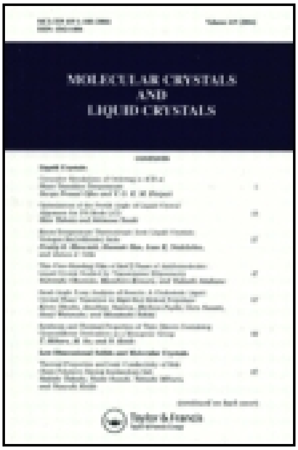

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Preparation and Characterization of Conductive Polymer Nano-Films

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Version of record first published: 18 Oct 2010

To cite this article: Sijoong Kwon, Sungwon Han, Daewoo Ihm, Eungryul Kim & Jinyeol Kim (2004): Preparation and Characterization of Conductive Polymer Nano-Films, Molecular Crystals and Liquid Crystals, 425:1, 77-83

To link to this article: http://dx.doi.org/10.1080/15421400490506531

Mol. Cryst. Liq. Cryst., Vol. 425, pp. 77/[355]–83/[361], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490506531

PREPARATION AND CHARACTERIZATION OF CONDUCTIVE POLYMER NANO-FILMS

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We investigate the electrically conductive polypyrrole (PPy) and poly (3,4-ethylenedioxythiophene, PEDOT) nano-films prepared in a continuous roll-to-roll process by vapor-phase polymerization method. Thin films of ferric chloride doped conductive PPy and PEDOT on plastic substrates, in which neither matrix polymers nor binders are used for the film forming process, are obtained at nano-level thickness. PPy and PEDOT film thickness was varying depend on reaction time and reaction temperature. The surface resistance change with time of exposure to monomer vapors, and the value was in the range of $10^3 \sim 10^5\,\Omega$*/sq. at 20–60 nm thick films and showed up to 600* Ω*/sq. for the* >600 *nm thick films. These thin films had a very highly ordered surface morphology. Especially, in the case of PEDOT film, the growth of highly ordered conductive PEDOT crystalline microstructure, which high anisotropy, parallel to the substrate film was fabricated, was observed by AFM.*

Keywords: AFM; conductive polymer; nano-films; poly(3,4-ethylenedioxythiophene); polypyrrole; vapor-phase polymerization

Received 1 October 2003; accepted 12 March 2004.

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INTRODUCTION

$\pi-$conjugated conducting polymers have received great attention because of their potential applications in electronic displays, electrode materials in batteries, smart windows, sensors, capacitors, molecular electronic circuit elements, and secondary batteries [1–5]. Opto-electronic devices often require polymeric transparent electrodes for improving device performance and furthermore fabricating devices with only polymer components [6–9]. There has been considerable excitement recently over the use of conducting polymers in a variety of technological applications such as electromagnetic interference shielding, conductive coating, antistatic agents, and infrared or radar absorbed materials. It is well known that mesoscopic and nanometric materials can have different physical properties than bulk materials, numerous potential technological and commercial applications. The several methods have been already introduced to prepare nano-materials [10–16]. Nanotubes of conducting polymers (polypyrrole and polyaniline) have been successfully prepared [10–12]. Thin films with desired properties and functionalities have been synthesized by various available methods, such as chemical oxidation, electrochemical synthesis, micellar polymerization, and deposition techniques [17–24]. However, a demand for improvement in quality of thin films has never ceased yet.

Among the several conducting polymers, polypyrrole (PPy) and polythiophene (PT) are one of these electrically conducting polymers which has been received much attention during the recent years. It could be a good candidate for the opto-electronic devices owing to its high conductivity, good stability in ambient conditions, and film-forming property. They are also known to be stable for a long time under ambient conditions [25]. In general, it has been known that conductive polymers can be synthesized by either an oxidative chemical or electrochemical polymerization of monomer in liquid-phase. However, recently, several researchers [25–28] introduced newer method of polymerization method in vapor-phase.

Poly(3,4-ethylenedioxythiophene)(PEDOT), as the polythiophene derivatives, also have been known as a good material for optoelectronic deveices owing to its high conductivity up to 500 S/cm and electrochemical stability with maintaining moderate transparency. PEDOT has a narrow band-gap due to the presence of the two electron-donating oxygen atoms adjacent to the thiophene unit. Commercially available PEDOT (as a colloidal form in water) with poly(styrenesulfonate; PSS) in water is environmentally stable and amenable to the formation of film coatings on glass or plastic surfaces for the antistatic, electrochromic devices and conducting electrode in light emitting diodes(LED) [29,30].

In this work, we investigate the electrically conductive PPy and PEDOT thin films prepared in a continuous roll-to-roll process by vapor-phase polymerization (VPP) method. Thin films of PPy and PEDOT doped with ferric chloride on plastic substrates are directly obtained at nano-level thickness. We also reported their surface morphology with thickness using the atomic force microscopy (AFM).

EXPERIMENTALS

Dopant/oxidizing agent (3 wt%$FeCl_3 \cdot 6H_2O$ in methanol) in the liquid phase do pretreatment on polymeric substrate films (polyethyleneterephthalate: PET) by dip- or micro-gravure roll coating. After drying for 3–5 minutes at $40 \sim 60^\circ C$, polymeric substrate films pretreated with $FeCl_3 \cdot 6H_2O$ were exposed to monomer vapor between 5 seconds to 5 minutes in the reaction chamber, vaporizing with monomer under the ambient conditions. The nano-films doped with ferric chloride are obtained at nano-level thickness. Following the polymerization, the grown films of conductive polymers were washed with methanol several times to remove unreacted oxidant, monomer and byproducts (e.g., $FeCl_2$), then dried for 3 min. under convection oven at $70 \sim 80^\circ C$. Pyrrole monomer (Aldrich, GR), EDOT monomer (Bayer, AG), $FeCl_3 \cdot 6H_2O$ (Aldrich, 98%), and methanol (Aldrich, 98%) were used without any further purification.

The thickness, surface morphologies, and conductivity of nano-films grown on the plastic substrates were measured using the atomic force microscopy (AFM) (Nanoscope IIIa DI, USA) and standard 4-probe technique (Loresta-GP, Mitsubishi Chemical). Their optical properties were measured with a Perkin Elmer Lambda 25 spectrophotometer.

RESULTS AND DISCUSSION

Iron (III) salts was conveniently used not only as "dopant" ions for conducting polymers having the heteroaromatic structures such as PPy and PEDOT but also as oxidant for polymerization. Because of pyrrole and EDOT monomers have relatively high vapor pressure, the polymerization of pyrrole and EDOT under *in situ* vapor phase can be readily initiated by exposing an oxidant to monomer vapor even though EDOT has relatively high vapor pressure than that of pyrrole. While 2.25 equivalents of an oxidant are theoretically required per mole of pyrrole and EDOT for their oxidative polymerization [31], the amount of the consumed oxidant is more than the theoretical value by 100% to 200%. During the polymerization, monomer was being oxidized to form a conductive polymer film. Within a few seconds, a thin film started to form on the polymeric substrate

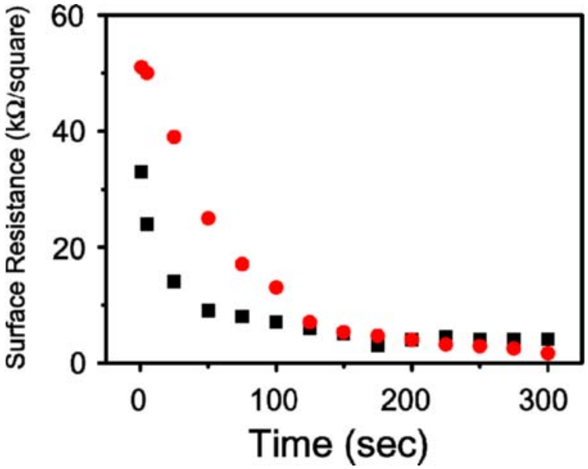

FIGURE 1 Conductivity vs. deposition time in the PPy(■)and PEDOT(•) prepared by vapor-phase polymerization at 3wt% $FeCl_3$.

films. The thickness of the films can be controlled between 30 and 80 nm depend on exposure (deposition) time to monomer. The change in surface resistance with exposure time to monomer vapors at 60°C is shown in Figure 1. At the initial stage of exposure to monomer, its surface resistance decreases very quickly with time due to the deposition of monomer. The surface resistance no longer decreases after approximately 100 seconds deposition. The surface resistance value was in the range of 10^4–10^5 Ω/square at the reaction times below 10 seconds and showed a value of $10^3\,\Omega$/square at the reaction times above 100 seconds. For the films that have the reaction times above 100 seconds the surface resistance is found to be practically independent of the deposition time of monomer. Especially, conductivity of PPy increased faster than that of PEDOT.

The conductive polymer film thickness was measured using an AFM. (Fig. 2 shows AFM image of PEDOT nano-films related with thickness) and the thickness also varied with polymerization time. Film thickness increased proportional to reaction time. Generally, the film thickness dependence of the conductivity was related with their mobility, the crystallinity of the film [32], surface scattering due to thickness being less than or comparable to mean free path of the charge carriers, discontinuities in the films, quantum size effect, island formation, and etc. [33]. In this case, these films contain the partially charged domains dispersed in neutral polymer chains. The metallic properties of conductive polymers have been attributed to the partially charged domains (polarons or bipolarons lattice structure) or a defect in conjugated chains of neutral polymer [34]. This may lead to the

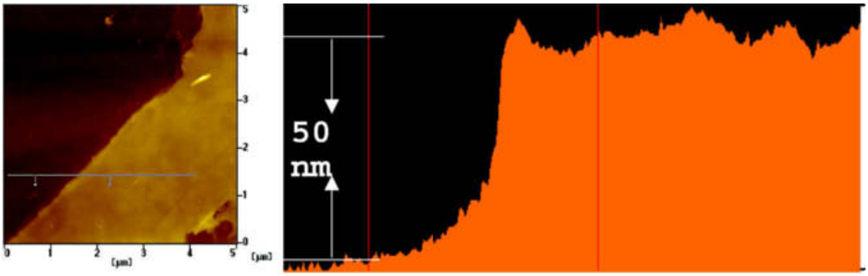

FIGURE 2 Thickness of thin film measured by AFM.

thickness dependence of conductivity. However, the conductivity as a function of polymerization time is ascribed to the difference in diffusion of monomer that affects the surface morphology of PPy and PEDOT. In addition, its conductivity can be varied by the fabricating methods. In this study, very high conductivities were obtained in the thin films fabricated by VPP method. Since the conductivity was related to the orientation or surface structure of polymers, we observed the morphology of films by AFM.

Figures 3(a) and (b) show a typical two dimensional perspective view of 2 × 2 μm^2 AFM images of the PPy and PEDOT films deposited for 100 seconds at 60°C. It can be seen that the polymer films have very homogeneous surface structures composed of thin layers of high integrity. The surface of the PPy film shows very smooth surface to result in a good reflection of light. The surface became mirror-like characteristics. These films also served as a strong adhesion layer to the plastic substrates such as PET, PI,

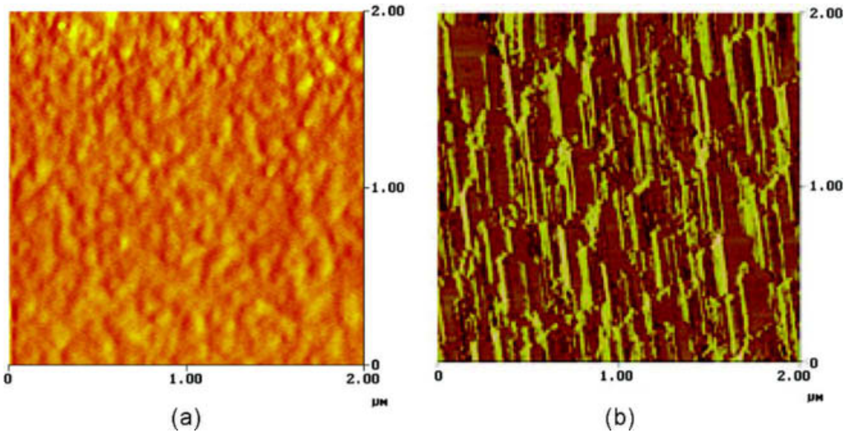

FIGURE 3 AFM images of (a) PPy and (b) PEDOT films prepared by vapor-phase polymerization at 60°C.

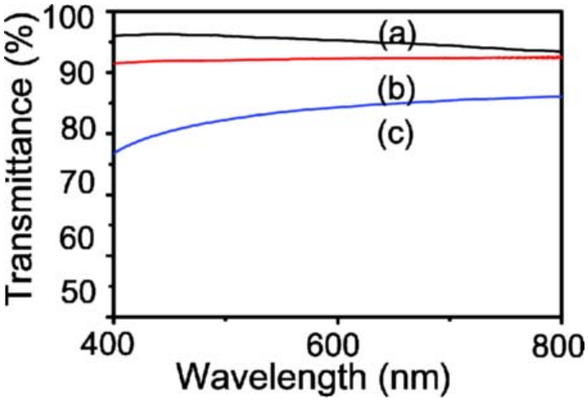

FIGURE 4 Transmittance of conductive polymer films of 50 nm thickness; (a) PET substrate only, (b) PEDOT coated PET, and (c) PPy coated PET.

PVC, etc. In the case of PEDOT, it is observed that highly ordered conductive PEDOT crystalline structure was grown. This conductive PEDOT crystalline structure of a rod shape can be identified in the initial step or reaction and it shows as the grown or deposited to the multi layer structure according to the increasing reaction time. The crystallinity in PPy and PEDOT films were not detected from the X-ray diffraction study, suggesting that both films prepared by VPP method are amorphous with smooth surface. As mentioned above, the conductive PPy and PEDOT thin films made by VPP method show the good electro-conductivity because it can be grown with the microstructure having uniform and compact morphologies.

In Figure 4 transmittance of PPy and PEDOT film were shown. Transmittance of thin nano films was controlled by the thickness of the film and the transmittance of both films prepared by this study show the transmittance up to 95%. Recently, thin polymer films having high transparency and conductivity have been used as the optical films or antistatic coating technologies for the flat panel display (FPD). As mentioned above, conductive PPy and PEDOT thin films made by VPP method show good electro-conductive and optical properties because of the growth of thin film with nano-level thickness and to the surface structure of high integrity. These properties are sufficient for the thin film to be applicable to the organic opto-electronic devices for the transparent polymeric transparent electrodes for improving performance and for achieving all-polymer devices. Actually, sophisticated applications are also envisaged for these materials, including preparation of electronic-static discharge, polymeric electroluminescent diode, and electroplating for metallization of insulators.

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