

DOPING LEVEL INCREASE OF POLY(3-METHYLTHIOPHENE) FILM DURING ELECTROCHEMICAL POLYMERIZATION PROCESS*

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Abstract The Raman spectra of poly(3-methylthiophene) (PMeT) films with different thicknesses, which have been electrochemically deposited on a flat stainless steel electrode surface by direct oxidation of 3-methylthiophene in boron trifluoride diethyl etherate (BFEE) at a constant applied potential of 1.38 V (versus SCE), have been investigated by excitation with a 633-nm laser beam. The spectroscopic results demonstrated that the doping level of PMeT film was increasing during film growth. This finding was also confirmed by electrochemical examination. Moreover, the Raman bands assigned to radical cations and dications in doped PMeT films were found approximately at 1420 and 1400 cm^{-1} , respectively. Radical cations and dications coexist on the backbone of PMeT as conductive species and their concentrations increase with the increase of doping level. Successive cyclic voltammetry was proved to be an effective approach to improving the doping level of as-grown thin compact PMeT film.

Key words Poly(3-methylthiophene), Raman spectra, Doping level, Radical cations, Dications

INTRODUCTION

Electrochemical polymerization is a useful and widely applied technique for synthesizing conducting polymer films^[1]. As-grown conducting polymer films are usually formed in doped state and can be applied directly without further treatment. It is known that the color and morphology of conducting polymer films will change with the progress of deposition^[2]. However, no work concerned the doping level change during the electrochemical growth process of conducting polymer film was reported.

Raman spectroscopy has been proved to be one of the most effective approaches for providing simultaneous and selective information about the structure of both doped and pristine states of conducting polymers and their charge distribution^[3]. Until now, many studies in this field were carried out by utilizing surface the enhanced Raman scattering (SERS) technique^[4]. However, SERS selectively enhances the Raman signals related to the oxidized species on the backbone of conducting polymers, and much rough electrode surface is needed for the oxidation and reduction cycles (ORC) technique^[5]. This is not the real case for the electrosynthesis of conducting polymers. In fact, by using traditional resonance Raman scattering high-quality spectrum also can be obtained.

Recently, we deposited poly(3-methylthiophene) (PMeT) films on flat stainless steel electrode surface by direct electrochemical oxidation of 3-methylthiophene in BFEE. The reason for using BFEE as the solvent and supporting electrolyte was that high-strength and free-standing PMeT film is obtainable from this medium^[6]. Raman spectroscopic and electrochemical studies indicate that PMeT film is formed almost in neutral state initially, then its doping level increases gradually to a constant value. The thickness scale for doping level change of PMeT film is about 500 nm. Similar phenomena were also observed for polythiophene and substituted polythiophene in BFEE and polypyrrole in acetonitrile and other solvents^[7]. However, no paper concerned the PMeT film in detail was published. In this paper, we report the experimental results on doping level increases of

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PMeT film during its electrochemical polymerization process.

EXPERIMENTAL

3-Methylthiophene (98%) was bought from Acros Organics. Boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$, BFEE) was a freshly prepared product of Beijing Changyang Chemical Plant (China), in which BF_3 concentration was 48.24% and water content was 0.24% (by volume). All the commercial materials described above were used as received.

Electrochemical polymerization and examination were performed in a one-compartment cell by using a Model 283 potentiostat-galvanostat (EG & G Princeton Applied Research) under computer control. The working and counter electrodes were two stainless steel sheets (AISI 430, 1.8 cm $\times$ 6 cm) placed 1 cm apart. Before each polymerization they were carefully polished with abrasive paper (1200 mesh) and cleaned by water, methanol and acetone successively, then dried by a blower. The typical electrolyte was BFEE containing 0.1 mol/L 3-methylthiophene, which was deaerated by dry nitrogen bubbling, and a slight nitrogen overpressure was maintained during the experiments.

Polymer films were grown uniformly on the working electrode surface at a constant applied potential of 1.38 V versus SCE. The thickness of the polymer films was calculated from the total charge passed through the cell (read directly from i -E curves by computer). Cyclic voltammograms (CV) were carried out using PMeT film coated stainless steel sheet as the working electrode and monomer-free BFEE solution as the supporting electrolyte. The doping level "y" of polymer film was determined through the relation of $y = 2Q_d/(Q_d - Q_0)$, where Q_d is the charge used for film deposition and Q_0 is the charge measured during the oxidation of the polymer^[8,9].

Raman spectra were recorded by using a RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC., England) employing a 633 nm laser beam and a charge coupled device (CCD) with 4 cm^{-1} resolution. Before Raman characterization, polymer films were taken out from the cell and washed repeatedly with diethyl ether to remove the electrolyte and monomer. The laser power was always kept very low (~ 0.1 mW) to avoid the destruction of samples. Some complex Raman peaks were divided into component Lorentzian peaks with proper background subtraction using an 'automatic fitting' program provided with the Raman spectrometer.

RESULTS AND DISCUSSION

Figure 1 shows 633 nm excited Raman spectra of PMeT films having different thicknesses. Weak fluorescence background and high signal-to-noise ratio are observable in these spectra. In spite of the complex chemical structures of polythiophenes, their Raman spectra are rather simple. The bands around 1400–1500 cm^{-1} are common features of Raman spectra of aromatic and heteroaromatic systems, which are always strong and dominate the whole Raman spectra^[10]. As can be seen from the spectrum of the 20 nm film, the most intense band (ν_2) is at *ca.* 1445 cm^{-1} , which can be assigned to the totally symmetric in-phase $\nu(\text{C}=\text{C})$ vibration of the bulk thiophene rings distributed over the whole polymer chain. This band is associated with the conjugated PMeT segments in neutral state (reduced state)^[3]. On increasing the film thickness, this band becomes broad and shows a red shift while its intensity decreases gradually. It is well known that Raman intensity is influenced by the scattering of the exciting light from the surface of the sample and from the transition of the vibration mode^[5]. In general, PMeT film with higher doping level has a rougher surface and always shows extensive light scattering from the surface. Therefore, the decrease of Raman intensity with the film thickness is due to the increase of film roughness and also the doping level.

Oxidative doping usually causes a redistribution of charge within the polymer backbone due to the formation of the domains with quinoid type band^[11]. Thus the $\text{C}_\alpha = \text{C}_\beta$ stretching shifts towards lower wavelength upon oxidation, which is in resonance with quinoid structure. By resolving the region of 1600–1200 cm^{-1} into Lorentzian components, two bands are clearly found at *ca.* 1420 cm^{-1} (Q_1) and *ca.* 1400 cm^{-1} (Q_2) (as shown in Fig. 2a and b). These two bands are attributed to the symmetric stretching mode of the $\text{C}=\text{C}$ bond associated

with oxidized (doped) species on the polymer chain. Figure 2 demonstrates that the intensity ratios of Q_1 (or Q_2) and ν_2 bands in the spectrum of a 50 nm film (Fig. 2a) are much lower than those in the spectrum of a 2100 nm film (Fig. 2b). The intensity ratios of Q_1 (or Q_2) and ν_2 bands increase with the increase of film thickness as illustrated in Table 1. On the basis of spectral observations described above, it is reasonable to conclude that the doping level of PMeT film increases with increasing film thickness.

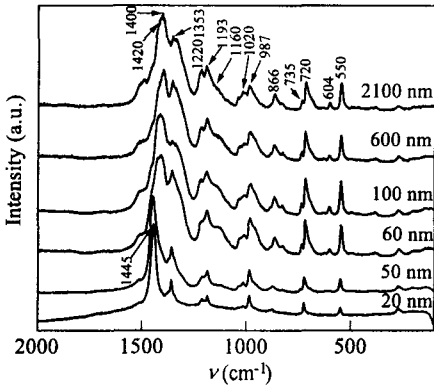


Fig. 1 633 nm Laser excited Raman spectra of PMeT films with different thickness

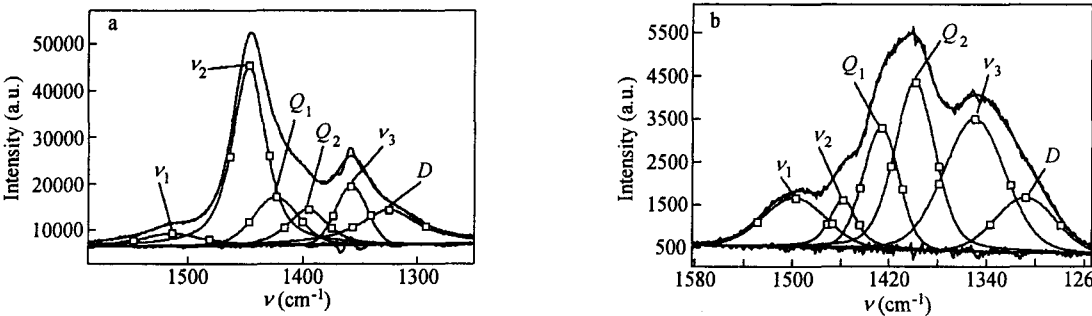


Fig. 2 Resolution of the bands in the region of 1250 cm^{-1} –1600 cm^{-1} into components of Lorentzian profiles for Raman spectra of PMeT
(a) Film thickness: 50 nm; (b) Film thickness: 2100 nm

Table 1. Raman bands intensity ratios in terms of PMeT film thickness						
Thickness (nm)	20	50	60	100	600	2100
$I(Q_1)/I(\nu_2)$	0.040	0.271	1.229	1.388	1.559	2.488
$I(Q_2)/I(\nu_2)$	0	0.203	1.416	2.730	2.991	3.437

As mentioned in the literature based on the results of oligothiophenes^[12], the Q_1 band at *ca.* 1420 cm^{-1} and the Q_2 band at *ca.* 1400 cm^{-1} are assigned to the radical cations and dications of doped PMeT, respectively. At low oxidative potentials, corresponding to low doping levels, the oxidized species present themselves mainly as radical cations while dications prefer to be formed at higher oxidative potentials, corresponding to high doping levels^[12]. In this case, the intensity ratio of Q_2 and Q_1 increases with the increase of film thickness (Table 1), indicating an increase of the doping level. The transfer of Raman intensity from the band near 1420 cm^{-1} to that near 1400 cm^{-1} , *i.e.* on going from radical cations to dications, indicates that for a given chain length the molecular domain perturbed by the ionization is topologically more extended in divalent ionized species than in the radical cation species^[13]. According to our experimental results, at low doping level not only the radical cations but also the dications can be formed, although the concentration of dications is much lower than that of radical cations (as shown in Fig. 2a). At high doping level, both dications and radical cations coexist (not single

radical cations^[14] or dications^[13]). Furthermore, the concentration of dications is slightly higher than that of radical cations in this case (as shown in Fig. 2b). These results indicate that radical cations and dications exist together as the conducting species on the polymer backbone through the whole polymerization process. At high doping level, the interaction between adjacent radical cations on the polymer chain leads to the formation of not only dications, but also a radical cation lattice. Thus the existence of radical cations can explain the metallic properties of polythiophenes very well while these properties can not be explained by a regular array of fully dications (a dication lattice) since one dication has no singly occupied electronic energy level^[14].

The doping level increase during the film growth process can also be confirmed by the relative intensity increase of other Raman bands. For examples, the intensity and width of the ν_1 band (which is attributed to $C_\alpha = C_\beta$ antisymmetric vibrations of aromatic thiophene ring) increase and its position shifts to lower frequencies as the film grows thicker. The broadening of the ν_1 band can be attributed to changes in conjugation length distribution in the PMeT chain. The conjugation length associated with π electron delocalization is favored when the polymer rings are coplanar, owing to the maximum overlapping of the C—C inter-ring carbon P_z orbital. The increase of doping level results in an increase of distorted parts in the polymer, thus reducing the coplanarity of the rings and therefore the conjugation length. Similarly, the intensity of the ν_3 band of the $C_\beta - C_\beta$ ring stretching vibration increases while its position keeps nearly stable as the thickness of the polymer film increases. Furthermore, the $C_\beta - H$ bending vibration at *ca.* 1182 cm^{-1} , the interring $C_\alpha - C_\alpha$ symmetric and antisymmetric stretching vibration at *ca.* 1206 cm^{-1} and 1146 cm^{-1} , the ring-methyl stretching vibration at *ca.* 983 cm^{-1} , ring C—S stretching vibration at *ca.* 866 cm^{-1} , ring out-of-plane bending vibration at *ca.* 604 cm^{-1} , ring-methyl in plane bending vibration and out of plane bending vibration at *ca.* 548 cm^{-1} and 274 cm^{-1} , the ring C—S—C deformation vibration at *ca.* 737 cm^{-1} and 718 cm^{-1} , also show increase in intensity and their positions shift to higher frequencies with the increase of film thickness, indicating that the doping level increases^[15, 16]. It should be noted that upon dedoping at -0.3 V versus SCE in monomer-free electrolyte, the Raman spectra of PMeT films became similar to each other, like the spectrum of 20 nm thick film shown in Fig. 1. This indicates that the spectra of pristine PMeT films are independent of film thickness. Therefore it further proves that the variation of the spectra of polymer films with different thickness is caused by different doping level.

The doping level of PMeT films with different thickness was also determined by the electrochemical technique (Fig. 3). When the thickness of polymer film increases from several nanometers to about 500 nanometers, the doping level goes up rapidly from nearly zero to about 25%. After 500 nm, the doping level of PMeT keeps almost stable. XPS examination also gave a similar result. These facts confirm the conclusion described above and are in good accord with the Raman phenomena.

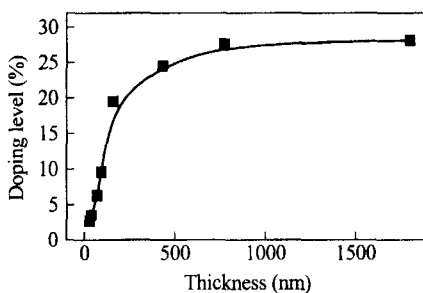


Fig. 3 Plot of the doping level of PMeT film versus film thickness

The low doping level of thin compact PMeT film can be further confirmed by the successive CV technique. Figure 4(a) presents the successive CV scans of a 40 nm PMeT film in monomer free BFEE. The potential scans were started at a positive potential and ended at the same potential so that the film can be finally obtained in doped state. A couple of redox waves appear in the potential scale of 0.33 V to 1.13 V, versus SCE. It is obvious that the current densities of oxidation and reduction waves increase with the continuation of potential scans. This indicates the increase of the charge needed to oxidize or reduce the polymer. Thus, it can be reasonably deduced

that the doping level of the original film is low and it can be increased significantly by CV potential scans. This result is also supported by Raman spectral study. As shown in Fig. 4(b), the Raman bands related to the oxidized (doped) species are strengthened significantly (2) after CV scans, in comparison with those in the spectrum of the same film before CV scans (a) [$I(Q_1)/I(\nu_2) = 0.128$, $I(Q_2)/I(\nu_2) = 0.039$ (before CV scans); $I(Q_1)/I(\nu_2) = 3.135$, $I(Q_2)/I(\nu_2) = 5.982$ (after CV scans)].

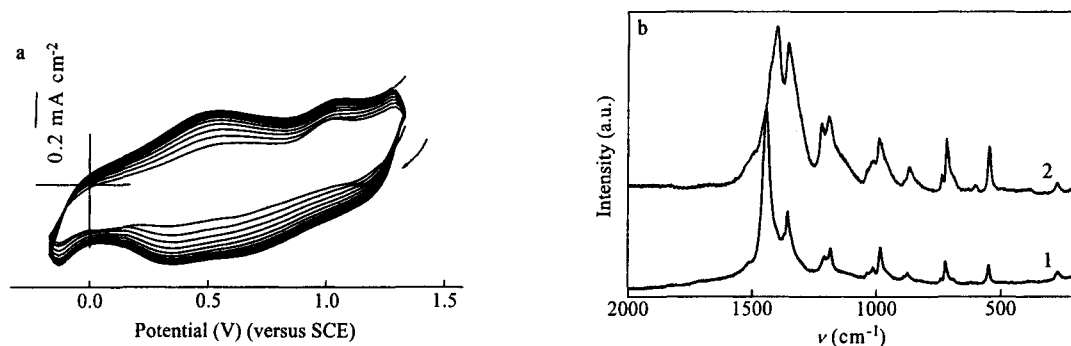


Fig. 4 (a) Successive cyclic voltammograms of PMeT film in monomer-free BFEE solution
Film thickness: 40 nm; potential scan rate: 100 mV/s, 12 cycles
(b) Raman spectra of the 40 nm film before (1) and after (2) CV scans

The same spectral and electrochemical phenomena were also observed by using different metals, such as Pt and Au, as the substrates. Furthermore, similar results were also observed from polythiophene, polypyrrole and poly(*para*-phenylene). Therefore, the possibility of interfacial reaction occurring between the polymer and electrode^[4] can be excluded. The doping level increase with film thickness is possibly due to the change of film morphology during its growth process. In the initial period of the polymerization process, a thin, compact and homogeneous PMeT film with long conjugated chain is formed on the electrode surface^[17] via a two-dimensional growth mechanism^[18]. The oxidation of the polymer is controlled by the diffusion of counter ions into the polymer matrix. This process is relatively difficult because of small free volume in the compact film. Therefore the film is formed with low doping level. At this time conductive species are mainly radical cations, including a small amount of dications. As the polymer film grows thicker via a three-dimensional mechanism in the later period^[19], it becomes a mixture of the long- and short-chain zones. The less ordered zones of the thick film are more porous than the thin film and the diffusion of counter ions and the solvent molecules into polymer film becomes much easier. Thus the doping level gradually increases with the film thickness. In this process the concentration of dications increases more rapidly than that of radical cations. Progressively, dications become the main conductive species. At the same time, radical cations also exist in thick polymer films. Finally, as the formed PMeT film can be oxidized up to a maximum doping level (0.28) when film thickness is higher than 2 μm , which means that about every section of four monomer units in the polymer chain contains one positive charge. This value is very close to that reported by Schmitz and Juttner^[20].

CONCLUSIONS

Raman spectroscopy was used to study electrochemically deposited PMeT films. Raman spectroscopic and electrochemical results indicate that the doping level of PMeT film increases with the increase of film thickness. The main reason for this phenomenon may arise from morphology variations during the polymer film growth process. As the main conductive species on the backbone of polymer films, radical cations and dications can coexist. Furthermore, cyclic voltammetry scans can effectively increase the doping level of thin compact PMeT film.

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