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Characteristics of an electropolymerized PPV and its light-emitting diode

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Poly(phenylene vinylene) (PPV) has been prepared successfully from *p*-xylylenebis(triphenylphosphonium bromide) in acetonitrile solution via an electroreduction polymerization. *p*-Xylylenebis(triphenylphosphonium bromide) also acted as an electrolyte in the solution. The resultant electropolymerized PPV film was transparent and dense, and had considerable adhesion to an indium–tin oxide (ITO) electrode. The electropolymerized PPV showed a blue shift both in the ultraviolet–visible absorption spectrum and photoluminescence, compared with the PPV prepared from a *p*-xylylenebis(tetrahydrothiophenium chloride) precursor route, indicating that it has a shorter π-conjugated chain length. The infra-red absorption spectra showed a stable P–C bond on the electropolymerized PPV chain. The Al/electropolymerized PPV/ITO light-emitting diode emitted green light with an emission maximum at 530 nm. Annealing the electroluminescence device in a high vacuum oven at 160°C for 3 h significantly enhanced the electroluminescence performance as a result of improvement of the interfacial contact between PPV and the Al metal electrode. Copyright © 1996 Elsevier Science Ltd.

(Keywords: electropolymerization; poly(*p*-phenylene vinylene); electroluminescence)

INTRODUCTION

Conjugated polymers have attractive potential applications in electronics and optoelectronics devices, with poly(*p*-phenylene vinylene) (PPV) being one of the promising candidates. The sulfonium precursor route[1], the most popular method to prepare PPV, is a base-induced polymerization of arylsulfonium salt monomer in aqueous solution. The polymerization reaction is terminated with dilute HCl aqueous solution and the solution is then dialysed against deionized water for several days. PPV film can be obtained from the PPV precursor after coating the solution and eliminating the sulfonium groups. Electronic and optoelectronic characteristics of the PPV film have been reported in the literature[2–5]. In addition to chemical polymerization electrochemical polymerization has also been reported for PPV preparation. In 1987 Nishihara *et al.*[6] reported a new method to synthesize PPV from $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*p*-xylene in tetrahydrofuran solution containing n-Bu_4NBF_4 electrolyte. The electropolymerized PPV film was recently fabricated into a polymer diode by this group[7]. However, the different synthetic methods may result in PPV with different π-conjugated chain lengths and chain configurations. These factors may affect the electronic and optoelectronic properties of the PPV.

In our early study[8] we reported the preparation of electropolymerized PPV from *p*-xylylenebis(tetrahydrothiophenium chloride). The resultant PPV diode is a good Schottky diode with a rectification ratio of 100, but it does not show electroluminescence. In this study, PPV is prepared in the undoped state via a simple and convenient electrochemical polymerization reaction from *p*-xylylenebis(triphenylphosphonium bromide) in acetonitrile solution. The resultant PPV is deposited on a cathodic (indium–tin oxide) (ITO) conductive glass electrode, on which the ionic monomer, *p*-xylylenebis(triphenylphosphonium bromide), undergoes an electroreduction polymerization. The ionic monomer *p*-xylylenebis(triphenylphosphonium bromide) also acts as an electrolyte in this process. The resultant PPV film is transparent and suitable for electronic as well as optoelectronic applications. The characteristics of the electropolymerized PPV film and its electroluminescence device will be discussed in this paper.

EXPERIMENTAL

Sulfonium precursor route for preparing chemically polymerized PPV

PPV precursor was prepared by the addition of 20 ml of 0.22 M NaOH aqueous solution into 20 ml of 0.2 M *p*-xylylenebis(tetrahydrothiophenium chloride) aqueous solution with 80 ml pentane. Both solutions were first cooled to 0–5°C in an ice bath. The reaction proceeded for 1 h and then was terminated by the addition of 0.1 M HCl aqueous solution to neutralize the reaction solution. After the pentane was decanted off, the PPV precursor aqueous solution was dialysed against deionized water for several days. Chemically polymerized PPV film was obtained by spin-coating the PPV precursor solution on an ITO glass electrode and then heating in a vacuum oven at 220°C for 2 h.

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Preparation of electropolymerized PPV

The solution for the electropolymerization was obtained by dissolving 0.05 g *p*-xylylenebis(triphenylphosphonium bromide) in 50 ml acetonitrile. A precleaned TN grade ITO (area $3.5 \times 2.5\,\mathrm{cm}^2$) conductive glass was used as a working electrode at the cathode, and a platinum plate (area $5.0 \times 4.0\,\mathrm{cm}^2$) was employed as a counter electrode at the anode. The two electrodes were separated by 2 cm. The electropolymerization reaction was carried out by a current with a fixed voltage level under ambient conditions. After the electropolymerization reaction, transparent PPV was obtained by heating the electropolymerized film in a high vacuum oven at 220°C for 2 h.

Preparation of PPV light-emitting diode

Both PPV films, i.e. chemically polymerized PPV (2000 Å) and electropolymerized PPV (2500 Å), on the ITO glass were coated with Al metal (2000 Å, area $7\,\mathrm{mm}^2$) by thermal evaporation in vacuum (4×10^{-6} torr) to give Al/PPV/ITO sandwich devices. Some of Al/PPV/ITO sandwich devices were annealed in a high vacuum oven at 160°C for 3 h.

Characterization

The thickness of the PPV film was measured with a Dektak 3030 surface profilometer. The morphologies of the electropolymerized PPV films were obtained using a Hitachi S-2500 scanning electron microscope, after coating the surfaces with a thin gold film. The cross-section profile of Al/PPV/ITO sandwich devices was characterized using a Hitachi S-4000 scanning electron microscope. Infra-red (i.r.) absorption spectra of the PPV were taken using a Bio-Rad FTS-165 FT-IR spectrometer. Ultraviolet–visible (u.v.–vis.) absorption of the PPV was measured using a Beckman 7400 spectrometer. A Jasco FR-770 spectrometer was employed to obtain both the photoluminescence spectra of PPVs with a xenon lamp at a wavelength of 365 nm and the electroluminescence spectra of Al/PPV/ITO light-emitting diodes. The *I* (current)–*V* (voltage) curves of the PPV sandwich devices were measured with a programmable Keithley 237 electrometer under ambient conditions. The electroluminescence intensities of Al/PPV/ITO sandwich devices were recorded using a photodiode detector connected with a Newport (model 1815-C) power meter.

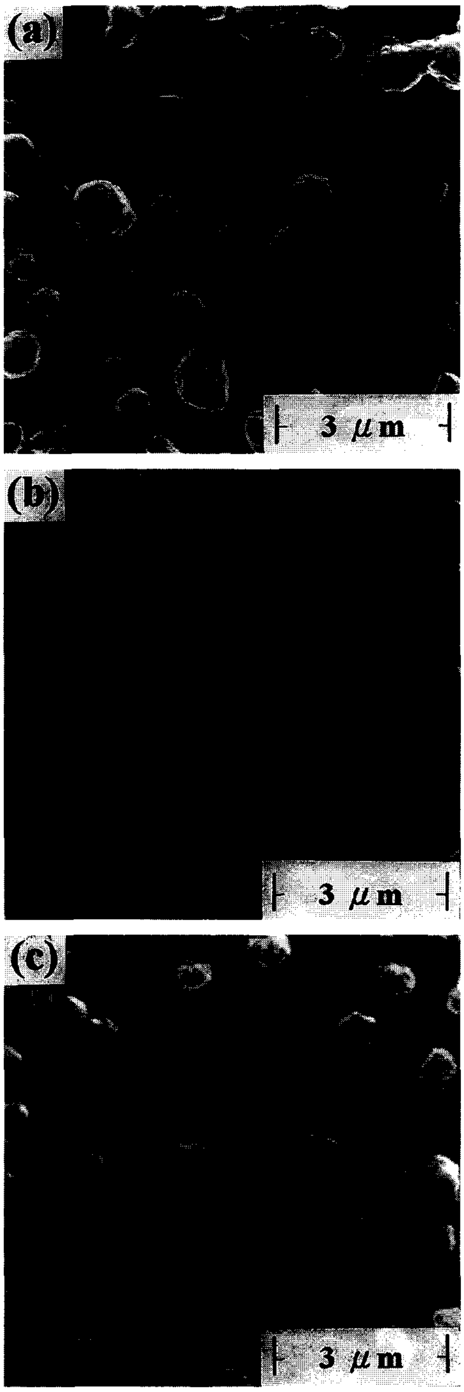

Figure 1 Scanning electron micrographs showing the growth of electropolymerized PPV on ITO glass after (a) 30 min, (b) 60 min and (c) 90 min of the electropolymerization reaction

RESULTS AND DISCUSSION

In this study, PPV was prepared via a new electroreduction polymerization from *p*-xylylenebis(triphenylphosphonium bromide) in acetonitrile solution. The electropolymerization was performed at a constant voltage level of 5.5 V; the current between the two electrodes typically changed from 6 mA at the beginning of the reaction to 2 mA at the end. The electropolymerized PPV was obtained by reducing the *p*-xylylenebis(triphenylphosphonium bromide) monomer. This ionic monomer showed a considerable ionization in the solution: no additional electrolytes were added in this electropolymerization reaction, thereby preventing doping of the resultant PPV by such electrolytes. The resultant PPV film in the undoped state was transparent, insoluble as well as infusible, and the film showed good adhesion to the ITO glass.

The dynamic growth behaviour of the electropolymerized PPV on the ITO glass was examined, and the surface morphologies are shown in *Figure 1*. As seen in *Figure 1a*, in the initial 30 min of the electropolymerization, isolated sphere-like PPV granules were formed on the ITO glass surface. As the electropolymerization reaction continued, *Figures 1b* and *c*, more PPV granules were formed which became connected with their neighbours, eventually forming a continuous dense PPV film on the ITO glass surface.

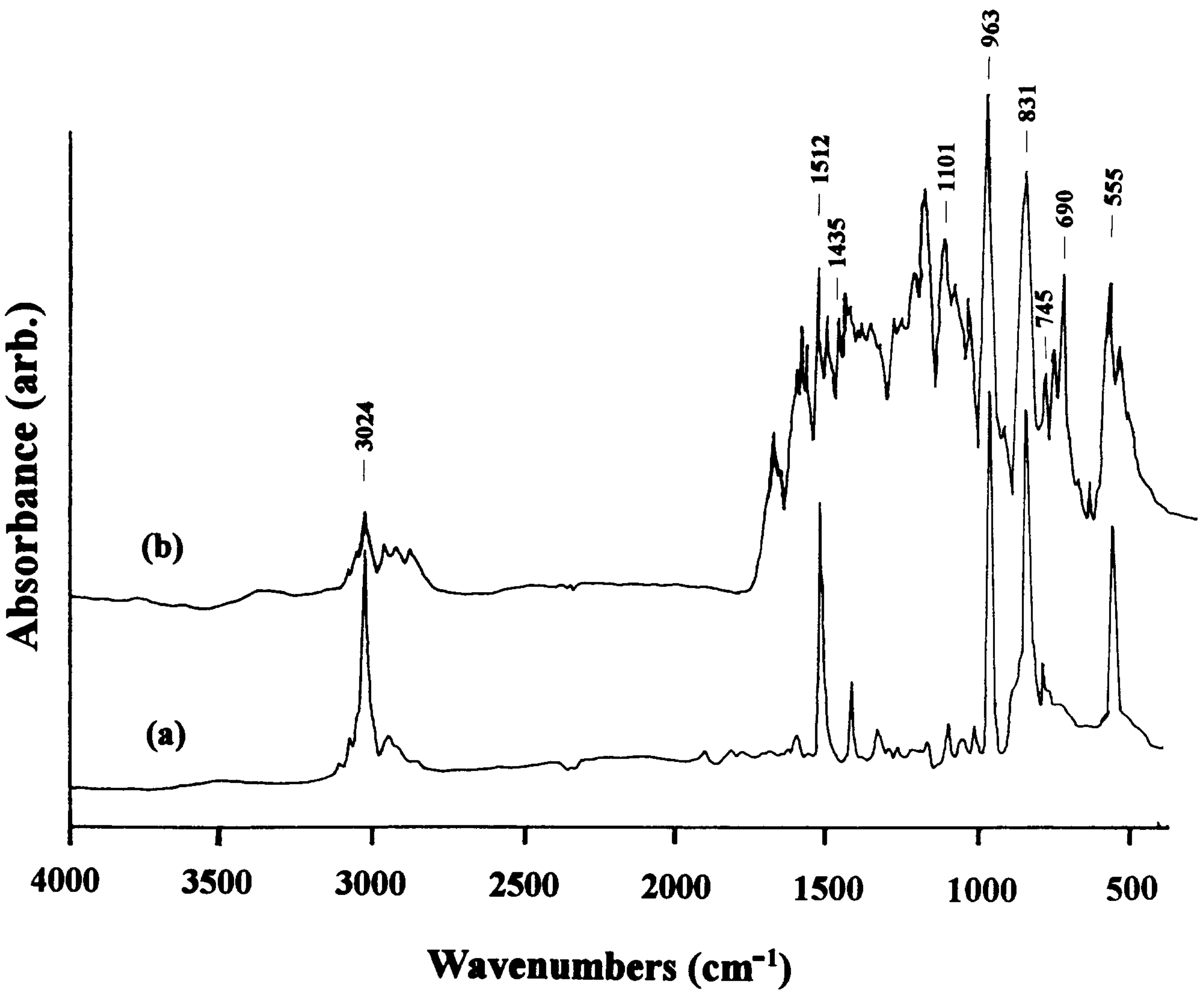

Figure 2 I.r. absorption spectra of the PPV prepared from (a) the sulfonium precursor route and (b) electrochemical polymerization

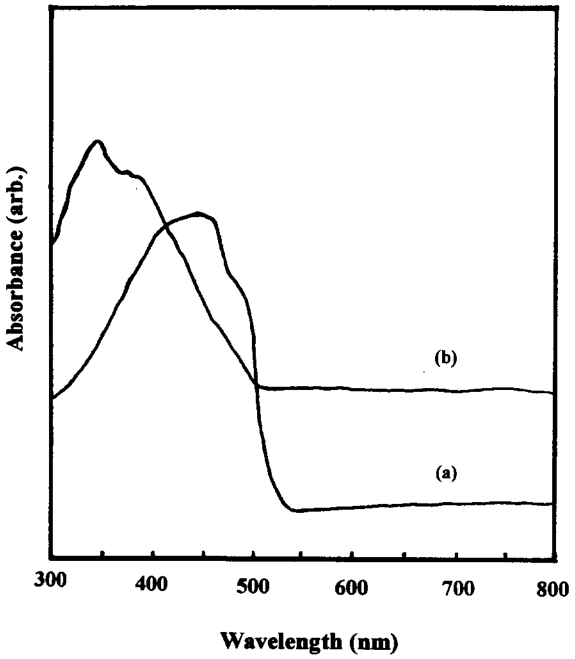

Figure 3 U.v.–vis. absorption spectra of the PPV prepared from (a) the sulfonium precursor route and (b) electrochemical polymerization

The chemical structures of the PPV prepared from the sulfonium route and the electropolymerized PPV were examined by i.r. spectroscopy, as shown in *Figures 2a* and *b* respectively. The absorption band near 963 cm^{-1}, resulting from C–H out-of-plane bending, is characteristic of the *trans* configuration of the vinylene group. The absorption band near 3024 cm^{-1} was due to the *trans*-vinylene C–H stretching mode. The bands near 831 and 1512 cm^{-1} were assigned to *para*-phenylene ring C–H out-of-plane bending and C–C ring stretching, respectively. The band near 555 cm^{-1} was attributed to the phenylene out-of-plane ring bending mode. These i.r. absorption bands were seen both in *Figure 2a* and *Figure 2b*. However, in *Figure 2b*, a band due to an aromatic ring in-plane stretching mode was seen at 1435 cm^{-1} for a P–Ar bond. Besides, the band near 745 cm^{-1} was assigned to P–C stretching of P–CH_2–Ar bonding. The appearance of bands near 1101 and 690 cm^{-1} was attributed to P–Ph stretching modes. When the electropolymerized PPV was further heated at 250°C for 8 h, its i.r. absorption spectrum was similar to that of the original material prepared at 220°C for 2 h. This indicates that the phosphorus–carbon bonds were retained in the polymer chains. Such bonds were stable even at higher temperature and under high vacuum, and

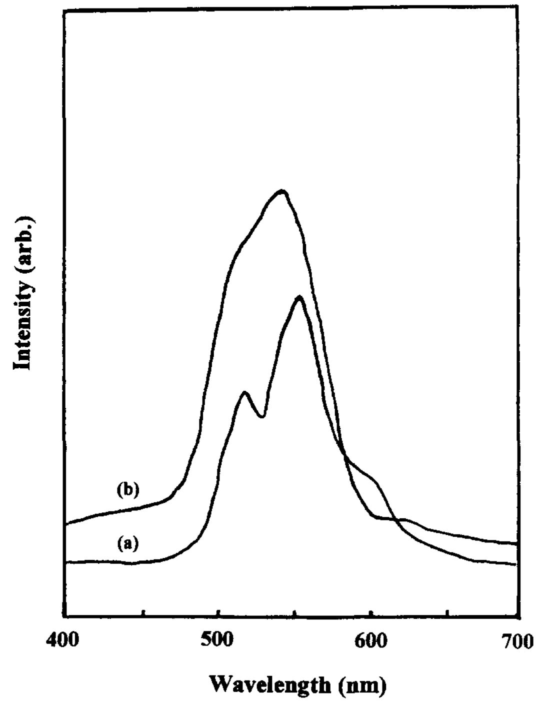

Figure 4 Photoluminescence spectra of the PPV prepared from (a) the sulfonium precursor route and (b) electrochemical polymerization

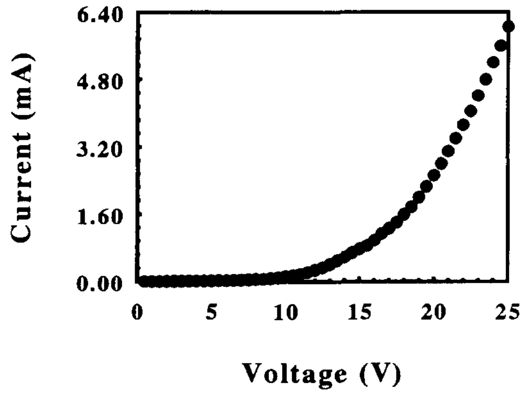

Figure 5 *I–V* curve of unannealed Al/PPV/ITO LED device

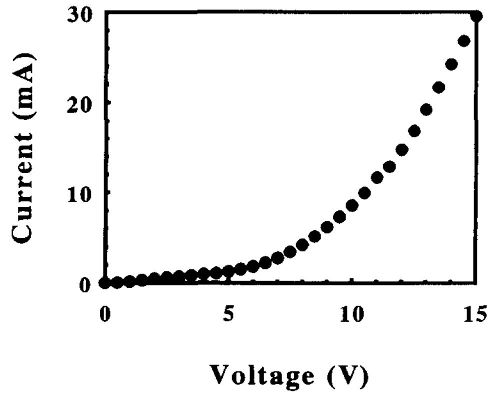

Figure 6 *I–V* curve of annealed Al/PPV/ITO LED device

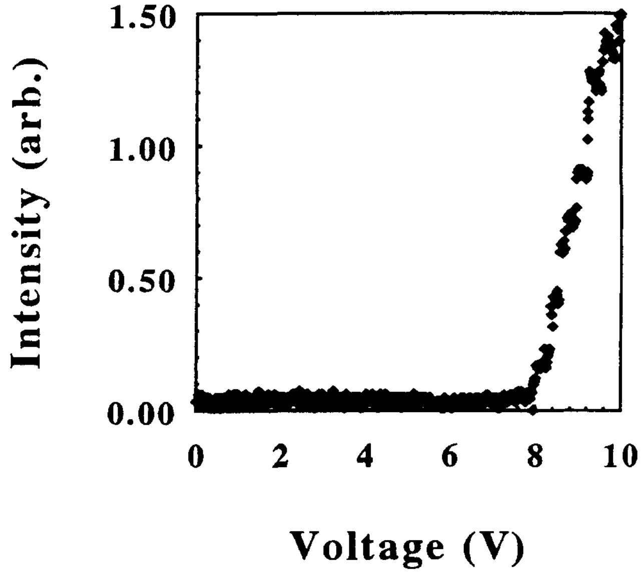

Figure 7 Luminescence intensity–voltage curve of annealed Al/PPV/ITO LED device

thus were not due to unreacted monomer or low-molecular-weight triphenylphosphorus.

The u.v.–vis. absorption spectra of the two types of PPV are depicted in *Figure 3*. The onset of u.v.–vis. absorption for the chemically polymerized PPV and the electropolymerized PPV was around 530 nm ($Eg = 2.34$ eV) and 515 nm ($Eg = 2.41$ eV), respectively. The blue shift in the u.v.–vis. absorption of the electropolymerized PPV indicated the formation of a short conjugated chain length.

The photoluminescence (PL) spectra of these two types of PPV are illustrated in *Figure 4*, where it can be seen that the electropolymerized PPV emitted a shorter wavelength (green) light than did chemically polymerized PPV (green-yellow). A Stokes shift between absorption and emission spectra was also observed in these systems, meaning that the photon energy of the emitted light is lower than that absorbed.

The steady-state *I–V* characteristics of the Al/electropolymerized PPV/ITO light-emitting diodes (LEDs) are shown in *Figures 5* and *6*. In these LED sandwich devices, Al and ITO were used as the cathode (electron-injecting electrode) and as the anode (hole-injecting electrode), respectively. In *Figure 5* the threshold voltage of the unannealed Al/electropolymerized PPV/ITO LED started at 13 V, corresponding to an applied electric strength of $\sim 5.2 \times 10^5$ V cm^{-1}. In comparison, the threshold voltage of the annealed Al/electropolymerized PPV/ITO LED occurred at 8 V, corresponding to an applied electric strength of $\sim 3.2 \times 10^5$ V cm^{-1}, as seen in *Figure 6*. The dependence of the electroluminescence (EL) intensity on the applied bias voltage for the annealed sandwich device is illustrated in *Figure 7*. When the applied bias exceeded the threshold voltage, the luminescence intensity was linearly proportional to the applied voltage, and the emitted light could be easily observed under normal room light. *Figure 8* showed the EL intensity of the annealed device as a function of applied current. The EL intensity of the LED device had a linear dependence on the applied current. In the PPV LED device the electrons from the metal electrode were injected into one side of the PPV layer to form negative polarons and the holes from the ITO electrode were injected into the opposite side of the PPV layer to form

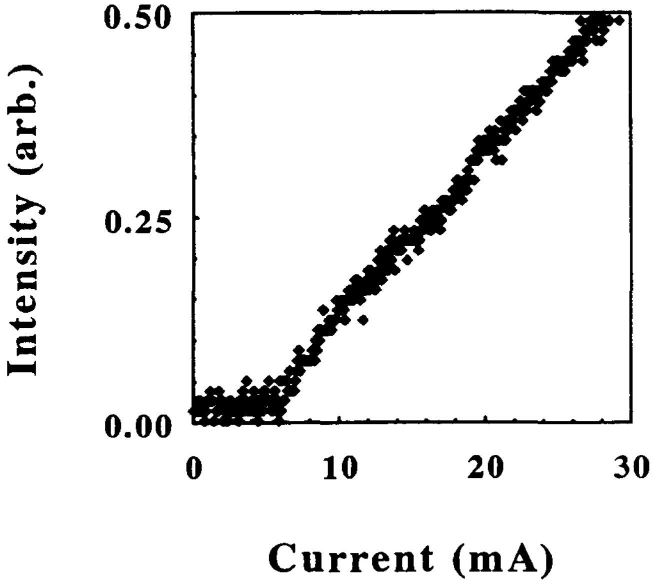

Figure 8 Luminescence intensity–current curve of annealed Al/PPV/ITO LED device

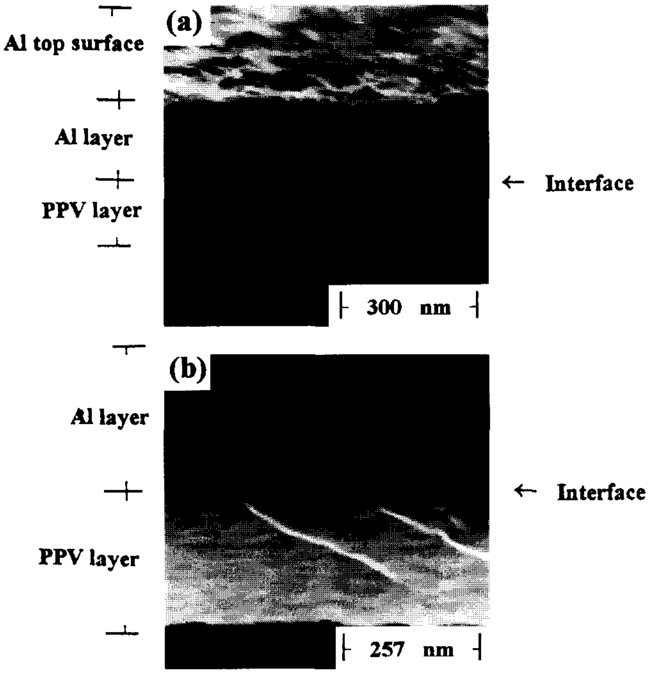

Figure 9 Scanning electron micrographs of the cross-section profile of (a) unannealed and (b) annealed Al/PPV/ITO sandwich devices

positive polarons[9]. Both negative polarons and positive polarons migrated under the influence of the applied electric field and combined on segments of the polymer chain to form the same singlet exciton which then could decay radiatively[9]. Therefore, the higher the applied current, the more the light was emitted.

When the EL characteristics of both unannealed and annealed electropolymerized PPV LED sandwich devices were examined, some significant improvements were observed in the performance of the annealed LED sandwich device. The initial light-emitting active area of the unannealed sandwich device was ~50%, and obviously increased to the full active area after annealing. Concurrently, the light emission intensity became more homogeneous. The failure of the unannealed sandwich device due to spike sparks was eliminated by the annealing process. Moreover, the annealing process reduced the threshold voltage of the polymer LED from 13 to 8 V, increased the light emission intensity and increased the long-term stability. Annealing of the Al/chemically polymerized PPV/ITO LED also resulted in a similar, remarkable improvement in performance.

The significant improvement in the performance of the annealed sandwich device could be explained by examination of scanning electron micrographs taken of the interface. As illustrated in *Figure 9a*, some gaps were present at the interface between PPV and the thermally evaporated Al metal prior to annealing. The interfacial gap between Al and PPV may be due to the formation of Al clusters on the PPV, such cluster formation having been reported in Al/polyimide and Au/polyimide systems[10,11]. The non-uniform formation of the Al film generated some interfacial gaps and reduced the effective contact area between Al and the polymer. The interfacial gap lowered the effective applied electric field strength on the device and consequently raised its operation voltage. The coarse Al metal may also have resulted in small spikes on the interface after thermal evaporation. These spikes caused the device to fail easily upon application of a voltage. In addition, the incomplete contact between PPV and Al metal reduced the active emission area and emission intensity. However, as seen in *Figure 9b*, after annealing the interface between PPV and Al metal exhibited good contact; thus annealing the Al/PPV/ITO sandwich device at 160°C for 3 h significantly improved the contact between PPV and Al metal. Therefore, the annealed device displayed a marked improvement in performance.

The EL spectra of both types of Al/PPV/ITO sandwich devices, *Figure 10*, were similar to their PL spectra. With a maximum emission at 530 nm, the EL of the electropolymerized PPV LED also showed a blue shift compared with that of the chemically polymerized PPV LED.

CONCLUSIONS

In this paper we have explored a new approach to prepare PPV and its electroluminescence device. The PPV was obtained successfully from *p*-xylylenebis(triphenylphosphonium bromide) in acetonitrile solution by electropolymerization. The electropolymerization was a reduction reaction with the ITO glass as a working electrode at the cathode. The resultant electropolymerized PPV deposited on ITO glass was a transparent and dense film suitable for electronic and optoelectronic applications.

The i.r. spectrum of the electropolymerized PPV revealed that it contained phosphorus–carbon bonds in the polymer chains. Experimental results indicated that the phosphorus–carbon bonds were stable and did not disappear even at higher temperature under high vacuum ($<10^{-8}$ torr), thus the phosphorus–carbon bonds were not due to unreacted monomers or low-molecular-weight triphenylphosphorus. The u.v.-vis. absorption spectrum of the electropolymerized PPV showed a blue shift compared with the spectrum of PPV prepared from the precursor route, showing that the electropolymerized

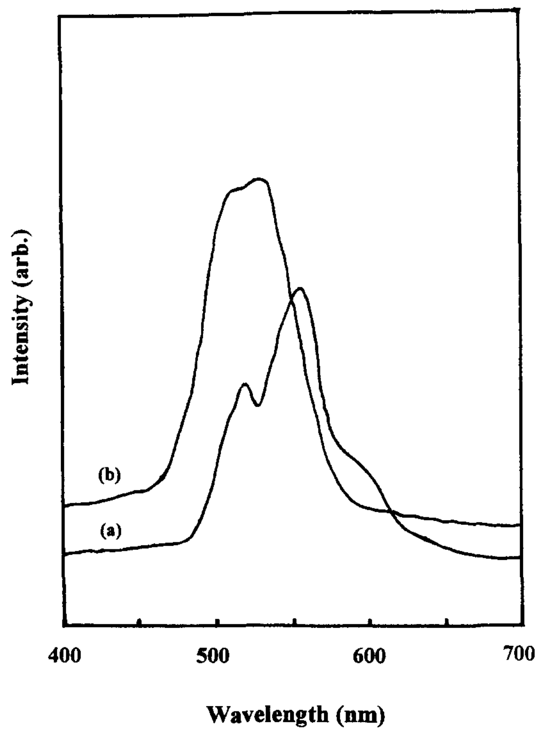

Figure 10 Electroluminescence spectra of (a) Al/chemically polymerized PPV/ITO and (b) Al/electropolymerized PPV/ITO LED devices

PPV had a shorter π-conjugated chain length. The PL spectrum of electropolymerized PPV was similar to the measured EL spectrum, where a green light was emitted with the emission maximum at 530 nm. Both the EL and PL spectra of the electropolymerized PPV also showed a blue shift, confirming a short π-conjugated chain length in the PPV main chain possibly as a result of the formation of P–C bonds. Annealing of the polymer LED improved the contact between PPV and Al metal, reducing the driving voltage and increasing the emitted light intensity.

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