Manipulation of Multicomponent Langmuir-Blodgett Films of Electrically Conductive Polymers: Polypyrrole and Poly(3-Hexylthiophene)

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ABSTRACT

Multicomponent Langmuir–Blodgett (LB) films containing polypyrrole, 3-octadecanoyl pyrrole, and poly(3-hexylthiophene) were fabricated via a novel in-situ polymerization process. In this process, pyrrole monomer is polymerized at the air–subphase interface in the presence of poly(3-hexylthiophene) by using a subphase containing 1 wt% $FeCl_3$. The resultant electrically conductive films could be readily deposited onto solid substrates as Z-type films by the vertical lifting method. By using visible absorption, x-ray diffraction, and FTIR measurements, it was found that all three components were present within the transferred films, with the polypyrrole chains assuming a preferential orientation parallel to the film surface. The conductivities of the mixed LB films were as high as 1.0 S/cm, and the stability of the conductivity was very good. Chemical doping of poly(3-hexylthiophene) within the film with strong oxidizing agents such as I_2 further enhanced the conductivity of the film.

INTRODUCTION

The Langmuir–Blodgett (LB) technique has allowed the exploration of many exciting new possibilities in the field of molecular electronic devices and sensors [1]. The molecular-level control afforded by this technique makes it possible to manipulate and create multifunctional thin films with unique molecular and supermolecular organizations from a diverse array of organic and polymeric materials. Recent work from this group has demonstrated that it is possible to manipulate electrically conductive polymers such as the poly(3-alkylthiophenes), polypyrrole, and polyaniline using LB methodologies [2–9]. LB films and multilayer heterostructures fabricated from these materials display unusual electrical properties such as exceptionally large conductivity anisotropies [2, 6], high dielectric constants [2] and rectifying characteristics [9]. The ultimate aim of this work is to develop the chemistry and processing techniques needed to control the structure and orientation of key electroactive materials within LB films. Of particular interest is the fabrication of multicomponent systems in which each component serves a controllable and well-defined function. By manipulating the types of molecules present in the film and their spatial organization with respect to each other, the response of the film to specific environments, both chemical and physical, can be tailored at the molecular level.

In this paper we describe the preparation of a new multicomponent system fabricated from pyrrole monomer, 3-octadecanoyl pyrrole, and poly(3-hexylthiophene). We have previously shown that mixed monolayers containing poly(3-hexylthiophene) and 3-octadecanoyl pyrrole can be successfully manipulated into multilayer LB films [5]. By using 3-octadecanoyl pyrrole (3ODOP) as the surface-active agent, it was possible to form stable monolayers containing as much as 90 mol% of the nonsurface-active conjugated polymer. An advantage of using 3ODOP as a surface-active agent is that it is possible to use this system to create multicomponent films containing electrically conductive chains of polypyrrole. We have previously shown, for example, that electrically conductive polypyrrole can be synthesized at the air–water interface by spreading mixtures of pyrrole monomer and 3-octadecanoyl pyrrole onto a subphase containing ferric chloride [6]. Through the use of mixed monolayers of 3ODOP, it should therefore be possible to incorporate a variety of different conjugated polymers into LB films containing electrically conductive chains of polypyrrole. The interactions promoted between these different electroactive polymers could be the source of new electrical and optical effects. The main purpose of this paper is to demonstrate that pyrrole polymerization chemistry can be successfully carried out in the presence of added conjugated polymers.

EXPERIMENTAL

The poly(3-hexylthiophene) (PHT) used in this study was synthesized via the ferric chloride route as described elsewhere [10]. The isolated polymer was purified by Soxhlet extraction with methanol and acetone for 3 days each. The PHT used in this study had an M_n of 21,000 g/mol and an M_w of 114,000 g/mol as determined by gel permeation chromatography, using tetrahydrofuran as a carrier solvent. The synthesis of the 3-octadecanoyl pyrrole (3ODOP) has been described in a previous

paper [6b]. The structures of the materials used in this study are presented in Scheme 1.

The monolayers were formed at the air–water interface of a Lauda film balance by spreading chloroform solutions of PHT, 3ODOP, and pyrrole (Py) (concentration: 1 mg of a mixture of PHT and 3ODOP per 2 mL chloroform). The water used as the subphase was purified with a Milli-Q purification system (Millipore Corp.) and had 1 wt% ferric chloride added as an oxidizing agent to promote pyrrole polymerization. Polymerization was carried out on the subphase for 5 minutes at 20°C. After polymerization, the subphase containing $FeCl_3$ was removed and replaced with purified water. This procedure was accomplished by slowly adding purified water at one end (the pressure sensor side) of the LB trough and removing the original subphase at the opposite end. Specifically, a 1-L glass bottle was connected to the end (close to pressure sensor) of the LB trough with a Teflon tube and a 1-L glass bottle with an aspirator was connected at the opposite end with a Teflon tube. While the new subphase was added to the LB trough from the glass bottle of the pressure sensor side, an equal volume of subphase was concurrently removed through a system of glass tubes, one of which extended to the bottom of the dipping well. After the monolayers and the LB trough were washed with 2 L of a 5% HCl solution followed by 1 L of purified water, the subphase was left for 30 minutes and then washed again with 2 L of purified water. This procedure removes most of the $FeCl_3$ from the subphase without significantly altering the area per molecule of the monolayer (maintained under a constant pressure) and with limited deformation of the monolayer.

The multicomponent monolayers were transferred onto solid substrates as Z-type LB films at 24 mN/m and 20°C by the vertical dipping method. A dipping speed of 5 mm/min was used. Drying times of 1 hour were used after depositing the first and second layer, and this time was reduced to 18 minutes for all subsequent dips. The multicomponent LB films were built onto hydrophobic glass slides that were prepared by treatment with 1,1,1,3,3,3-hexamethyldisilazane for optical absorption, x-ray diffraction, and conductivity measurements. Zinc selenide plates and platinum-coated slides were used as substrates for FTIR measurements.

Visible absorption spectra were recorded using an Oriel Instaspec System 250 multichannel spectrophotometer. Small-angle x-ray diffraction measurements were made with Rigaku Routalex RU300 unit with CuK_α radiation. FTIR measurements
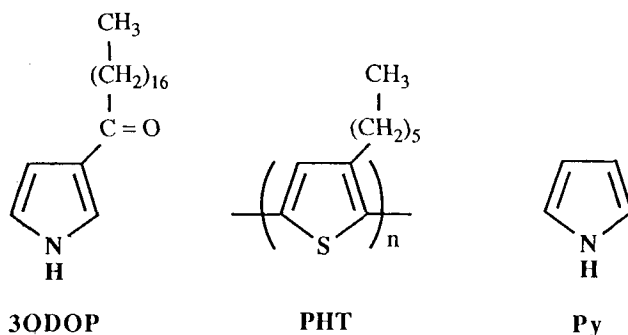
SCHEME 1.   Chemical structures of 3ODOP, PHT, and pyrrole monomer.

were made with a Nicolet 510P FTIR spectrometer with a MCT-B detector. A Spectra Tech Model 500 spectra reflectance accessory was used for the grazing incident reflection measurements (GIR). The GIR and transmission FTIR spectra were generated on multicomponent LB films consisting of a total of five layers. Film thicknesses were estimated with a surface profilometer (Dektak) on LB films with thicknesses greater than 2000 Å .

The multicomponent LB films were also chemically doped with I_2. The LB films were exposed to the I_2 vapor for 10 minutes under partial vacuum. D.C. in-plane conductivities were measured with a Keithley Model 602 electrometer via the standard four-probe technique.

RESULTS AND DISCUSSION

Electrically conductive polypyrrole can be formed at the air–water interface of an LB trough by spreading a solution containing excess pyrrole monomer and a suitable surface-active molecule onto an oxidizing subphase containing $FeCl_3$. In this procedure the surface-active molecule simply provides an environment suitable for the pyrrole polymerization and promotes the spreading of the resultant conducting polypyrrole chains into ultrathin layers [6]. The net result is a heterogeneous surface film comprised of electrically conductive chains of polypyrrole adsorbed onto a condensed monolayer of the surface-active molecules. As will be demonstrated shortly, this process can also be carried out in the presence of nonsurface-active conjugated polymers such as the poly(3-alkylthiophenes), thereby making it possible to fabricate complex, multicomponent surface films containing more than one type of electroactive polymer.

Figure 1 displays the pressure–area isotherms of 3ODOP on a pure water subphase, a 2/1 mole ratio 3ODOP/PHT mixed monolayer (based on the molecular weight of the PHT repeat unit) on a pure water subphase, and a 10,000/2/1 mole ratio Py/3ODOP/PHT monolayer spread on a 1 wt% ferric chloride subphase. As a basis for comparison, the area per molecule axis of the mixed monolayers is based solely on the number of 3ODOP molecules spread onto the subphase. This makes it possible to determine the effect that the added PHT and polypyrrole have on the ability of this material to organize into a condensed monolayer. As can be seen, although the limiting area per molecule has expanded slightly to about 36 $Å^2$/molecule, the collapse pressure and general features of the 3ODOP/PHT monolayer and the polymerized Py/3ODOP/PHT monolayer look remarkably similar to the isotherm of pure 3ODOP. The surface film of the pyrrole polymerized monolayer, however, exhibits a distinct black color (easily observed when the film is taken past its collapse point), indicating that conductive polypyrrole chains are indeed being formed at the air–subphase interface. From the behavior of the isotherms, it therefore appears that the 3ODOP molecules of the multicomponent systems are free to assume their usual monolayer organization on the surface whereas the electroactive polymer chains, for the most part, reside beneath the monolayer. In other words, the conductive polypyrrole chains synthesized at the air–water interface are forced beneath the condensed monolayer of 3ODOP molecules that is formed during film compression.
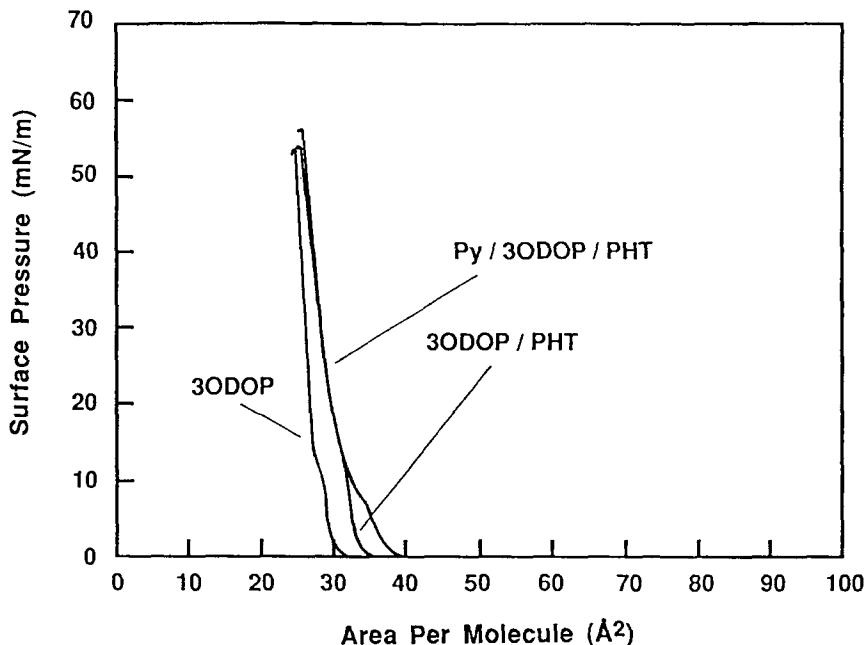
FIG. 1.   Pressure–area isotherms of 3ODOP, a (2/1) mixture of 3ODOP/PHT, and a (10,000/2/1) mixture of Py/3ODOP/PHT.

To further investigate the chemical and structural nature of the pyrrole-poly-merized system, monolayers were transferred onto solid substrates as Z-type LB films. The top curve in Fig. 2 shows the transmission FTIR spectrum of a Py/3ODOP/PHT (10,000/1/3) multicomponent LB film with five transferred layers. The presence of asymmetric and symmetric CH_3 and CH_2 stretching vibrations in the 2800–3000 cm^{-1} region indicates that the 3ODOP and/or the PHT molecules are successfully transferred into the multilayer films. Also note that this spectrum exhibits a collection of strong absorption bands in the 900–1800 cm^{-1} region and a broad absorption band that extends from about 1800 cm^{-1} into the near-infrared region. These absorption bands can be directly attributed to the presence of electri-cally conductive chains of polypyrrole [6]. The latter feature is, in fact, the tail of the polypyrrole bipolaron band that is centered in the near-infrared region and is a well-known signature of electrical conductive polypyrrole [11].

Information about molecular orientation within the multicomponent LB films was obtained via a comparison of the transmission and reflection (GIR) FTIR spectra. The bottom curve in Fig. 2 displays the GIR FTIR spectrum of a Py/3ODOP/PHT (10,000/1/3) LB film with five layers. Transmission and GIR FTIR measurements have been shown to provide direct information about the molecular orientation of the various molecules present in multicomponent LB films [7]. The information is obtained by comparing the intensities of absorption bands character-istic of key functional groups observed in both 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 GIR. On the other hand, func-
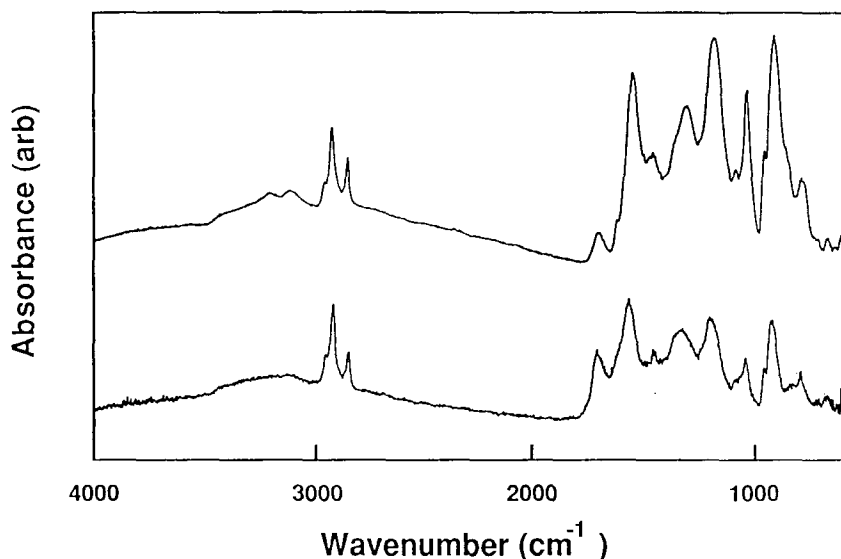
FIG. 2.   Transmission (upper) and GIR (lower) FTIR spectra of Py/3ODOP/PHT (10,000/1/3) multicomponent LB films with five layers.

tional groups oriented perpendicular to the film substrate will exhibit stronger absorption bands in GIR than in transmission.

As can be seen in Fig. 2, the absorption band (3200 cm^{-1}) due to the N—H stretching vibrations of the pyrrole head groups of 3ODOP is noticeably stronger *and more defined in transmission than in GIR. It should be noted that the* N—H *stretch of conducting polypyrrole is too weak and diffuse to be observed by FTIR.* Thus, the infrared activity in this region can be attributed solely to the 3ODOP molecules. The carbonyl absorption of the 3ODOP head group (observed as a weak shoulder at about 1630 cm^{-1} in the transmission spectrum) is also seen to be stronger in transmission that reflection. Spectra taken from films with slightly less polypyrrole present (not shown) also show this type of polarization dependence, albeit much more dramatic due to the fact that the strong absorption bands of the polypyrrole molecules are not masking it out. These results suggest that at least some of the pyrrole head groups of the 3ODOP molecules are preferentially oriented within the film and exhibit a tendency to lie parallel to the plane of the film surface [8].

The asymmetric and symmetric CH$_2$ and CH$_3$ stretching vibrations of the hydrocarbon tail groups of the 3ODOP and PHT molecules are found in the 3000–2800 cm^{-1} region. In this case, a strong polarization dependence is not observed, suggesting that the hydrocarbon tail groups are randomly oriented within the film. Previous studies of pure Y-type LB films of 3ODOP have shown that the hydrocarbon tail groups are highly oriented and preferentially tilted away from the film surface normal with an unusually large tilt angle [8]. In the polypyrrole multicomponent system, the intensity of the asymmetric CH$_2$ stretching vibration at 2920 cm^{-1} is slightly greater in GIR than in transmission, while the intensity of the symmetric CH$_2$ stretching vibration at about 2850 cm^{-1} is slightly weaker in GIR than in transmission. *Although very weak, this is the characteristic signature of tilting*

3ODOP molecules (the symmetric and asymmetric CH_2 stretching vibrations are contained within the same plane but are oriented perpendicular to each other within the plane; this provides a means to determine if the molecules are tilting in a preferred direction within the film) [8]. Thus, it is possible that the some of 3ODOP molecules are adopting their usual molecular organization and only the alkyl groups of the polythiophene molecules are randomly oriented. Unfortunately, it is not possible to independently probe the orientations of the alkyl groups of the 3ODOP and PHT molecules. Given the fact the 3ODOP head groups appear to be preferentially oriented within the LB film, it seems reasonable to conclude that some of the 3ODOP molecules are ordered within the film and that the disorder revealed by the methylene stretching vibrations is primarily due to the alkyl groups of the polythiophene molecules. In any event, it is clear that the fraction of 3ODOP molecules that assume a well-oriented organization is very small.

The most significant observation to be made in Fig. 2 is the strong polarization dependence observed from the bands associated with the conducting chains of polypyrrole. These bands are markedly greater in transmission than in GIR. Thus, it appears that the conductive polypyrrole chains exhibit a strong tendency to become oriented parallel to the film surface. In order to confirm this observation, optical spectra of the LB films were measured with p- and s-polarization light at angles of 45 and 0° to the film surface. These measurements revealed a polarization dependence consistent with polypyrrole chains oriented within the plane of the film, thereby confirming the above observation. Specifically, it was found that the dichroic ratio (ratio of the absorbance of the LB film measured at 45° with p-polarization light to that measured with s-polarized light) at 700 nm was about 0.77. Based on the intensities of the polypyrrole bands relative to those of the other components, we estimate that for the above indicated conditions, each deposited monolayer is comprised of about 50–70% polypyrrole (depends strongly on polymerization time and spreading solution).

Figure 3 shows the absorption spectrum of a Py/3ODOP/PHT (10,000/1/3) multicomponent LB film. The absorption band of the $\pi-\pi^*$ transition of the PHT conjugated backbone at about 480 nm is clearly observed in this figure as is a broad absorption at longer wavelengths that is associated with electrically conducting polypyrrole. This latter band is characteristic of a highly oxidized polypyrrole backbone that is supporting localized defect states in the form of bipolarons. The presence of a strong $\pi-\pi^*$ transition for the PHT molecules indicates that they are not oxidized/doped by $FeCl_3$ during the fabrication process and therefore exist within the LB film in their neutral, nonconducting state. Thus, the multilayer films are comprised of electrically conductive polypyrrole chains and neutral, nonconducting polythiophene chains. It should be noted at this point that the intensities of the visible absorption bands of this system as well as the vibrational bands observed in the FTIR spectra were found to scale linearly with the number of layers transferred to a substrate. This shows that the deposition process is very reproducible from layer-to-layer.

The x-ray diffraction pattern of a Py/3ODOP/PHT (10,000/1/3) multicomponent LB film is shown in Fig. 4. The multicomponent film exhibits only a single diffraction peak at a 2θ value of about 3° which gives a single layer repeat distance of about 29 Å . Interestingly, this corresponds nicely to the measured average thickness per layer of about 30 Å obtained using a surface profilometer. LB films of
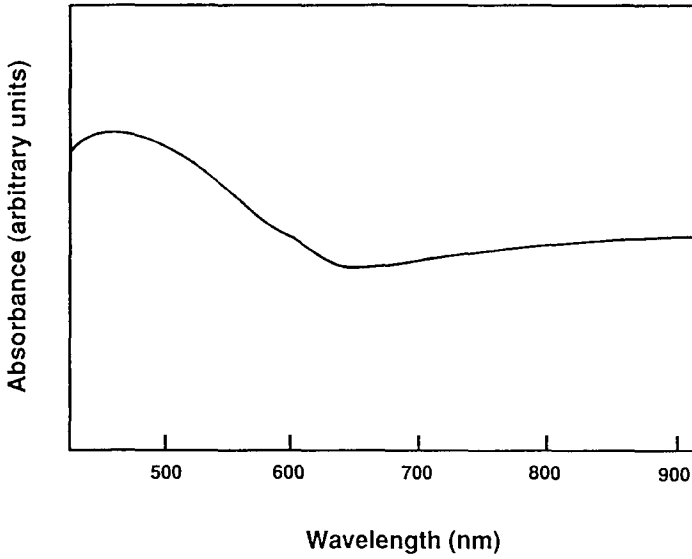
FIG. 3. Absorption spectrum of a Py/3ODOP/PHT (10,000/1/3) multicomponent LB film with 10 layers.
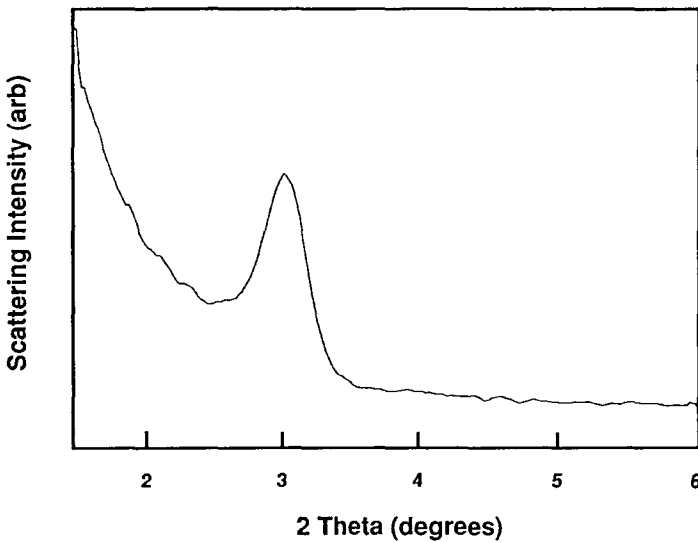

FIG. 4. X-ray diffraction pattern of a Py/3ODOP/PHT (10,000/1/3) multicomponent LB film with 10 layers.

pure 3ODOP have been found to exhibit a layer repeat distance of about 14 Å (28 Å bilayer distance). If it is assumed that the 3ODOP molecules adopt their usual layer thickness within the multicomponent LB film and the polymer chains are physically adsorbed to this condensed layer, then it appears that the PHT and polypyrrole molecules contribute a total of about 15 Å to the thickness per trans-ferred layer. This seems highly unlikely, however, since the multicomponent films transfer in a Z-type mode and are much more disordered than the pure LB films of 3ODOP. The observed weak diffraction peak therefore most likely represents the bilayer stacking of some 3ODOP molecules that have managed to reorganize into their normal multilayer structure within the multicomponent film.

The following conclusions can be made about the structure of the multicompo-nent LB films. PHT in its undoped form, 3ODOP, and electrically conductive polypyrrole molecules are all successfully and reproducibly transferred from the air–water interface into the multilayer LB films. The polypyrrole molecules formed at the air–water interface assume a preferential orientation parallel to the film surface after multilayer fabrication. The 3ODOP molecules show some evidence for preferred orientation within the LB film, although at a very low level which appears to be mostly due to the formation of phase-separated molecular stacks. No evidence was found to support the idea that the PHT molecules are preferentially oriented within the film. All of these results suggest that the surface-active 3ODOP molecules and the PHT conjugated chains simply act as processing vehicles that allow the formation and transfer of electrically conductive layers of polypyrrole. The net result is a relatively disordered multilayer organization in which undoped chains of poly(3-hexylthiophene) and 3ODOP molecules are randomly mixed with domains of electrically conductive polypyrrole chains.

In-plane conductivity measurements of the multicomponent LB films revealed that conductivities close to 1.0 S/cm can be realized in the as-transferred multilayers (typically around 0.7 S/cm). The conductivity in this case is due solely to the conductive polypyrrole chains as the PHT molecules are transferred in their noncon-ductive state. The in-plane conductivities were found to depend on the polypyrrole polymerization time, with films that were polymerized for at least 5 minutes achiev-ing the highest conductivities. Times longer than 10 minutes, however, produced monolayers that were too stiff to deposit onto substrates. The conductivities of the multicomponent LB films were found to be quite stable in air. Figure 5, for exam-ple, displays the conductivity stability of a Py/3ODOP/PHT (10,000/1/3) multi-component LB film. For comparison purposes, a film with a conductivity similar to that achieved with the 3ODOP/polypyrrole system is shown. After 60 days, the conductivity of the LB film is seen to only drop a small amount in air. It is interest-ing to note that the highest conductivities achieved with this more complex system were significantly higher than those typically obtained with the 3ODOP/polypyrrole system (typically about 10^{-2} S/cm). The stability of the conductivity in air for the multicomponent system was also much better than that observed with the 3ODOP/polypyrrole system. Apparently, the presence of PHT molecules favorably influ-ences the transport behavior and stability of the conducting polypyrrole chains. Alternatively, it might simply reflect the fact that a better quality polypyrrole is formed at the air–water interface when PHT is present. More work is clearly needed to ascertain the origin of this interesting effect.
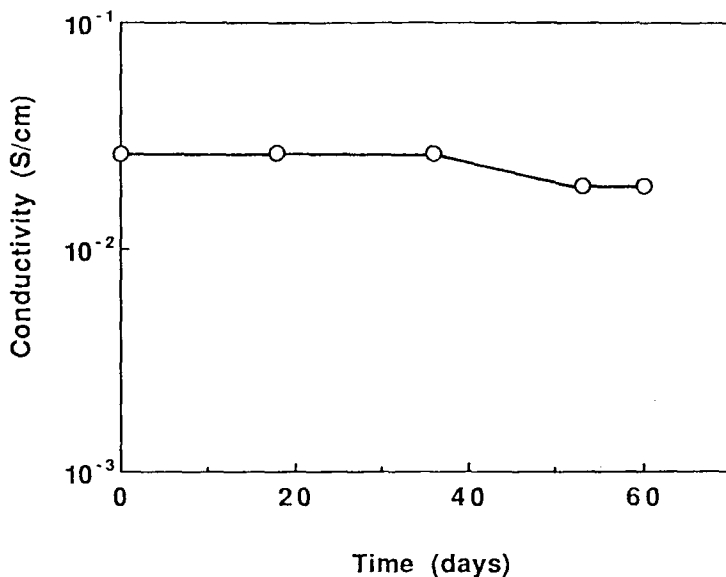
FIG. 5. Conductivity stability of a Py/3ODOP/PHT (10,000/1/3) multicomponent LB film with 5 layers.

The multicomponent LB films can also be further doped after deposition with dopants such as I_2 and $NOPF_6$. In case of I_2 doping, the conductivity of the LB film doubled, and the absorbance due to the $\pi-\pi^*$ interband transition of the PHT conjugated backbone decreased, consistent with the chemical doping of this material. This demonstrates that the electrical properties of the multilayer films can be further modified via the doping of the PHT molecules. In the case of I_2, the conductivity of the doped film decreased rapidly in air and reverted back to its original state in a few hours. Dopants such as $NOPF_6$, on the other hand, produce films with much better conductivity stability.

CONCLUSION

We have demonstrated that multicomponent LB films containing poly(3-hexylthiophene) and electrically conductive polypyrrole can be fabricated using a process involving the polymerization of pyrrole monomer on an LB trough. This represents one of the few LB systems that actually manipulates directly a conjugated polymer in its highly conductive form. In addition, the films can be further doped by exposure to strong oxidizing agents which render the PHT molecules electrically conductive. This new system may prove useful in the fabrication of novel molecular electronic devices and chemical sensors.

ACKNOWLEDGMENTS

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