to structural or single chain conformational changes that manifest themselves by altering the electronic structure of the conjugated polythiophene layers.

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