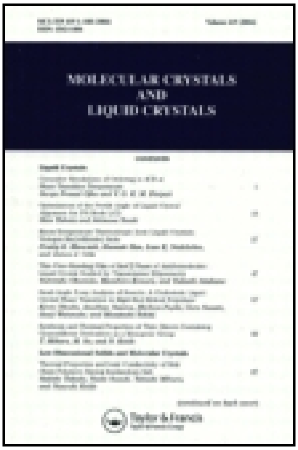

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Progress Towards the Fabrication of Langmuir-Blodgett Thin Films of Conducting Polymers

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The molecular organizations and electrical properties of multilayer LB films fabricated from monolayers comprised of a mixture of conjugated polymer chains and surface active molecules have been examined. LB films created from electrically conductive polypyrrole-based monolayers were found to consist of well ordered domains of the surface active component (3-octadecanoyl pyrrole) and partially oriented polymer chains. The multilayer films of this system were found to exhibit very large dielectric constants (>100) at low frequencies and enormous conductivity anisotropies. These unusual electrical properties can be directly attributed to the supermolecular organization of the film which consists of polypyrrole chains sandwiched between well ordered layers of the 3-octadecanoyl pyrrole molecules. LB films created from poly(3-alkyl thiophene)-based monolayers were found to be comprised of poorly ordered polymer domains randomly dispersed throughout a well ordered matrix of the surface active component (cadmium stearate). The level of conductivity reached by chemical oxidation and the magnitude of the resultant conductivity anisotropy were found to be strongly influenced by the type of dopant used and the manner in which it was introduced into the film. Doping from the solution phase produced the most highly conducting thin films but also dramatically altered the molecular organization of the film. Gas phase doping, on the other hand, could be accomplished without major modifications of the original heterogeneous structure of the film thus creating more anisotropic electrical properties.

1. INTRODUCTION

Over 50 years ago, Irving Langmuir and Katherine Blodgett established the methodologies needed to fabricate highly ordered, multilayer thin films of organic surface active molecules. Since that time, the Langmuir-Blodgett (LB) approach has been used extensively to control the thickness and molecular architecture of ultrathin films of organic insulators.[1] Most recently, this novel technique has been utilized to manipulate the order and molecular organization of thin films of electroactive and optically responsive organic materials.[2] Towards this latter goal, we have developed a number of new techniques[3,4] that can be used to manipulate electrically conductive polymers into LB films. This research is in direct response to the now well recognized need to identify new techniques for the processing of conducting polymers into thin film forms with well defined and controllable molecular organizations. Such films are expected to play an important role in the emerging areas of photonics and molecular electronics.

To date, we have successfully fabricated multilayer LB films from polypyrrole and a variety of the alkyl substituted polythiophenes. In the former case,[3] an excess of pyrrole monomer is polymerized at the air-water interface of an LB trough in the presence of a surface active pyrrole molecule and ferric chloride. The oxidizing ferric chloride subphase serves to polymerize the pyrrole monomer and render the resultant polypyrrole electrically conductive, whereas the surface active pyrrole, typically 3-octadecanoyl pyrrole, facilitates the spreading of the conducting polymer into a uniform monolayer. The electrically conductive mixed monolayer films can then be transferred into Y-type multilayer films using standard vertical lifting methods. The LB films containing the poly(3-alkyl thiophenes), on the other hand, are fabricated from mixed monolayers comprised of cadmium stearate and the conjugated polymer.[4] In this case, monolayer films are formed by spreading solutions containing various mole ratios of the performed polymer and stearic acid onto a pure water subphase containing cadmium chloride. The resultant mixed monolayers are then fabricated into Y-type LB films and, when desired, rendered electrically conductive via suitable doping techniques.

In both cases, the multilayer thin films are heterogeneous systems comprised of well ordered domains of the surface active molecules and less ordered domains of the conducting polymer. Thus, the multilayer structure created by the LB transfer technique and the heterogeneous nature of each molecular layer combine to produce a novel molecular organization that strongly influences the electrical and optical properties of the thin film. In this paper we describe a few example of some recent progress that has been made towards gaining an understanding of how the structure of these new thin films influence their electrical properties.

2. EXPERIMENTAL

Conducting films of polypyrrole were formed at the air-water interface of an LB trough by spreading a mixture of pyrrole and a surface active derivative of pyrrole, 3-octadecanoyl pyrrole (3ODOP) (5000/1 pyrrole/3ODOP molar ratio), onto a subphase containing 1% ferric chloride. The details of this procedure and the techniques used to form multilayers from this system can be found in our previous publications.[3] A different method was used to form monolayers of the poly(3 alkyl thiophenes) (PAT).[4] In this case, monolayers are formed by spreading mixtures of the performed polymer and a surface active molecule, stearic acid (SA) (molar ratios ranging from 1/2 up to 5/1 PAT/SA), onto the surface of the LB trough. Multilayers were then fabricated from these mixed monolayers using standard LB transfer techniques. In contrast to the polypyrrole/3ODOP system in which electrically conductive monolayers are created at the air-water interface, the poly(alkyl thiophene)/stearic acid system must be doped after the completion of the multilayer thin film to render it conductive.

All of these LB films form stable monolayers that can be readily transferred onto a variety of substrates such as glass, zinc selenide, or platinum-coated glass slides. This wide choice of substrates permits a flexibility in forming thin film devices which can be used to determine the electrical and spectroscopic properties of the conductive films. For example, sandwiching the film between two metallic layers produces a capacitor in which the multilayer film acts as the dielectric medium. Such capacitors were produced by first depositing the polymer multilayer onto a platinum-coated glass slide and then evaporating a thin film of aluminum on top of the multilayer to complete the device. Electrical contact was made to the top electrode by gently pressing a fine gold wire to the aluminum. The capacitance and resistance of these devices were recorded as a function of frequency to determine the frequency dependence of the dielectric constant and transverse conductivity. In-plane conductivity measurements were made on multilayer films deposited on an insulating glass substrate. Electrical measurements were made between 20 Hz and 1 MHz with a Hewlett-Packard 4275A or 4284A impedance analyzer, whereas a Keithley model 602 electrometer was used for DC conductivity measurements.

Fourier Transform Infrared (FTIR) spectroscopy was performed on LB films deposited onto either infrared transparent substrates such as zinc selenide (transmission measurements) or reflecting substrates such as platinum-coated glass slides (reflection measurements). In the reflection mode a grazing angle of 8° was used. Details about how transmission/reflection FTIR measurements can be used to determine the molecular orientation of molecules in LB films can be found in the literature.[5] All the infrared spectra were measured with a Digilab FTS-40 FTIR spectrometer equipped with a room-temperature deuterated triglycine sulfate detector. Films were scanned 256 times with a 4 cm^{-1} resolution.

3. RESULTS AND DISCUSSION

The LB films fabricated from either polypyrrole or the alkyl substituted polythiophenes can be best described as multiphase, molecularly layered thin films. In both cases, the multilayer films contain well ordered domains of a surface active molecule and relatively disordered domains of the electroactive polymer. In order to relate the electrical and optical properties of these new heterogeneous thin films to their structures, it is necessary to determine the molecular organization and level of order present in each phase and the organization of the two phases with respect to each other. Thus, the structure of the thin film must be probed at both the molecular and supermolecular level.

3.1 Spectroscopic studies

Transmission/reflection FTIR measurements provide direct information about the molecular order and orientation of the various molecules present in the film. Such information is obtained by comparing the intensities of absorption bands characteristic of key functional groups observed in both the transmission and reflection spectra. Functional groups whose transition dipole moments are found essentially in the plane of the film will exhibit stronger vibrational bands in transmission than in reflection. Functional groups oriented perpendicular to the film substrate, on the other hand, will exhibit stronger absorption bands in the reflection spectrum as compared to the transmission spectrum. Figures 1 and 2 show the reflection and transmission spectra of multilayer films fabricated from monolayers of polypyrrole/3ODOP, poly(3-hexyl thiophene)/deuterated stearic acid (2/1 mole ratio of PHT/DSA) and poly(3-octadecyl thiophene)/deuterated stearic acid (2/1 mole ratio of PODT/DSA) in select regions of the infrared spectrum. Also included in Figure 2 are the transmission and reflection FTIR spectra of a multilayer thin film of pure deuterated stearic acid. The FTIR spectra of all of these LB films show a strong polarization dependence indicating preferential ordering of the molecules within the films.

In the case of the polypyrrole/3ODOP system (Figure 1), the absorption bands due to the N-H and carbonyl stretching vibrations of the 3ODOP pyrrole head groups (3200 cm^{-1} and 1630 cm^{-1} respectively) are both significantly stronger in transmission than in reflection. If it is assumed that the carbonyl group and the pyrrole ring are coplanar, these results would suggest that the pyrrole head groups

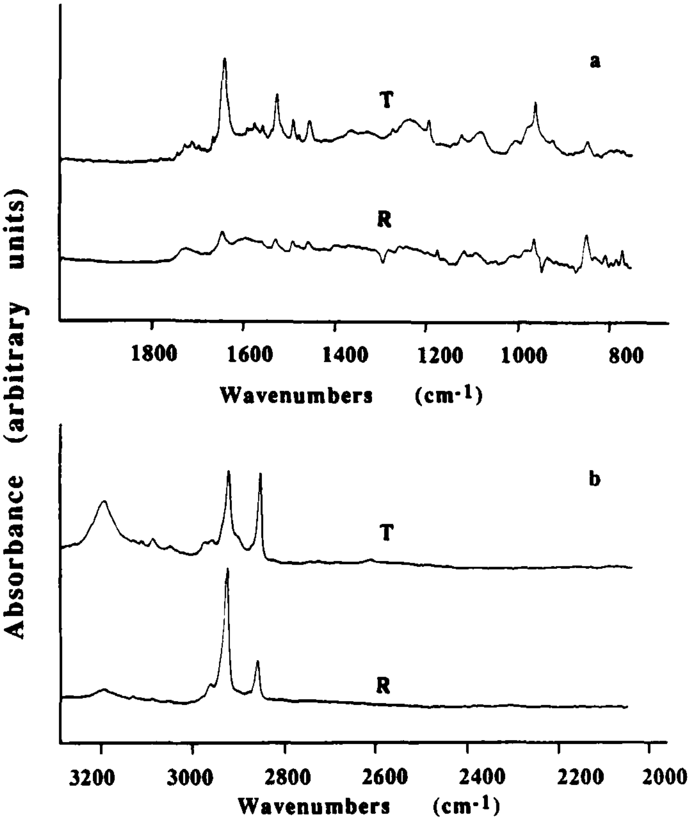

FIGURE 1 Transmission (T) and reflectance (R) FTIR spectra of PPY/3ODOP LB Films.

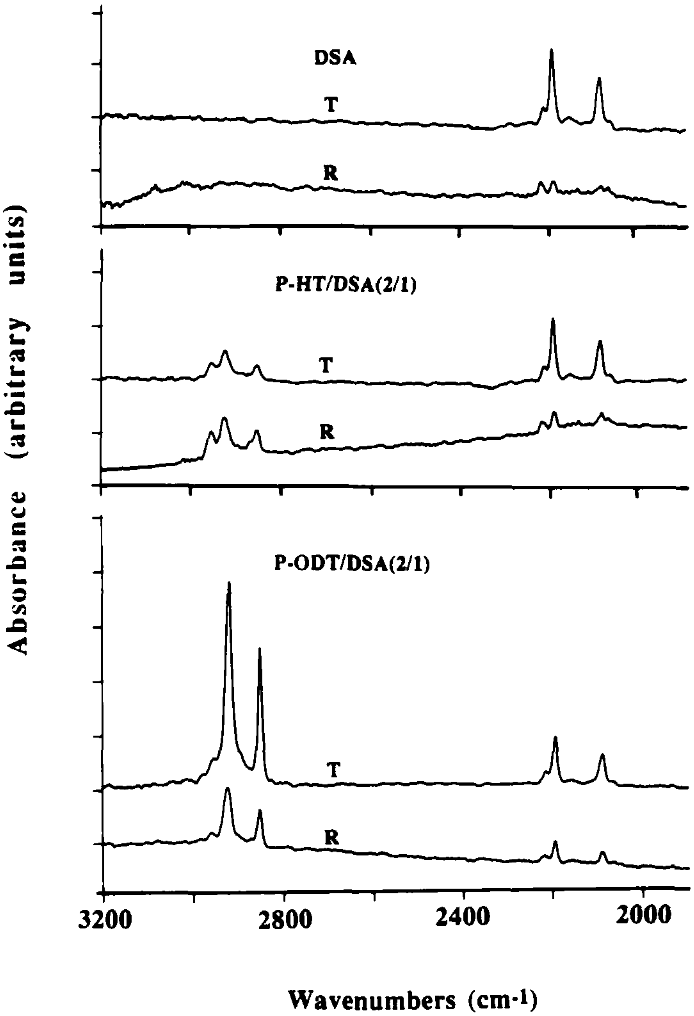

FIGURE 2 Transmission (T) and reflectance (R) FTIR spectra of LB Films fabricated from pure deuterated stearic acid (DSA), Poly(hexyl thiophene)/DSA (2/1) and poly(octadecyl thiophene)/DSA (2/1).

of the 3ODOP molecules are oriented preferentially within the plane of the film; i.e., they are lying parallel to the plane of the substrate. Alternatively, a non-coplanar arrangement of the carbonyl and pyrrole ring would indicate that the rings are oriented edge on to the substrate. A determination of the exact orientation of the head groups awaits a more detailed assignment of all of the in-plane and out-of-plane pyrrole ring vibrations. In any event, it is clear that the pyrrole rings of the 3ODOP molecules are preferentially oriented within the multilayer thin films.

An examination of the C-H stretching region (between 2800–3000 cm^{-1}) in

Figure 1b reveals that the hydrocarbon tails of the 3ODOP molecules are also preferentially oriented within the multilayer films. As can be seen, the intensity of the asymmetric CH_2 stretching vibration at 2920 cm^{-1} is greater in reflection than in transmission while the intensity of the symmetric CH_2 stretching vibration at 2851 cm^{-1} is significantly weaker in reflection than in transmission. Since the asymmetric and symmetric CH_2 vibrations have dipole moments that are orthogonal with respect to each other and are both contained within the plane that is perpendicular to the fully extended hydrocarbon chain axis,[7] the above observations suggest that hydrocarbon tail groups of the 3ODOP molecules are oriented perpendicular to the plane of the substrate and are tilted away from the substrate normal with an unusually large tilt angle. Although a complete analysis of these data has not yet been conducted, these results suggest a tilt angle of at least 45° from the substrate normal. This conclusion is further supported by low angle scattering results obtained from a multilayer of pure 3ODOP which indicate a bilayer repeat distance of about 28 Å. To achieve this bilayer stacking, the molecules would have to pack with a tilt angle of about 55° from the surface normal. The FTIR spectra of multilayer thin films of pure 3ODOP display a similar polarization dependence as the mixed films indicating that the 3ODOP molecules retain their usual molecular organization in the presence of the polypyrrole chains. Preliminary NEXAFS analysis[6] of the mixed LB films also supports the existence of surface active molecules packed with an unusually large tilt angle.

The broad infrared vibrational bands characteristic of electrically conducting polypyrrole found in the region between 1000 and 1400 cm^{-1} are also seen to be significantly more intense in transmission than in reflection. This would suggest that the heterocyclic backbones of the polypyrrole chains are preferentially oriented with their long axes within the plane of the substrate. Thus, FTIR analysis indicates that the LB fabrication technique creates multilayer structures in which both the 3ODOP molecules and the polypyrrole chains assume specific orientations. A complete analysis of the FTIR data will be presented in a future publication.

Figure 2 displays the FTIR spectra of multilayers fabricated from the poly(3-alkyl thiophene)/stearic acid based system. In order to separately examine the orientation of the hydrocarbon tails of the cadmium stearate molecules and of the alkyl sidegroups pendent to the polythiophene backbone, the multilayer films were fabricated with deuterated stearic acid. Since the vibrational bands of the hydrocarbon tails of the deuterated stearic acid molecules are shifted to lower wavenumbers relative to the hydrocarbon sidegroups of the polythiophene molecules, it is possible to independently examine the orientation of both molecules. The asymmetric and symmetric CD_2 and CD_3 stretching vibrations of the hydrocarbon tail groups of deuterated stearic acid are found in the 2000–2300 cm^{-1} region while the asymmetric and symmetric CH_2 and CH_3 stretching vibrations of the hydrocarbon tail groups of the various alkyl substituted polythiophenes are found in the 2800–3000 cm^{-1} region.

As indicated by the strong polarization dependence observed in Figure 2 for a pure multilayer thin film of deuterated cadmium stearate, this material forms well ordered multilayers comprised of highly oriented molecules. The FTIR reflection/transmission spectra are comparable to those obtained from multilayers of nondeuterated cadmium stearate which is known to form highly ordered Y-type multilayer thin films. In the transmission spectrum, the asymmetric (2193 cm^{-1}) and the symmetric (2088 cm^{-1}) CD_2 stretching vibrations are significantly more intense than the asymmetric (2214 cm^{-1}) and the symmetric (2066 cm^{-1}) CD_3 stretching vibrations. In the reflection spectrum, on the other hand, the intensities of the asymmetric and the symmetric CD_2 stretching vibrations are comparable to the asymmetric and the symmetric CD_3 stretching vibrations. Such a polarization dependence is known to occur[5] when the fully extended hydrocarbon tails are oriented close to the normal of the substrate surface. Thus, this is a well known signature of a multilayer thin film containing highly oriented surface active molecules with their hydrocarbon tail groups oriented nearly perpendicular to the substrate surface. It is interesting to note the difference between the polarization dependence of the vibrational bands characteristic of the hydrocarbon tails of the 3ODOP molecules (see Figure 1) and those characteristic of the hydrocarbon tails of the deuterated cadmium stearate molecules. This difference in polarization behavior is directly related to the different tilt angles experienced by these molecules in their respective environments. In both cases, however, well ordered domains of the surface active molecules are clearly indicated.

When the poly(3-alkyl thiophene) molecules are mixed with deuterated stearic acid and formed into multilayers, the resultant LB films show a polarization dependence that is dependent on the length of the alkyl chain pendent to the polymer backbone. In the case of poly(3-hexyl thiophene), it can be seen in Figure 2 that the CH_2 and CH_3 stretching vibrations of the hydrocarbon groups of the polythiophene molecules observed between 2800 cm^{-1} and 3000 cm^{-1} do not show any significant polarization effect indicating a random orientation of these groups. The vibrational bands due to the deuterated cadmium stearate molecules (between 2000 and 2300 cm^{-1}), on the other hand, show a polarization dependence that is very similar to that observed in a pure multilayer of deuterated cadmium stearate; albeit not quite as dramatic (as judged by the ratio of CD_2/CD_3 intensities in the reflection spectrum) due to the effects of disorder that are introduced when such high loadings of polymer are used (2/1 mole ratio of PHT/DSA). At lower polymer levels, the polarization dependence is identical to that of a highly ordered film of deuterated cadmium stearate.

For the multilayer thin film formed with a 2/1 mole ratio of PODT/DSA, it can be seen that the level of molecular orientation of the deuterated cadmium stearate molecules is greatly reduced as is clearly indicated by the observation of a CD_2/CD_3 intensity ratio that is essentially independent of polarization. The weak but significant polarization dependence of the CH_2/CH_3 intensity ratio, however, indicates that the hydrocarbon tails of the polymer molecules are partially oriented within this film. We have found that the level of orientation of the alkyl groups of the PODT molecules increases with increasing polymer content whereas the level of orientation of the hydrocarbon tails of the deuterated cadmium stearate molecules increases with decreasing polymer content. Thus, the most ordered deuterated cadmium stearate domains are found in films containing low polymer contents whereas the most ordered polymer domains are found in films containing high polymer contents. Apparently, the cadmium stearate molecules begin to mix with the long hydrocarbon tails of the PODT molecules at high polymer contents thereby restricting their ability to form separate, well ordered domains.

To summarize, the LB multilayer thin films created from PPY/3ODOP are comprised of highly oriented 3ODOP molecules and partially oriented electrically conductive polypyrrole chains. The hydrocarbon tails of the surface active 3ODOP molecules in this case are oriented perpendicular to the substrate surface with an unusually large tilt angle of about 55° from the surface normal whereas the polymer chains are preferentially oriented with their fully extended backbones contained within the plane of the substrate. The multilayer thin films fabricated from mixed monolayers of cadmium stearate and various poly(3-alkyl thiophenes), on the other hand, are comprised of highly oriented cadmium stearate molecules and randomly organized polythiophene molecules. In this case, the hydrocarbon tail groups of the surface active cadmium stearate molecules are oriented nearly perpendicular to the substrate normal. In general, the highest level of molecular orientation of the surface active molecules is found in films containing a low molar percentage of polymer molecules with short alkyl sidegroups. Evidence for orientation of the hydrocarbon groups of the polythiophene molecules was only found when the polymer was fitted with very long alkyl groups such as an octadecyl group which apparently becomes partially oriented in films containing a high polymer content.

3.2 ELECTRICAL MEASUREMENTS

As might be anticipated, the heterogeneous multilayer structures of the LB films fabricated from these two different electroactive polymers have a direct influence on the electrical properties of the films. For example, measurements of the in-plane electrical conductivity of the multilayer thin films fabricated from the PPY/3ODOP system reveal a value of about 10^{-2} S/cm. The transverse conductivity, on the other hand, ranges from 10^{-7} to 10^{-10} S/cm depending on the details of the fabrication procedure.[6] This remarkable conductivity anisotropy, in some cases exceeding over 10^{8}, provides direct evidence that the multilayer structure is also highly anisotropic. Electrical measurements coupled with spectroscopic and x-ray diffraction studies therefore suggest that the electrically conductive polypyrrole chains are sandwiched between well ordered molecular stacks of the insulating 3ODOP molecules. In such an organization, conduction can occur readily in the plane of the film since the conducting polypyrrole chains form a continuous or near continuous layer. Conduction across the film thickness, however, would be restricted by the presence of the insulating domains of 30DOP.

The frequency dependence of the dielectric constant and transverse conductivity of a multilayer thin film of PPY/3ODOP are shown in Figure 3. The dielectric constant is seen to be very low at high frequencies but increases continuously with decreasing frequency eventually reaching a very large value of about 150. The transverse conductivity, on the other hand, steadily decreases with decreasing frequency approaching its measured DC transverse conductivity of 10^{-10} S/cm at the lowest frequencies. This behavior may be interpreted as resulting from the limited mobility of charge carriers in the transverse direction of this structure. The charge carriers can traverse short distances by hopping or tunneling between localized

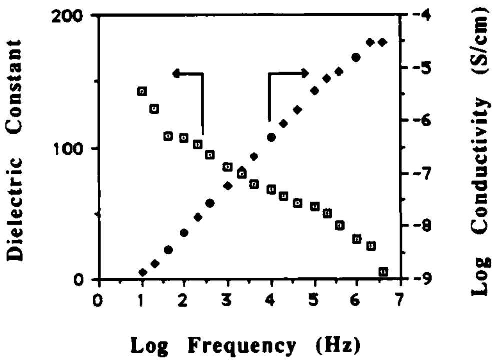

FIGURE 3 The dielectric constant and transverse conductivity of the polypyrrole/3ODOP multilayer thin film as function of frequency.

defect sites, however, movement over longer distances is impaired by the presence of the insulating barriers. The AC conductivity at higher frequencies is dominated by a strong contribution from localized charge transport while at lower frequencies, the more limited amount of charge transport over longer distances dominates. The large dielectric constant of the film at low frequencies results from the accumulation of space charges at the interfaces of the conducting and insulating domains. At low frequencies, the movement of charge carriers (most likely bipolarons) and possibly mobile ionic species in the conducting phase is fast enough to follow the AC field, however, with progressively higher frequencies, the motion of the less mobile species is frozen out thereby eliminating their contribution to the dielectric constant. Again it can be seen that the novel molecular organization created by the LB technique has a dramatic influence on the electrical properties.

Unlike the polypyrrole based LB films in which the electroactive polymer is manipulated directly in its electrically conductive doped form, the LB films fabricated from the alkyl substituted polythiophenes must be doped after their fabrication to make them electrically conductive. It is therefore necessary to consider how the molecular organization of the film has been modified by the type of dopant used and the way that it is introduced into the film. The two basic methods that have been used to render these films conductive are gas phase doping with $SbCl_5$ or I_2 and solution phase doping from acetonitrile solutions of $NOPF_6$.

The conductivity of a film containing a 2/1 mole ratio of poly(3-hexyl thiophene)/stearic acid that has been doped with $NOPF_6$ from solution exhibits a conductivity of about 1 S/cm which is over three orders of magnitude greater than the conductivity reached after doping with $SbCl_5$ from the gas phase (about 1×10^{-3} S/cm). Optical measurements show that the polymer chains in both cases are completely oxidized by the doping process (in both cases, the interband transition is completely eliminated).[8] In addition, the conductivity anisotropy measured from the multilayers doped with $SbCl_5$ is at least two orders of magnitude greater than the films doped with $NOPF_6$. The conductivity anisotropy of films doped with $SbCl_5$ is estimated to be somewhat greater than 10^4. Note that the conductivity anisotropy of the polythiophene based LB films is significantly lower than that of the PPY/3ODOP multilayers. This reflects the fact the polypyrrole chains tend to be sandwiched between the domains of 3ODOP molecules whereas the polythiophene domains are more interdispersed in the cadmium stearate matrix.

The differences in the electrical properties of the PHT/SA LB films may be explained by the deleterious effects of liquid phase doping on the molecular organization of the films. In the case of gas phase doping, the basic heterogeneous film structure created by LB technique remains intact while doping in a solution necessarily requires that the film be saturated with a solvent. It is this interaction with the solvent which disrupts the film organization thereby making the film more disordered and much less anisotropic. Thus, the solution doped films exhibit electrical properties more characteristic of bulk poly(3-hexyl thiophene) due to the fact that the polymer chains are more uniformly distributed throughout the film after doping. The electrical properties of multilayers doped from the gas phase, however, are still dominated by the heterogeneous multilayer structure established by the LB technique. X-ray diffraction patterns recorded before and after doping have confirmed these conclusions.[8]

4. CONCLUSION

The multilayer LB films fabricated to date from electrically conductive polymers are comprised of well ordered domains of a surface active component and relatively disordered domains of the conducting polymer. When films are fabricated directly from electrically conductive polypyrrole, the polymer chains become partially oriented within the plane of the film and tend to be sandwiched between molecular stacks of the surface active molecules (3-octadecanoyl pyrrole). This results in a multilayer structure whose electrical properties are highly anisotropic. In some cases, conductivity anisotropies of over 10^8 have been observed. Multilayer thin films fabricated from mixed monolayers of the alkyl substituted polythiophenes, on the other hand, are comprised of disordered domains of the polymer molecules randomly dispersed throughout a well ordered matrix of the surface active molecules (cadmium stearate). In this case, doping with suitable oxidizing agents must be carried out to create electrically conducting LB films. The level of conductivity reached by doping and the resultant conductivity anisotropy are determined by the type of oxidant used and the manner in which it is introduced into the film. Doping from solution creates the most conducting films but also completely disrupts the original molecular organization. The original heterogeneous multilayer structure, however, can be retained by doping from the gas phase. This results in lower conductivities due to the influence that the heterogeneous structure has on the transport of charge carriers through the film.

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