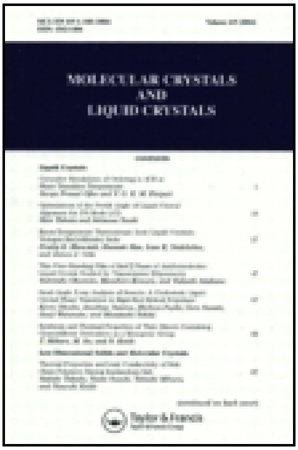

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Effect of Different Treatment of PPV Layer on the Electro-Optical Properties of Electroluminescence Device

L. S. Park [a], K. S. Shin [a] & S. K. Park [a] [b]

[a] Department of Polymer Science, Kyungpook National University, Taegu, Korea

[b] Department of Electronic Engineering, Kyungpook National University, Taegu, Korea

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EFFECT OF DIFFERENT TREATMENT OF PPV LAYER ON THE ELECTRO-OPTICAL PROPERTIES OF ELECTROLUMINESCENCE DEVICE

L. S. PARK, K. S. SHIN AND S. K. PARK*
Department of Polymer Science, Department of Electronic Engineering*,
Kyungpook National University, Taegu, Korea

Abstract Thermal conversion process of PPV precursor, insertion of poly(N-vinyl carbazole) PVK layer under PPV and doping of PPV upper surface with lithium salt before metal electrode formation were studied. With decreasing thermal conversion temperature of PPV, increase of EL intensity, decrease of threshold voltage and blue shift of EL spectra were observed. The insertion of hole transport/electron blocking PVK layer under PPV increased the maximum applicable voltage to the EL device.

Keywords : Electroluminescence device, poly(p-phenylene vinylene), surface treatment, thermal conversion of PPV, solution doping.

INTRODUCTION

Since the first report of the polymer light-emitting diodes based on poly(p-phenylene vinylene) PPV by Cambridge group, a number of different polymers have been synthesized including molecularly doped system.[1-4] M. Esteglamatian et. al. observed shift of PL peak by doping PPV with lithium salt.[5] Q. Pei et al. obtained low threshold voltage and improved durability through electrochemical doping on opposite sides of a thin film of conjugated polymer.[6] In this article, we report the effect of thermal conversion process of PPV, insertion of poly(N-vinylcarbazole) PVK layer under PPV, and doping of PPV layer with lithium salt on the EL device.

EXPERIMENTAL

Synthesis of PPV Precursor and Thermal Conversion to PPV

α,α'-Dichloro-p-xylene (5g ; 28.56mmol) and tetrahydrothiophene (13.14g ; 149mmol) were added into 80 ml of methanol and stirred for 19 hr at 50 °C under N_2 atmosphere. The reaction mixture, after cooling, was poured into cold acetone and the precipitate was filtered and dried under vacuum for 48 hr to give 6.64 g of p-phenylene dimethylene-1,1-bis(tetrahydrothiophene-1-ium)dichloride (Yield = 66.2 %). Elemental analysis : C, 54.69 ; H, 6.88; S, 18.25% (calculated) and C, 54.69; H, 7.26;

S, 17.87% (Found). To the disulfonium salt (5.0 g, 14 mmol) solution in methanol (45 ml) was added dropwise aqueous NaOH solution (0.4 mol/L; 14 mmol) over 20 min. period at 0 °C. The reaction mixture was stirred further for 60 min. and give a highly viscous PPV precursor solution. The precursor solution was dialyzed against deionized water at room temperature for 3 days with a cellulose membrane (cut limit ca. 12,000 g/mol). Dialyzed PPV precursor solution (0.5 wt%) was spin coated on the ITO glass. The ITO glass coated with PPV precursor was placed in a vacuum chamber and thermally converted to PPV at different temperature (140 °C ~ 260 °C) for 3hr.

Treatment of PPV Layer and Fabrication of EL Device

ITO glass (30 Ω/□, 1.08 mm thickness) was cut into 2.5 cm×2.5 cm size and the electrode area was etched by electrolysis method . It was cleaned in a ultrasonic bath with acetone, methanol and mixture of isopropyl alcohol and water (1:1 by vol.). Different types of EL device with PPV as emitting layers were fabricated. First, the EL device for observing the effect of thermal conversion temperature was described above. Second, for the insertion of PVK layer under PPV emitting layer, PVK solution (0.5 wt% in dichloroethane) was spin coated on the ITO. It was dried at room temperature for 20 min in the vacuum oven and then PPV precursor aq. solution was spin coated. The PPV layer was thermally converted at 140 °C for 3 hr. Third, for doping of PPV layer, 0.5 wt% PPV precursor aq. solution containing 0.02 wt% of LiClO4 was spin coated directly on ITO and then thermally converted at 260 °C for 3 hr. The Mg metal electrode was deposited by E-beam method on all of these devices at 20 Å/sec rate to 4,000 Å thickness. The structure of a typical EL device and polymer materials are shown in Fig. 1.

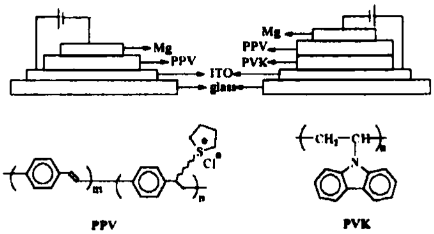

FIGURE 1 Structure of EL devices and polymer materials

Characterization and Measurement

Elemental analyses of monomer and polymers were taken on a Carlo Elba Model 1106. Current and luminance were measured with Model 8902A Digital Multimeter and Minolta Luminance Meter LS-100 equipped with close-up lens (No. 110, ϕ 40.5mm) at room temperature, respectively. Electroluminescence spectrum was obtained by Optical Multichannel Analyzer (EG & G, USA) equipped with OMA4 CCD detector.

RESULTS AND DISCUSSION

The intensity of EL device was dependent on the thermal conversion temperature of PPV layer in the order 140 °C > 180 °C > 220 °C > 260 °C as shown in Fig. 2(A).

The current vs. voltage plot showed same order as the EL intensity plot. From Fig. 2(A), it is noted that the threshold voltage of EL device decreased as the PPV conversion temperature decreased (ca. 6 volt for PPV converted at 140 °C). The EL spectrum analysis showed shift of maximum peak toward short wavelength with decreasing conversion temperature (Fig. 2(B)). The decrease of threshold voltage and EL spectral shift were suggestive of unconverted sulfonium salts in the PPV layer. This was confirmed by the elemental analysis data of PPV films converted at different temperature (Table 1).

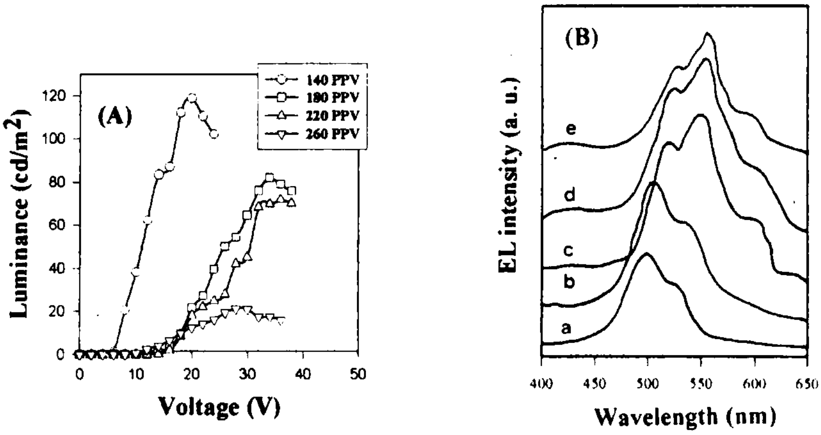

FIGURE 2 (A) : Luminance vs. voltage profile of EL device with PPV layer converted thermally at different temperature. (B) : electroluminescence spectra of EL device with PPV layer converted thermally at (a) 100 °C, (b) 140 °C, (c) 180 °C, (d) 220 °C and (e) 260 °C.

Table 1 Elemental analysis data of PPV film thermally Converted at different temperature.

Sample	Temp. (°C)	C	H	S
100 PPV	100	74.54	5.53	2.50
140 PPV	140	83.74	5.57	0.26
180 PPV	180	91.27	5.81	0.00
220 PPV	220	92.46	5.88	0.00
260 PPV	260	93.61	5.94	0.00

Thus the EL device made with PPV converted at 140 °C (140 PPV) may have similar characteristics as reported by Q. Pei.[6] The EL device with 140 PPV showed high EL intensity, but the maximum applicable voltage was lower than the ones with PPV converted at higher temperature (Fig. 2(A)). Thus a thin film of hole transport/electron blocking layer (PVK) was deposited under PPV which was then converted at 140 °C. This EL device showed increased maximum applicable voltage, but decreased EL intensity (Fig. 3(A)). This may be due to insufficient hole injection through the PVK and PPV interface. To see the effect of presence of $LiClO_4$ salt in the PPV layer converted at high temperature of 260 °C, PPV precursor aq. solution containing 0.02

wt% $LiClO_4$ was spin coated directly on the ITO glass. The EL device in which PPV was solution doped with $LiClO_4$ showed lower threshold voltage compared to the EL device with pure PPV layer converted at same temperature of 260 °C, but the maximum applicable voltage and EL intensity became low .(Fig. 3(B))

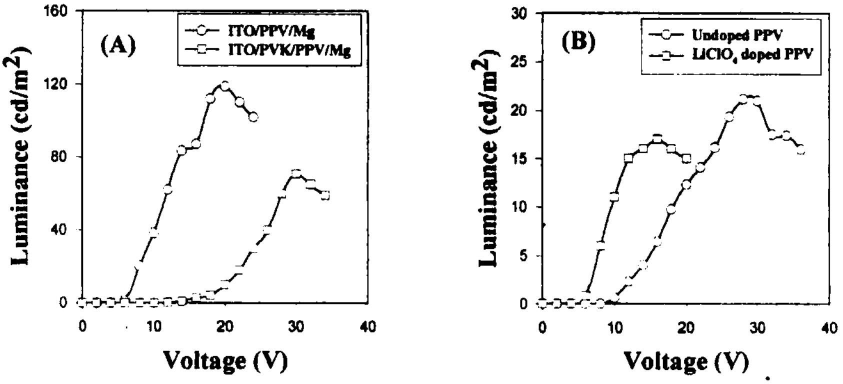

FIGURE 3 (A) : Effect of hole transport/electron blocking PVK layer under PPV emitting layer (PPV converted at 140 °C). (B) : Effect of $LiClO_4$ doping of PPV layer in the ITO/PPV/Mg EL device (PPV converted at 260 °C)

CONCLUSIONS

In conclusion, EL intensity of ITO/PPV/Mg device was dependent on the thermal conversion temperature of PPV in the order 140 °C > 180 °C > 220 °C > 260 °C. The threshold voltage was lowest (ca. 6 volt) in the device with PPV converted at 140 °C . Blue shift of EL spectra was detected as the PPV conversion temperature decreased. Incorporation of hole transport/electron blocking layer (PVK) under PPV (converted at 140 °C) increased the maximum applicable voltage to the EL device, but decreased EL intensity. $LiClO_4$ doping of PPV (converted at 260 °C) gave low threshold voltage, but the maximum applicable voltage and EL intensity became low.

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