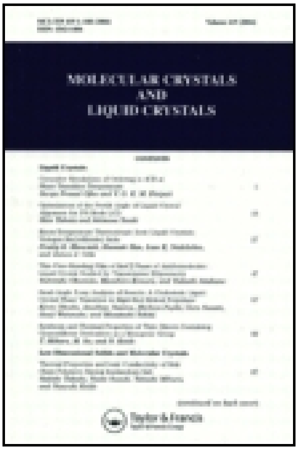

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Two Different Phases of a Conducting Polymer Film Formed by Electrocasting Method

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Poly(3-hexylthiophene) has been renowned for having excellent electrochemical reactivity and optoelectronic functionalities. The existence of a pre-peak pair at ~0.7 V in the polymerization CV could be noticed in several references. Because this pre-peak pair is almost enveloped into the broad main peak pair. Especially the existence of them in the CV obtained from monomer free electrolyte is hardly noticed. There have been many different interpretations for the existence of the pre-peak pair. This research was to examine the appearance of the pre-peak by using new approach of electrocasting of polymer from solution.

Keywords: adsorbed phase; electrocasting; P3HT; pre-peak current; soluble

INTRODUCTION

Conducting polymers are known as functional organic materials with special chemical and physical functionalities which have been

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understood as characteristics of inorganic semi-conductors [1–5]. Among these conducting polymers, poly(3-alkylthiophenes) (PATs) have attracted much attention due to its ease of processing and good solubility [6–9]. Especially, poly(3-hexylthiophene) shows good solubility to several organic solvents, such as tetrahydrofuran (THF) and chloroform [9–11]. The electrochemical properties of this polymer were examined by means of cyclic voltammetry [10,12,13]. The existence of a pre-peak pair at $\sim$0.7 V in the polymerization cyclic voltammogram (CV) could be noticed. These pre-peaks are almost enveloped into the broad main peaks. Many different interpretations have been proposed for the existence of the pre-peak pair by many different groups, for example polymer relaxation, adsorption phenomena, different crystallinity, and etc. [14,15].

Our research is to examine the appearance of the pre-peak by using new approach of electrocasting method. This method utilized the dramatic solubility change of the polymer due to the change of its redox state. Direct oxidation of the solution species could change the soluble reduced form into the insoluble oxidized form. Therefore thin film of the oxidized polymer was formed on the electrode surface. The electrocasting process could be used in making very thin film with a lower potential than the one for electrochemical polymerization. The low potential deposition allowed us to have thin film of the polymer which has comparable amount of pre-paeak phase species. In this research, the deposition processes of the electrocasting were studied with CV and SEM images.

EXPERIMENTAL

Poly(3-hexylthiophene) (P3HT) was obtaied by following the method in references [16–20]. All chemicals used in this work were ACS grade. Polymer solution for electrocasting was prepared by dissolving 0.15 g P3HT and 0.1 mole of lithium chloride into 100 ml of THF. Gold film coated on polyester plate was put into the polymer solution and used as working electrode. A piece of Pt plate was used as a counter electrode and an Ag/AgCl (sat'd KCl) electrode was adopted as a reference electrodes. Cyclic voltammetry was adopted for electrocasting the thin film directly from the polymer solution. Applied potentials could oxidize conducting polymer, P3HT in the solution. Individual cyclic voltammogram for electrocasted polymer film was obtained in an electrolyte of 0.1 M $LiClO_4/CH_3CN$. The surface coverage was tested by analyzing CV obtained in $K_3Fe(CN)_6$ electrolyte. Electrochemical experiments were done by EG&G Model 263 or BAS 100/W potentiostats. All electron microscopic images were obtained by using SEM (JSM 6700 F, JEOL, Japan).

RESULTS AND DISCUSSION

P3HT film was first prepared by electrochemical polymerization of monomers (0.1 M 3HT) in electrolyte solution (0.1 M $LiClO_4/CH_3CN$). Figure 1(a) shows the electrochemical polymerization process; the oxidation current of the monomer 3HT increases rapidly at around 1.5 V and this oxidation initiates rapid polymerization. As the potential cycles repeated, the monomer oxidation rate was increased gradually at the same potential. This indicates the rapid oxidation of monomer and polymerization occurred at the same time. After the first cycle, the CV showed a broad redox current peak pair at about 0.8–1.0 V. The CV shown in Figure 1(b) was obtained from the polymer formed on the electrode in a monomer free electrolyte of 0.1 M $LiClO_4/CH_3CN$. In this CV, no pre-peak was observed because it is very small in height compared to that of the main peak in polymer CV and thus it had been readily enveloped into large main peak.

Potential cycles of narrow potential windows (0.3 V–(0.7 ~ 1.1) V) were used to induce slower deposition of the polymer compared to the electrochemical polymerization. Ten cycles for each electrocasting were performed at the scan rate of 10 mV/sec. Direct electrolysis of the polymer dissolved in solution induced the polymer film deposition on the electrode substrate at the lower potentials compare to those of polymerization. The film deposition procedure is shown in the CV in Figure 2. In this electrocasting process, potentials of 0.7 V can induce

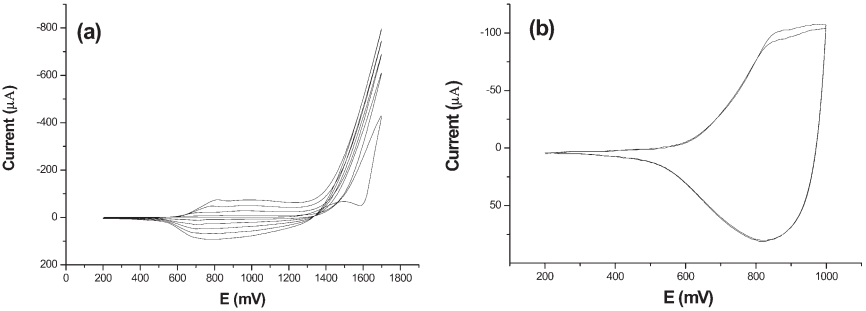

FIGURE 1 CV for the electrochemical polymerization (a), and CV of P3HT in monomer free solution (b). Electrolytes; 0.1 M $LiClO_4/CH_3CN$. Scan rate; 50 mV/sec.

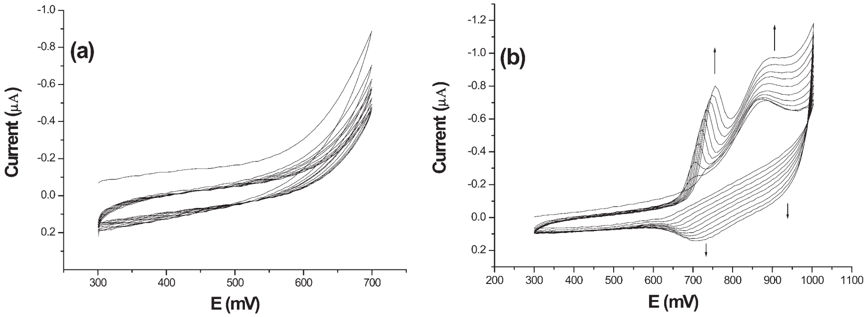

FIGURE 2 Electrocasting CV of solution species of P3HT with 0.3 ~ 0.7 V (a) and with 0.3 ~ 1.0 V (b). Scan rate; 10 mV/sec.

low anodic current due to slow oxidation of the polymer occurred only at the energetically preferred positions of the electrode. When the switching potential was changed to higher ones up to 1.1 V, anodic pre-peaks appeared in all CV's. One of them was shown in Figure 2(b). As the potential cycle repeated, the redox peaks were regularly increased due to the film growth. Anodic pre-peak appearing in near 0.7 V is now observable in this CV, because the elecrocasting of low potential allowed slow deposition reaction of polymer onto the electrode compared to the rapid deposition of monomer polymerization. And this pre-peak could not be enveloped into the main peak. Thus the cathodic pre-peak is observable.

Electrochemical analysis in polymer free electrolyte and coverage test were done on the polymer films obtained by the electrocasting method. Current responses for polymer redox reaction are appeared in Figure 3(a). Peak positions were a little different from the ones in Figure 2(b) because of using different electrolyte (the polymer free electrolyte of ACN). The polymer formed by the lowest 0.7 V shows very low response compared to others. When the switching potential is changed to higher values, the current peaks were appearing at 0.45 V and 0.8 V. Figure 3(b) shows the pre-peaks are appeared almost at the same position of 0.45 V and their hysteresis is almost negligible. This implies that the redox species ($E^{\circ} = 0.45\,V$) had been formed almost thin layer phase rather than vertically grown one [21]. CV for 1.1 V in the same figure did not show the pre-peaks. Because the potential was high enough to cause fast oxidation rate of the polymer and results in three-dimensional growth preferring in vertical direction. Fast oxidation of polymer near the electrode makes fast depletion of the oxidizing species and this causes the growth preferring in

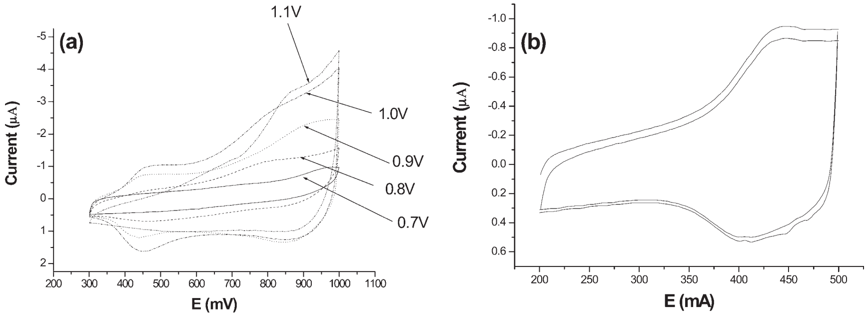

FIGURE 3 CV of electrocasted P3HT with different potential window of 0.3∼0.7, 0.8, 0.9, 1.0, and 1.1 V (a) and window of 0.3∼1.0 V in polymer free solution (b). Scan rate; 50 mV/sec.

vertical direction. In this case, the rate for lateral growth is relatively slower than the vertical one. Scan rate dependent current test is illustrated in Figure 4(a). The anodic pre-peak current varies linearly with respect to the scan rate, *v* as in Figure 4(b). But, the current of main peak does not vary linearly. Therefore, the pre-peak is due to the redox of the adsorbed phases of P3HT on gold electrode. The main peaks are of course due to the redox of vertically grown thick polymers [22,23].

Coverage tests were done by performing CV test for these films in 5 mM in $K_3Fe(CN)_6$ solution, and results are in Figure 5, [24]. In this experiment reversible redox property of $Fe(CN)_6^{3-}$ species was used. The electrode prepared with 1.0 V switching potential gave the

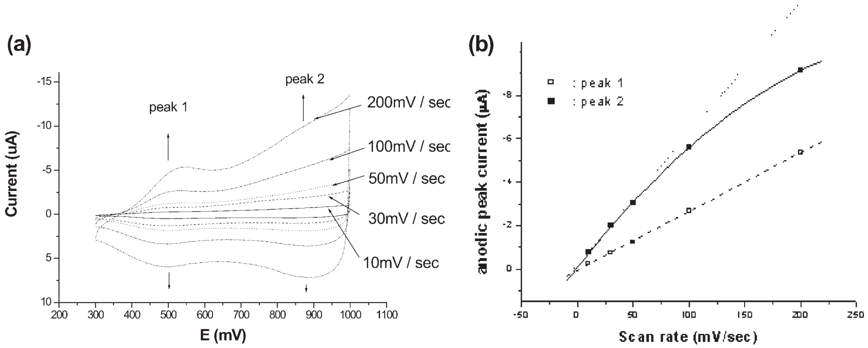

FIGURE 4 CV of electrocasted P3HT in 0.1 M $LiClO_4/CH_3CN$ (0.3∼1.0 V) (a), and scan rate dependent peak current (b).

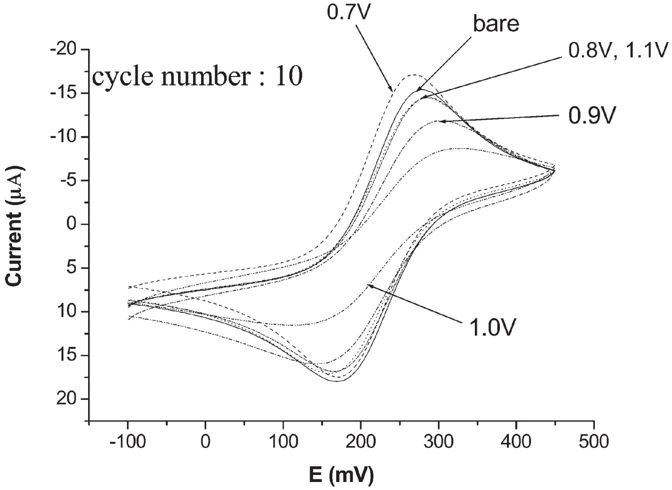

FIGURE 5 Coverage test of electrocasted P3HT in 5 mM $K_3Fe(CN)_6$/0.1 M KCl/H_2O, scan rate; 50 mV/sec.

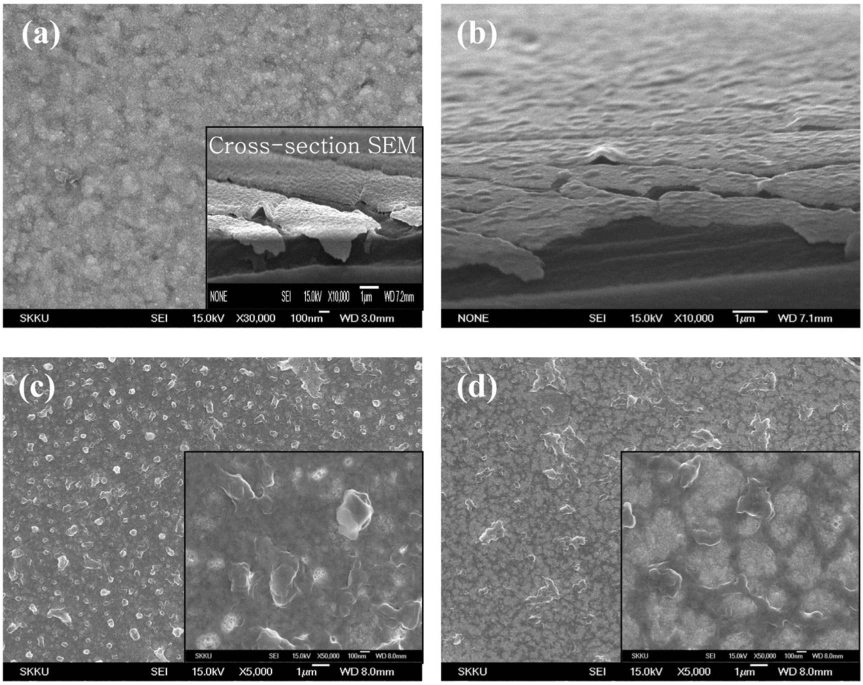

FIGURE 6 SEM image of (a) bare gold electrode, (b) P3HT formed with 0.3∼0.7 V, (c) 0.3∼1.0 V, (d) 0.3∼1.1 V.

smallest current response, because the substrate surface is almost covered with polymer. The reason for electrode prepared at 0.9 V showing quasi-reversible response is that some part of the substrate surface is exposed to the reacting species. The electrode of 1.1 V appears to be like bare electrode because the deposited polymer is mainly in vertically grown phase.

SEM images of the polymer films are obtained to confirm the deposition procedure. Figure 6(a) is for the bare gold electrode, and (b) is the image for electrocasted film with 0.7 V switching potential. Only adsorbed small points are formed all over the Au surface. In higher potentials, vertically growing centers begin to appear. Switching potential of 1.0 V shown in (c) produced polymer covered surface with vertical growing centers on it. And 1.1 V allowed fast growing rate, so the vertically preferred growing on the substrate electrode was the dominate phase as in (d).

CONCLUSION

The electrocasting process could be used in preparing thin film with a lower potential than the one for electrochemical polymerization. The film deposition with low potential electrocasting allowed film growth preferred in lateral direction and produced adsorbed phase. The main peaks of the polymer CV are usually responsible for polymer of the three-dimensional growth phase preferring in vertical direction. These ultra thin films of conducting polymers could be applied to the nano/micro device fabrication.

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