

## Formation of Novel Electrically Conductive Langmuir–Blodgett Multilayer Thin Films of Poly(3-alkylthiophenes)

Itsuo Watanabe, Keith Hong, and Michael F. Rubner\*

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, U.S.A.

Langmuir–Blodgett multilayer thin films have been fabricated from mixed monolayers containing stearic acid and various poly(3-alkyl thiophenes); the resultant multilayer films exhibit well defined spacings, as indicated by X-ray diffraction, and can be chemically oxidized to produce electrically conductive multilayer thin films.

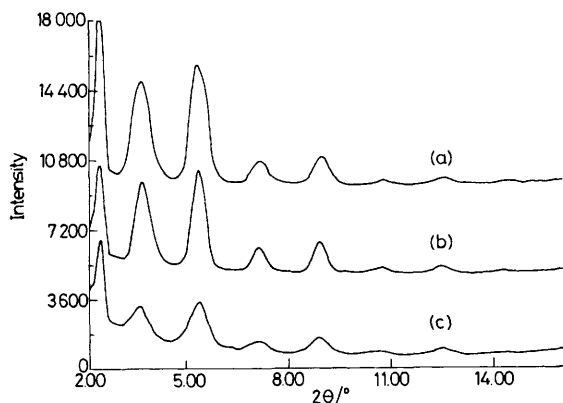
Recently, a good deal of progress has been made towards the development of stable, processible electrically conductive polymers. Many of the important advances in this area have centred on the design and synthesis of new conjugated polymers whose structures have been suitably modified to introduce processibility without compromising the electrical conductivity of the system. Most notably, the recent development of soluble and melt processible electrically conductive polymers based on 3-alkyl substituted polythiophenes<sup>1,2</sup> and similar derivatives<sup>3</sup> of the polyheterocycles has heralded a new direction for conducting polymer research. These materials allow for the first time an opportunity to process conducting polymers into technologically useful forms with novel electrical and optical properties. To date, however, only conventional solution casting and melt processing techniques, which offer very little control over the molecular order and organization of the polymer, have been utilized to process these new polymers. We have recently shown that it is possible to process electrically conductive alkyl substituted polypyrroles into multilayer thin films using the Langmuir–Blodgett (LB) technique.<sup>4</sup> We now report a novel approach that can be used to fabricate soluble electrically conductive poly(3-alkylthiophenes) into LB multilayer thin films with well defined and controllable molecular architectures. Thus, for the first time, it is possible to control the molecular organization and superstructure of a conducting polymer system.

The alkyl substituted polythiophenes used in this work, poly(3-butylthiophene)(P-3-BT), poly(3-octylthiophene)(P-3-OT), and poly(3-octadecylthiophene)(P-3-ODT) were prepared according to the methods of Eisenbaumer *et al.*<sup>1</sup> LB monolayer and multilayer thin films were fabricated using a Lauda film balance. Monolayers were spread from chloroform

solutions of the mixtures on a purified aqueous subphase containing  $2 \times 10^{-4}$  M CdCl<sub>2</sub>. Details of the fabrication and structures of these new multilayer thin films will be presented elsewhere.

In order to manipulate polymeric systems into LB multilayer thin films, it is normally necessary to utilize amphiphilic molecules which are capable of forming monolayers at the air–water interface of the LB trough. Thus, in principle, heterocyclic molecules such as pyrroles and thiophenes that have been substituted at the 3-position of the ring with long alkyl groups should be capable of forming stable monolayers. We have found that this is true for substituted pyrroles<sup>4</sup> as the pyrrole ring is sufficiently hydrophilic to promote monolayer formation. However, in the case of substituted thiophenes, in which the heterocyclic ring lacks the strong dipole associated with the N–H bond of the pyrrole ring, the molecules cannot be formed directly into monolayers. The spreading of, for example, a solution containing P-3-ODT onto the air–water interface of an LB trough simply results in the formation of aggregated islands of polymer which only exhibit a surface pressure when they are forced together at very small molecular areas.

Remarkably, however, we have found that stable monolayers can be formed with a variety of alkyl substituted polythiophenes if they are mixed with suitable portions of stearic acid. Specifically, it is possible to form stable, condensed monolayers from soluble poly(3-alkylthiophenes) with alkyl chain lengths ranging from four (butyl) to eighteen carbons (octadecyl). Depending on the particular alkyl substituted polythiophene, it is possible to incorporate as much as 80 mol% of the conjugated polymer into the mixed monolayer and still obtain highly ordered multilayer thin films. The structures of the resultant multilayer films fabri-



**Figure 1.** Small angle X-ray scattering curves of multilayer thin films (34 layers) containing a 1 : 2 molar ratio of poly(3-alkylthiophene) to stearic acid; (a) P-3-BT, (b) P-3-OT, and (c) P-3-ODT.

cated from these mixed monolayers are highly dependent on the composition of the mixed monolayer and the length of the substituent attached to the polythiophene rings.

Capacitance and optical absorption measurements made on stepped films as a function of the number of layers deposited indicate that the substituted polythiophene molecules are transferred reproducibly into the multilayer films. Figure 1 shows the small angle X-ray scattering (SAXS) curves obtained from multilayer (34 layers) thin films fabricated from mixed monolayers of various poly(3-alkylthiophenes) and stearic acid in a 1 : 2 molar ratio. The presence of at least seven lamellar reflections in these curves clearly demonstrates that we have formed a well defined layered structure with bilayer repeat distances centred around 49 Å. Preliminary near-edge X-ray-absorption fine-structure analysis<sup>5</sup> (NEXAFS) indi-

cates that the hydrocarbon tails of the stearic acid molecules are highly oriented within the film. These highly ordered thin films can be readily doped with oxidizing agents such as nitrosyl hexafluorophosphate to produce electrically conductive multilayer thin films. To date, we have been able to reach conductivities of about 5 S cm<sup>-1</sup> by chemical doping.

Highly ordered multilayer thin films of electroactive polythiophenes can be easily fabricated from mixed monolayers containing alkyl substituted polythiophenes and surface active molecules such as stearic acid. The resultant structures are highly anisotropic and can be rendered electrically conductive by suitable oxidizing agents. The ability to fabricate electroactive polymers into LB films means that it is now possible to control the molecular organization and hence the optical and electrical properties of these interesting materials.

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