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MOLECULAR ORGANIZATION AND ELECTRICAL PROPERTIES OF MIXED LANGMUIR-BLODGETT MULTILAYER THIN FILMS OF POLYPYRROLE

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ABSTRACT. The molecular organization of Langmuir-Blodgett multilayer thin films containing electrically conductive polypyrrole chains dispersed throughout insulating domains of surface active pyrrole molecules was examined by several thin film spectroscopic techniques. Reflection-absorption FTIR and NEXAFS spectroscopy have revealed that the 3-ODOP (3-octadecanoyl pyrrole) surface active pyrrole molecules are highly oriented within the film with their fully extended hydrocarbon chains tilted away from the surface normal with an unusually large tilt angle of about 55°. Evidence for preferred orientation of the polypyrrole chains was also found. The multilayer films 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 molecular organization of the film which consists of polypyrrole chains sandwiched between well ordered layers of 3-ODOP molecules.

1. Introduction

Recent improvements in the environmental stability and processibility of conducting polymers have stimulated renewed excitement in this very interesting class of materials. New synthetic methodologies based on precursor polymers and derivatized polymers have resulted in materials that can be readily manipulated into a variety of useful forms without severely compromising their electrical properties [1]. In addition, the availability of a number of new processible polymers means that it is now possible to control, via suitable processing techniques, the molecular organization and ordering of these materials. This, in turn, is expected to dramatically improve their overall electrical and mechanical properties. For example, the manipulation of processible conjugated polymers into films and fibers in which the polymer chains are fully extended along a preferred axis has already been shown to produce materials with enhanced mechanical strengths and dramatically increased electrical conductivities [1]. In order to truly exploit the novel electrical and optical properties of these materials, however, it is also necessary to develop processing techniques that can be utilized to form them into highly ordered thin films with controllable molecular organizations. Indeed, the realization of many molecular electronic and thin film sensor schemes is strongly linked to the availability of such films.

The Langmuir-Blodgett (LB) technique provides one of the few ways to manipulate organic materials into uniform thickness, thin film forms with controllable molecular architectures. Essentially, one simply disperses suitable molecules onto the air-water interface of a Langmuir trough and, by reducing the area available to the molecules, forces them to form an ordered condensed monolayer at the water surface. The monolayers are then sequentially transferred onto a substrate to produce a multilayer thin film; the thickness and molecular organization of which are precisely controlled by the number and type of monolayers deposited. Thus, using this approach, it is possible to form complex molecular architectures comprised of ordered layers of functionally different molecules exhibiting properties simply not found with the parent molecules in their normal molecular organizations.

To date, we have developed a number of different strategies that can be utilized to manipulate conducting polymers into multilayer LB films. All of these variations can be conveniently divided into two main categories: the manipulation of surface active conjugated polymers and the manipulation of non-surface active conjugated polymers. In the former case, the monomers or polymers used to make the LB films are structurally modified to create amphiphilic molecules that form true monolayers at the air-water interface. For the surface active monomers, polymerization is typically carried out at the air-water interface by adding an oxidizing agent into the water subphase resulting in an electrically conductive monolayer that is subsequently transferred into multilayers. It should be noted that it is also possible to first build multilayers from the surface active monomers and then electrochemically polymerize them as has been shown by Shimidzu and coworkers [2]. Alternatively, the surface active monomers can be prepolymerized and then directly manipulated via the LB technique. In the second main approach, soluble, non-surface active polymers are mixed with suitable portions of traditional surface active molecules such as stearic acid to from stable mixed monolayers that can be easily formed into LB films. This latter technique does not require any structural modification of the polymer and is generally applicable to any of the soluble conjugated polymers. A variation of this theme involves the adsorption of a non-surface active conducting polymer onto the monolayer of a surface active molecule and the transfer of this entire mixed bilayer assembly into a multilayer thin film.

Examples of the above processing schemes include the LB manipulation of mixed monolayers of stearic acid and the poly(3-alkyl thiophenes). In this case, it has been found [3] that mixed monolayers containing as much as 80 mole% of the conjugated polymer can be fabricated into multilayer thin films with well defined layer structures. The final molecular organization of these multilayer films consists of well ordered, highly aligned stacks of stearic acid molecules throughout which relatively disordered domains of the conducting polymer are dispersed. These films are, in fact, very reminiscent of biological membranes in which large protein molecules are dispersed throughout highly ordered bilayers of surface active phospholipid molecules. The conjugated polymer domains, however, do not achieve the level of ordering provided by nature in the protein molecules. The polymerization of pyrrole in the presence of a surface active pyrrole molecule at the air-water interface of an LB trough is an example of another approach that has successfully resulted in multilayer thin films of conducting polymers [4]. This system also produces a mixed monolayer, in this case, comprised of electrically conductive polypyrrole chains and insulating surface active pyrrole molecules.

In order to develop the full potential of these new thin film structures, new analytical approaches are necessary which allow detailed studies of the relationship between the molecular architecture on the one hand and the supermolecular ordering on the other. A number of techniques such as reflection/absorption FTIR spectroscopy [5] and Near Edge X-ray Absorption Fine Structure spectroscopy [6] (NEXAFS) have already been shown to be effective in determining the level of molecular order and orientation in insulating LB films. We are currently applying these techniques [7] along with other synchrotron radiation techniques to the study of these new electrically conductive LB films.

In this paper, we examine the structure and properties of LB films formed from the polypyrrole based system. It will be shown that by comparing the results of a number of different structural probes, it is possible to establish the structure/property relationships in these very interesting thin films.

2. Experimental

We have previously demonstrated [4] that electrically conductive polypyrrole films can be formed at the air-water interface of an LB trough by simply dispersing a solution containing a surface active pyrrole monomer and a large excess of pyrrole onto a subphase containing ferric chloride ($FeCl_3$). The ferric chloride acts to both polymerize the mixture at the air-water interface and simultaneously oxidize the resultant polymer thereby rendering it electrically conductive. Pyrrole monomer is needed to facilitate polymerization at the air-water interface as neither the surface active pyrrole monomer nor pure pyrrole will polymerize independently under the conditions used to prepare the films. A large molar excess of pyrrole monomer is used due to the high degree of water solubility exhibited by this material. Two types of surface active pyrrole monomers have been examined; 3-octadecyl pyrrole (3ODP) and 3-octadecanoyl pyrrole (3ODOP).

The key to creating electrically conductive polypyrroles that can be readily manipulated into multilayer structures using the LB technique lies with the proper choice of surface active pyrrole. For both surface active monomers, we find that electrically conductive films are only created at the air-water interface when a reaction is carried out between pyrrole and the surface active pyrrole with a mole ratio close to 5000/1. FTIR studies [4] clearly demonstrate that the 3ODP molecules are copolymerizing with the added pyrrole whereas the 3ODOP molecules only serve to promote the formation of polypyrrole homopolymer. Due to the higher reactivity of the former system, the reaction creates relatively thick (about 200 Å) surface films of polypyrrole rich copolymer that are extremely difficult to process into LB multilayer thin films. The latter system, on the other hand, produces uniform monolayer films at the air-water interface that can be easily transferred into multilayers using a conventional vertical lifting technique. Thus, the pyrrole/3ODOP system is preferred for fabricating multilayer thin films.

The synthesis of the surface active pyrrole monomers used in this study as well as the polymerization procedure have been described in detail elsewhere [4]. Polymerization was carried out on the water surface of a Lauda film balance at 20°C by spreading a solution of pyrrole and substituted pyrrole onto a subphase containing 1 wt % ferric chloride. Monolayers were transferred onto solid substrates as Y-type LB films at 25 mN/m and 20°C. A dipping speed of 5 mm/min was used to transfer the films. Drying times of at least two hours were used between the first and second dips. This time was reduced to one hour for all subsequent dips. Details of the electrical measurements will be published elsewhere.

3. Results and Discussion

The level of molecular order and orientation in LB films can be readily probed by reflection/absorption FTIR spectroscopy. In this technique, LB films are deposited onto two different substrates; an infrared transparent ZnSe plate and an infrared reflecting platinum coated glass slide. Transmission spectra are then recorded on the sample deposited on ZnSe and grazing incidence reflection spectra (with an incident angle of 8° to the substrate surface) are recorded on the sample deposited on the platinum coated slide. In the transmission mode, the electric field vector is exclusively polarized in the plane of the substrate and hence only those molecular vibrations that have a component of their transition dipole moment in the plane of the film will be activated. In the reflection mode, however, the electric field vector is polarized essentially perpendicular to the substrate therefore only probing molecular vibrations that have a component of their dipole moment normal to the substrate plane. Thus, by comparing the infrared spectra obtained in these two experiments, it is possible to ascertain the type and level of molecular orientation present in the film.

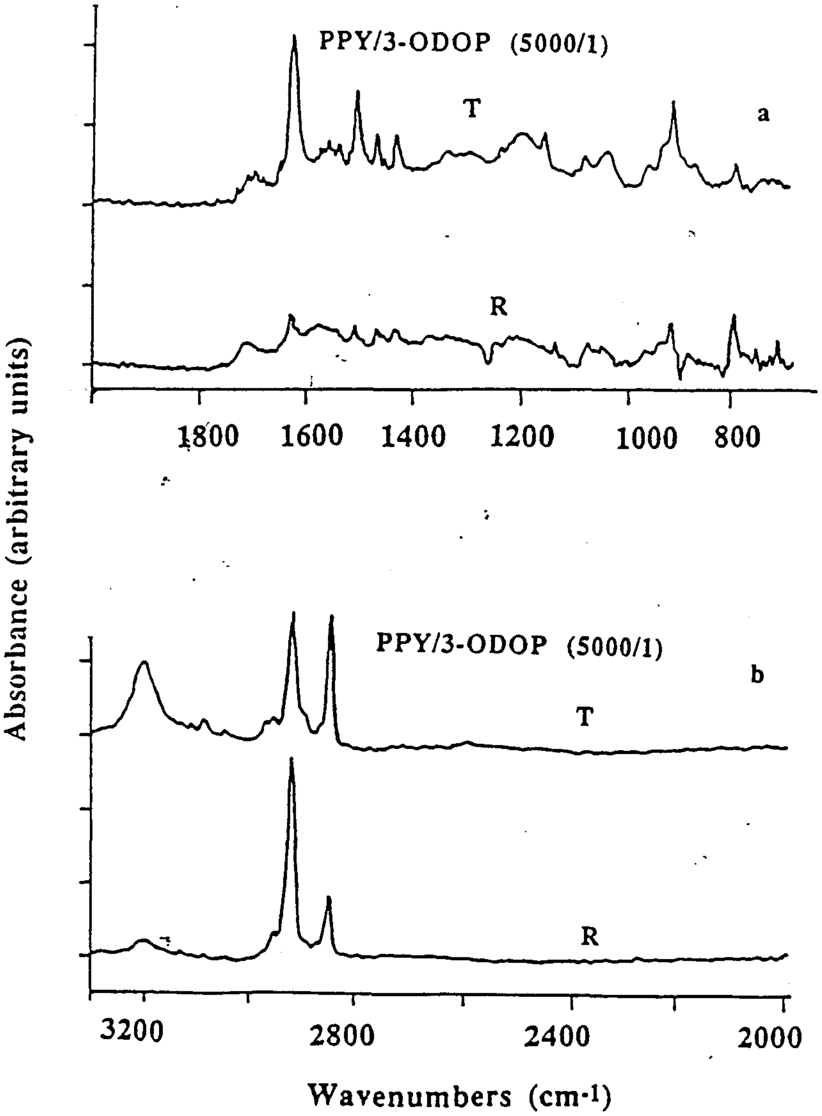

Figure 1. Transmission (T) and Reflectance (R) spectra of polypyrrole/3-ODOP multilayer thin films.

Figure 1 shows the reflection (R) and transmission (T) spectra of the polypyrrole/3ODOP system in two separate regions of the infrared spectrum. In Figure 1b, it can be seen that the absorption due to the hydrogen bonded N-H stretch (around 3200 cm^{-1}) of the 3ODOP pyrrole rings is significantly stronger in transmission than in reflection implying that the pyrrole rings are preferentially lying flat in the plane of the multilayer film i.e., the rings are oriented nearly parallel to the substrate. In addition, a clear polarization dependence is observed in the C-H stretching region (between 2800-3000 cm^{-1}) indicating some preferred orientation of the hydrocarbons tails of the 3ODOP molecules. Specifically, the asymmetric CH_2 stretch (2921 cm^{-1}) is seen to be about equal in intensity to the symmetric CH_2 stretch (2844 cm^{-1}) in transmission but of much larger intensity in the reflection spectrum. 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, it would appear that the hydrocarbon tail groups of the surface active 3ODOP molecules are tilted away from from the substrate normal with a unusually large tilt angle. Although a complete analysis of these data has not been conducted, these results suggest a tilt angle of a least 45° from the substrate normal. This conclusion is further supported by low angle x-ray scattering results obtained from a multilayer of pure 3-ODOP which indicate a bilayer repeat distance of about 28Å. To achieve this bilayer stacking, the molecules would have to pack with a tilt angle of about 55° from the surface normal. Thus, the 3ODOP molecules are well ordered within the electrically conductive mixed LB film, essentially retaining the level and type of molecular orientation present in a pure 3-ODOP multilayer film.

The infrared spectra depicted in Figure 1a also show a strong polarization dependence. The absorption band due to the carbonyl stretching vibration of the 3ODOP molecules at about 1630 cm^{-1} is significantly stronger in transmission than in reflection. In addition, the major pyrrole ring vibrations of the 3ODOP molecules between 1600 and 1400 cm^{-1} are also much stronger in transmission than in reflection. These observations are consistent with the pyrrole rings of the 3ODOP molecules being oriented preferentially in the plane of the substrate (assuming that the carbonyl and pyrrole ring are coplanar). If the carbonyl is not coplanar with the ring, it is possible that the rings may be oriented edge on to the substrate; a determination of the exact orientation of the head groups awaits complete assignments of all of the in-plane and out-of-plane pyrrole ring vibrations. It can also be seen that the polypyrrole chains of this mixed LB film tend to be aligned with their heterocyclic backbones lying parallel to the plane of the substrate. This is indicated by the fact that the absorption bands characteristic of oxidized polypyrrole (between 1400 and 1000 cm^{-1}) are much more intense in transmission than in reflection. Thus, both the 3ODOP molecules and the polypyrrole chains show evidence of preferred orientation in the multilayer structure.

X-ray absorption studies also provide valuable information about molecular orientation in LB films. These studies focus on the near edge structure of the core level absorption spectrum. In NEXAFS spectroscopy, core level electrons are excited by the incident photons to unoccupied orbitals near the ionization threshold. This technique takes advantage of the high degree of polarization of the x-ray beam emanating from a synchrotron storage ring. The excitations examined in this work are core level excitations to the unoccupied σ^* and π^* orbitals. By scanning the incident photon energy and monitoring the Auger electrons resulting from the relaxation processes of the excitation, the empty states, such as C-C σ^*, C=C σ^* and $\pi^*$and (C-H)*, can be identified and the direction of the bonds relative to the substrate plane can be determined.

Figure 3 shows the carbon *k*-edge NEXAFS spectra obtained from a multilayer of the polypyrrole/3ODOP system. Unlike the spectra obtained from a multilayer thin film of 3-octadecyl pyrrole monomer (3ODP), where a strong polarization dependence was clearly observed [7], the two spectra of polypyrrole/3-ODOP obtained with different polarizations are essentially identical. Generally, such a result would imply that the hydrocarbon tails of the 3ODOP molecules are disordered within the multilayer thin film. However, an alternative explanation is that the fully extended hydrocarbon tails are oriented perpendicular to the substrate direction with an unusually large tilt angle between 45 to 55 degrees from the surface normal. In light of the FTIR results, which show a clear indication of preferential orientation of the surface active pyrrole molecules, it is reasonable to conclude that the latter explanation is the correct one. Thus, the combined techniques of reflection-absorption FTIR spectroscopy, NEXAFS and low angle x-ray diffraction provide valuable insights into the structure of the conducting LB films.

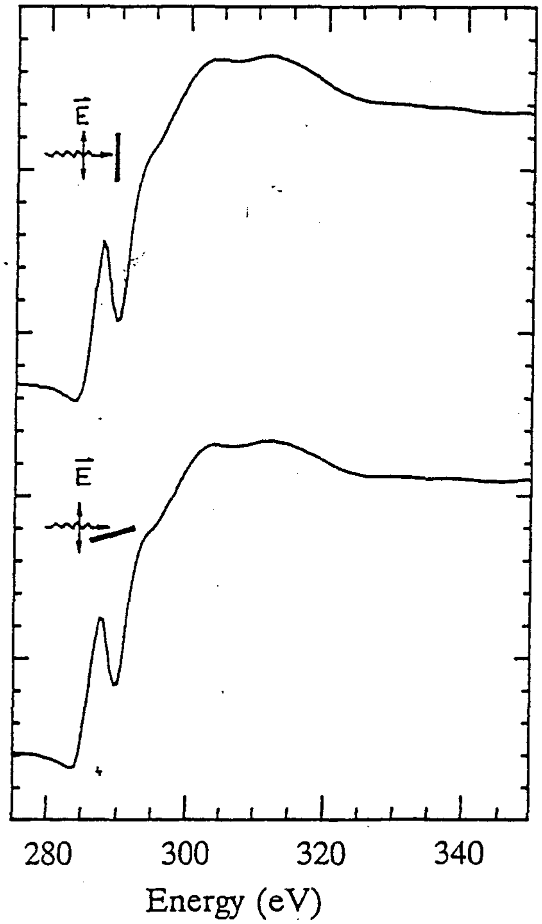

Figure 2. Carbon *K*-edge NEXAFS spectra at normal and glancing angle incidence for a 20 layer film of polypyrrole/3-ODOP

The above structural studies suggest that the polypyrrole/3ODOP multilayer thin films contain ordered regions of the 3ODOP molecules and partially oriented regions of electrically conductive polypyrrole molecules. The exact supermolecular organization of these two separate domains, unfortunately, can not be easily deduced from these measurements. A clue to how the two domains are organized with respect to each other within the multilayer structure, however, is provided by electrical measurements. For example, measurement of the in-plane electrical conductivity of typical multilayer films reveals a value of about 10^{-2} S/cm. The transverse conductivity, on the other hand, was found to be less than 10^{-10} S/cm. This remarkable conductivity anisotropy over 10^{8} clearly indicates that the structure of the film is also anisotropic.

Based on structural studies and electrical measurements, the current picture that emerges is that the multilayer thin films are comprised of polypyrrole chains sandwiched between well ordered insulating domains of 3ODOP molecules. In such an an organization, conduction could 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 3ODOP.

In order to evaluate the dielectric properties of the multilayer thin films fabricated from the polypyrrole/3ODOP system, monolayers were transferred onto a platinum coated glass slide to create a thin film with two steps of 44 and 60 layers. The thin film therefore consisted of two sections, each with a different film thickness; one about 1980 Å thick and the other about 2700 Å thick (each deposited monolayer is 45 Å thick). After drying the film in vacuum for two days to remove residual water, an array of aluminum electrodes having active areas of 0.02 and 0.04 cm^{2} was deposited onto the film via standard vacuum evaporation techniques. Each capacitor thus represents a sandwich structure of the type Pt/ LB film /Al.

The dielectric constant plotted as a function of frequency is presented in Figure 2. As can be seen, the dielectric constant displays a strong frequency dependence. At low frequencies, the dielectric constant is very large (around 150), it then drops to an apparent plateau in the range between 10^{4} and 10^{5} Hz with a value of about 50 and finally decays to values less than 5 in the MHz range. The frequency dispersion observed in this system reflects the influence of frequency on the movement of carriers and possibly ionic species to the various interfaces present in the sample. At low frequencies, the movement of these species across their respective domains is fast enough to allow them to easily follow the oscillating electric field. With progressively higher frequencies, however, the motion of some of the less mobile species is frozen out thereby eliminating their contribution to the dielectric constant.

It is tempting to attribute the large dielectric constant of this heterogeneous LB film at low frequencies to the accumulation of space charges at the interfaces of the conducting and insulating domains. As indicated earlier, the molecular organization in this case is best described as domains of conducting polypyrrole chains sandwiched between layers of the insulating hydrocarbon tail groups of the surface active 3ODOP molecules. Thus, carriers move through the polypyrrole domains, most likely via the hopping of positively charged bipolarons, until they encounter an interface with an insulating region of the film at which point they become trapped.

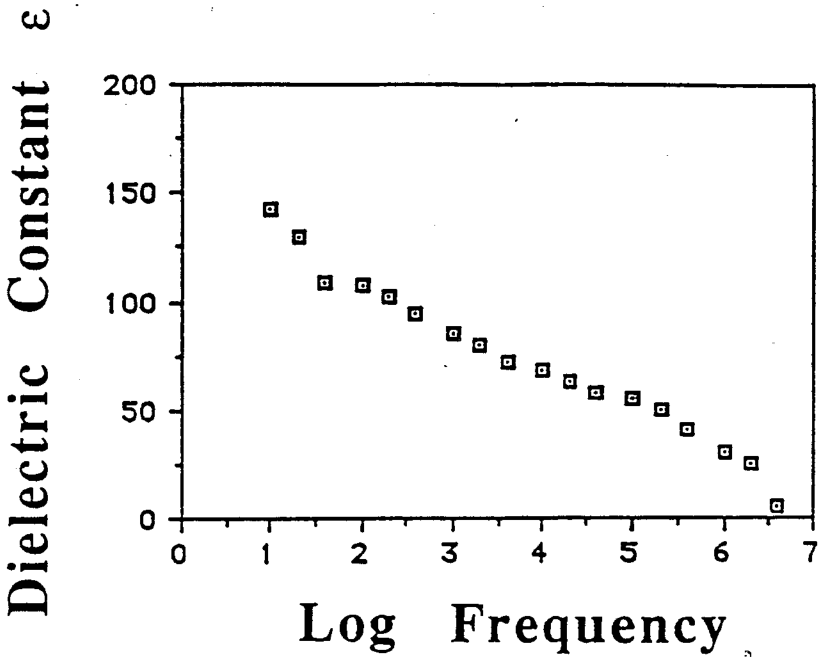

Figure 3. The dielectric constant of the polypyrrole/3ODOP multilayer thin film as function of frequency

4. Conclusions

Reflection-absorption spectroscopy and NEXFS studies have shown that LB films created from mixed monolayers of electrically conductive polypyrrole and 3-ODOP surface active molecules form multilayer structures comprised of polypyrrole domains dispersed throughout well ordered domains of 3-ODOP molecules. The resultant heterogeneous structures give rise to unusually large dielectric constants due to the trapping of mobile charge carriers at the various interfaces present in the film.

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