

Preparation and Electrical Conductivity of Langmuir–Blodgett Films of Poly(3-alkylthiophene)s

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ABSTRACT: Five poly(3-alkylthiophene)s (P3ATs) with different alkyl side chains were synthesized. Pure P3ATs alone are not well suited for manipulation by the Langmuir–Blodgett (LB) technique, but their mixed systems with arachidic acid can be used to prepare high-quality Y-type films with the vertical dipping method, which was proved by UV-visible spectra and small-angle X-ray diffraction patterns. Conductivities of the LB films were measured using a two-probe method at room temperature. The conductivities exhibited obvious anisotropy and could increase by 2–4 orders of magnitude after iodine vapor doping. The influence of alkyl chain length on the conductivity in the LB films was revealed. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1–6, 1998

Key words: poly(3-alkylthiophene); LB films; conductivity; doping

INTRODUCTION

Since the first discovery of metal-like conducting behavior in doped polyacetylene,¹ conducting polymers have been attracting much attention because of the large number of potential applications. Polythiophene (PT) exhibits thermal and air stability. As to processibility, solubility and/or fusibility can be achieved by adding alkyl groups on the backbones of the polymer molecules. Therefore, poly(3-alkylthiophene)s (P3ATs) are promising materials for electronic application and have been stimulating much research interest.^{2–5}

Because the functional properties of materials are closely related to their micro-structures, a technique by which the polymer molecules can be fabricated into a highly ordered structure is expected. The Langmuir–Blodgett (LB) technique offers one of the few ways of obtaining such ordered, ultrathin, and thickness-controllable films.^{6–8} In this article,

we report on the formation and electrical conductivity of the LB films consisting of five P3ATs with different alkyl side chains and arachidic acid (AA) as well as the influence of side-chain length on the conductivities.

EXPERIMENTAL

Five species of 3-alkylthiophene monomers, 3-butylthiophene, 3-octylthiophene, 3-dodecylthiophene, 3-hexadecylthiophene, and 3-octadecylthiophene, were synthesized via the coupling of appropriate alkylmagnesium bromides with 3-bromothiophene in the presence of the catalyst Ni(dPPP)Cl₂ [dPPP = Ph₂P(CH₂)₃PPh₂] following the procedure of Tamao et al.⁹ Soluble poly(3-butylthiophene) (P3BT), poly(3-octylthiophene) (P3OT), poly(3-dodecylthiophene) (P3DDT), poly(3-hexadecylthiophene) (P3HDT), and poly(3-octadecylthiophene) (P3ODT) were prepared according to the method of Hotta et al.¹⁰ All polymers were purified by Soxhlet extraction with methanol and acetone for 24 h, respectively. The molecular weights were determined by gel permeation chromatography (GPC) using tetrahydrofuran as a

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carrier solvent and were in the range of 8000–100,000. Chloroform was used as a solvent for solutions of P3AT and AA in different molar ratios (based on the molecular weight of the PT repeat unit).

Surface pressure–area isotherm measurements and deposition experiments were performed on a computer-controlled KSV 5000 instrument (Finland). A known amount of a P3AT–AA mixed solution (~ 1.6 mM) was spread onto an aqueous subphase containing 5×10^{-4} M CdCl₂. After complete evaporation of the solvent, the floating layer on the subphase was compressed at a speed of 20 mm min⁻¹ and the π -A isotherm was recorded at $20 \pm 0.5^\circ\text{C}$ in the meantime. At a surface pressure of 15–20 mN m⁻¹, Y-type LB films were built onto hydrophobic substrates for the requirements of various measurements. UV-visible spectra were recorded on an

HP-8451A spectrometer. Small-angle X-ray diffraction (XRD) measurements were performed with a D/max- ν B X-ray diffractometer using CuK α radiation. Atomic force microscopy (AFM) images were obtained with a Nanoscope III (Digital Instruments Inc.). The conductivities of the LB films were measured by a dc two-probe method on a Solartron Schlumberger 7081.

RESULTS AND DISCUSSION

Isotherms

The surface pressure–area isotherms of five P3ATs and their mixed systems with AA in different molar ratios (based on the molecular weight of the P3AT repeat unit) are shown in Figure 1. In the case of pure P3ATs, the mean molecular

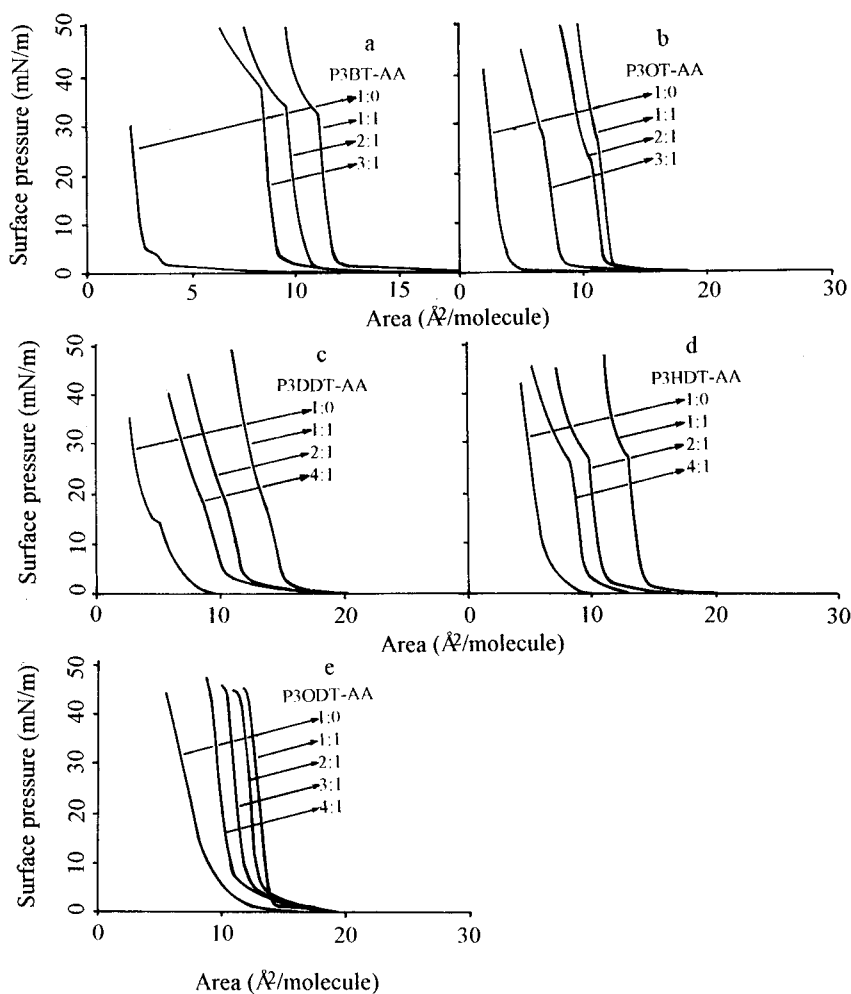


Figure 1 Surface pressure–area isotherms of P3AT–AA mixtures with different molar ratios: (a) P3BT–AA; (b) P3OT–AA; (c) P3DDT–AA; (d) P3HDT–AA; (e) P3ODT–AA.

Table I Average Limiting Areas per Molecule of P3AT-AA Mixed Systems (\AA^2)

System	1 : 0	1 : 1	2 : 1	3 : 1	4 : 1
P3BT-AA	4.2	11.7	10.3	8.8	
P3OT-AA	4.0	12.2	11.5	8.0	
P3DDT-AA	7.6	15.0	11.9		10.6
P3HDT-AA	6.9	13.9	11.0		9.7
P3ODT-AA	9.5	13.9	13.0	12.2	10.9

areas (MMA) obtained from Figure 1 are 4.2, 4.0, 7.6, 6.9, and 9.5 \AA^2 for the five derivatives, respectively. These values are obviously smaller than the area of the thiophene ring calculated from the Corey-Pauling-Koltum (CPK) model ($\sim 14.7 \text{\AA}^2$).¹¹ This result demonstrates clearly that P3ATs do not form true condensed monolayers at the air-water interface and only a part of the repeat units on the main chain is in contact with the water surface due to the rigidity of the main chain. Because a longer alkyl side chain can add more flexibility to the polymer backbone and must make it easier for P3AT molecules to unfold at the air-water interface, the MMA value of P3ODT is closer to that calculated from the CPK model than are those of the other four derivatives.

Meanwhile, it can be seen from Figure 1 that the stable condensed films of a variety of P3AT-AA mixtures were formed at the air-water interface and did not collapse until 40–50 mN m^{-1} , even containing as much as 80 mol % of the P3AT component, implying the possibility of the LB technique manipulation. The average molecular areas of various mixed monolayers obtained from Figure 1 are listed in Table I and basically follow a simple additivity rule, taking the data of pure AA and P3ATs into account. So, in the mixed monolayers, thiophene rings tend not to spread into a true monolayer and the P3AT and AA molecules are not miscible at the molecular level but rather form separate domains, which was proved by the AFM image of the LB film shown in Figure 2. Except for the P3ODT-AA mixtures, there is an inflection point on each of the isotherms which is due to the phase transition at a certain pressure, indicating that molecular reorganization is taking place within the monolayers. Because the thiophene ring is not sufficiently hydrophilic, it is reasonable that at a critical surface pressure the polymer molecules are squeezed out of the mixed monolayer and form a multilayer structure in which P3AT molecules are randomly stacked on the top of the ordered condensed monolayer of AA.

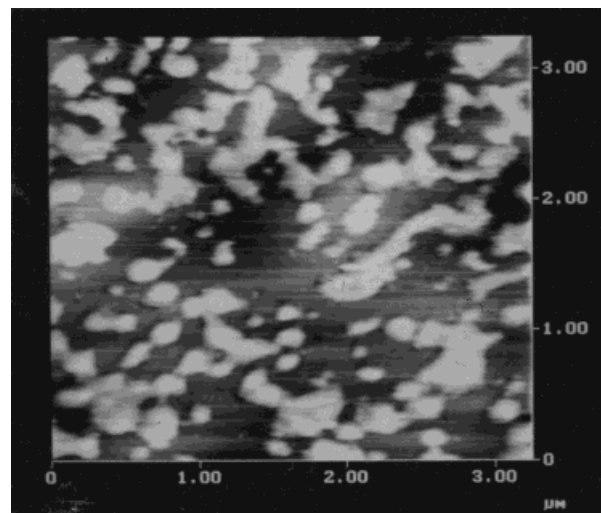
As to the P3ODT-AA system, the long alkyl chain pendent to the polymer backbone strongly interacts with the hydrocarbon tail of AA, preventing the rejection of P3ODT molecules at higher pressure. No inflection point appears on the isotherms.

LB Films

Because of the limitation of the molecular structure features, it is difficult to fabricate high-quality LB films of pure P3AT with the vertical dipping method. The transfer ratio of P3ODT was 0.1–0.3 in the Z-type deposition and smaller for the other four derivatives. However, in the pressure range of 15–20 mN m^{-1} , monolayers of P3AT-AA mixtures can be easily transferred onto various substrates, forming Y-type LB films. Transfer ratios of 0.8–1.0 were obtained for downstroke and upstroke up to 50 layers.

Figure 3 displays the UV-visible absorption spectra of two P3AT-AA systems both in chloroform solutions and in the LB films. The $\pi-\pi^*$ transition absorption peak of P3AT in the LB films shows a slight broadening and obvious redshift compared with that in solution. This is probably due to the different molecular environment in each state and the interaction of the molecules in the LB films.

A UV-visible absorption measurement is usually used to assess the reproducibility of the transfer process. As shown in Figure 4, the linear relationship between the maximum absorbance and

**Figure 2** AFM image of the LB films of P3ODT-AA (3 : 1).

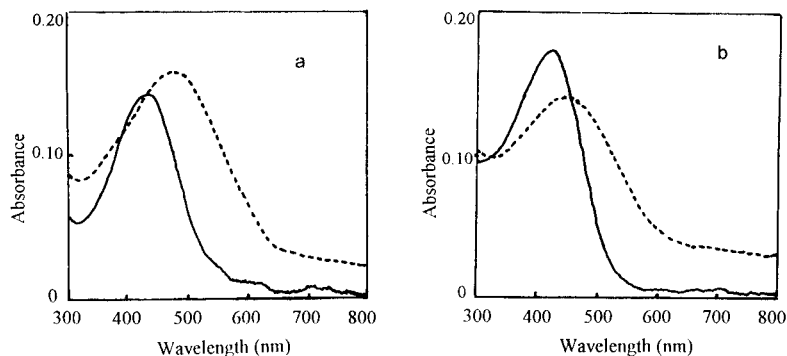


Figure 3 UV-visible absorption spectra of (a) P3BT-AA (1 : 1) and (b) P3ODT-AA (1 : 1): (—) in chloroform; (----) in the LB films (20 layers).

the number of layers transferred clearly demonstrates that all the monolayers were reproducibly and uniformly transferred onto the substrates. Similar results were observed from other mixed systems with different molar ratios.

Figure 5 depicts the small-angle XRD patterns of 30-layer LB films in three P3AT-AA (1 : 1) systems. A set of Bragg reflections, more or less, was readily observed, indicating that the LB films exhibit a well-defined layered structure. Apparently, as the length of the alkyl side chain increases, the number and intensity of the diffraction peaks also increase, implying more order in the LB films of the P3ODT-AA mixture. This is due to the strong interaction between the long alkyl chain and the hydrocarbon tail of AA. Moreover, the bilayer d -spacings calculated from the XRD data are both about 56 Å, irrespective of alkyl spaces of P3AT, and the same as that ob-

tained from the LB films of pure cadmium arachidate. It can be deduced that the domains of P3AT molecules are uniformly dispersed among a highly ordered matrix of cadmium arachidate molecules and the origin of diffraction observed should come from well-oriented AA multilayers.

Conductivity of LB Films

The conductivities of the mixed LB films along the directions of perpendicular (σ_{\perp}) and parallel (σ_{\parallel}) to the film plane were measured in both the undoped and doped states by the dc 2-probe method. The results are listed in Table II (the film thickness used in the calculation was estimated from the XRD data and the number of deposited layers).

The P3AT-AA mixed LB films are insulating as a neutral state; however, they can be converted

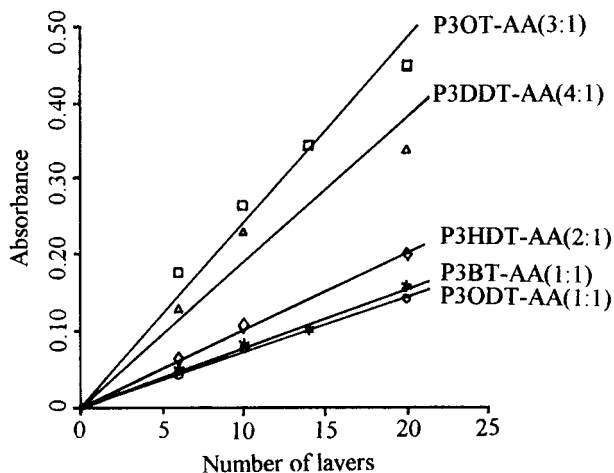


Figure 4 Relationship between the maximum absorbance and the number of transferred layers of P3AT-AA LB films.

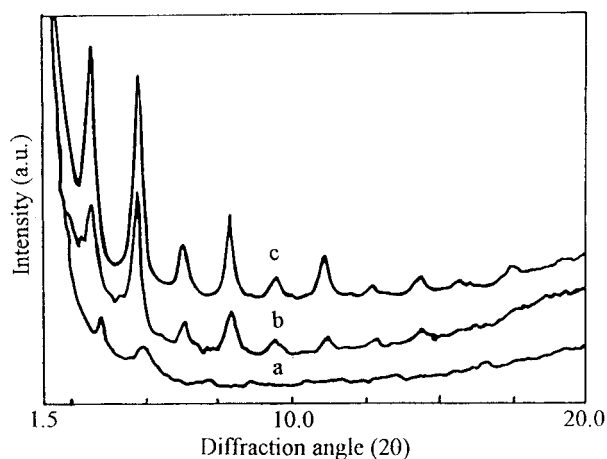


Figure 5 Small-angle X-ray diffraction patterns of 30-layer LB films of (a) P3BT-AA (1 : 1), (b) P3OT-AA (1 : 1), and (c) P3ODT-AA (1 : 1).

Table II Conductivities of the LB Films in Undoped and Doped States

States	$\sigma_{//}$ (S cm ⁻¹)	σ_{\perp} (S cm ⁻¹)	$\sigma_{//}/\sigma_{\perp}$
P3ODT/AA (1 : 1)			
Neutral	2.22×10^{-6}	3.70×10^{-15}	10^9
Doped with I ₂	9.99×10^{-5}	3.70×10^{-13}	10^9
P3ODT/AA (3 : 1)			
Neutral	5.99×10^{-7}	7.48×10^{-15}	10^8
Doped with I ₂	1.69×10^{-2}	7.11×10^{-10}	10^8
P3HDT/AA (1 : 1)			
Neutral	1.00×10^{-6}	6.18×10^{-15}	10^9
Doped with I ₂	1.67×10^{-2}	2.47×10^{-9}	10^7
P3DDT/AA (1 : 1)			
Neutral	4.51×10^{-6}	1.59×10^{-13}	10^7
Doped with I ₂	2.31×10^{-3}	1.25×10^{-12}	10^9
P3OT/AA (1 : 1)			
Neutral	6.50×10^{-5}	5.93×10^{-13}	10^8
Doped with I ₂	4.39×10^{-3}	6.91×10^{-11}	10^8
P3OT/AA (3 : 1)			
Neutral	4.39×10^{-4}	9.57×10^{-12}	10^8
Doped with I ₂	1.12×10^{-2}	2.44×10^{-10}	10^8
P3BT/AA (1 : 1)			
Neutral	4.91×10^{-6}	2.52×10^{-13}	10^9
Doped with I ₂	5.39×10^{-2}	6.34×10^{-10}	10^8
P3BT/AA (2 : 1)			
Neutral	1.11×10^{-5}	1.85×10^{-11}	10^6
Doped with I ₂	8.63×10^{-3}	1.40×10^{-10}	10^6
Doped with FeCl ₃	1.50×10^{-1}	$<10^{-10}$	10^9

into electrically conductive films by doping with chemical oxidants such as I₂ or FeCl₃. Upon doping with iodine vapor, the conductivities of the LB films increased by 2–4 orders of magnitude. The conductivity in LB films exhibits an obvious anisotropy: The ratios of $\sigma_{//}/\sigma_{\perp}$ are in the range of 6–9 orders of magnitude whether in undoped or doped states. It is also clear from Table II that (1) as the portion of P3AT becomes larger in the mixed systems the conductivity is enhanced, which is ascribed to the insulating nature of AA, and (2) in same molar ratio, the conductivity increases with a decreasing alkyl side-chain length. Because the dimensionality and coplanarity of the conjugated main chain are dependent on the side chain and its conformation, the alkyl side group will have an effect on the electronic band scheme and interchain interaction, resulting in the dependent relationship between the conductivity and the length of the alkyl side chain.¹²

Polyalkylthiophene was reported to be oxidized to form polaron and bipolaron gap states, which is used to explain the conducting behavior.¹³ The existence of polaron and bipolaron states can be proved by the corresponding absorption peaks.

However, we have not observed a new absorption peak from the UV-visible-near IR spectra of P3AT–AA LB films after I₂ vapor doping. The relevant conducting mechanism is being studied further.

CONCLUSION

We synthesized five poly(3-alkylthiophene)s with different side chains. It was found that only by mixing with typical film-forming materials such as AA that P3ATs can be fabricated into uniform multilayers with high quality using the vertical dipping method. In the most cases, the P3AT and AA molecules are not fully miscible at the molecular level, that is, disordered P3AT molecules were dispersed among the well-ordered domains of the cadmium arachidate molecules. The conductivities of P3AT–AA LB films exhibit high anisotropy and are strongly dependent on the side-chain length of the polymer molecules. At room temperature, the conductivities of the LB films increased by 2–4 orders of magnitude after being doped with iodine.

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