

# PREPARATION OF LIGHT-EMITTING DIODES WITH POLY(P-PHENYLENE VINYLENE)

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## 1. INTRODUCTION

Tang and Van Slyke first reported an organic double-layer electroluminescent(EL) device in 1987.[1] They achieved a luminance of  $1000 \text{ cd/m}^2$  at a voltage below 10 V. The EL quantum yield is about 1%(0.01 photon/electron).

PLED's were fabricated with the  $\pi$ -conjugated semiconducting polymers, e.g., PPV, polythiophene, poly(p-phenylene), and their derivatives and polymers having conjugated  $\pi$ -electron systems. Among them, poly(p-phenylene vinylene)(PPV) is the first electroluminescent polymer and seems to be of importance for elucidating the light-emitting mechanism. PPV emits light when current is applied regardless to its synthetic route; soluble precursor route[2,3], chemical vapor deposition[4], electropolymerization[5].

Because of the simple structure of the single-layer type PLED, we tried to make only the single-layer type PLED with high efficiency. PPV was chosen for the emitting polymer layer.

Polymer thin films can be obtained easily by conventional methods. If a free-standing PPV film can be utilized as emitting layer, we can fabricate PLED with ease in low cost.

What are the key steps toward making efficient PLED? How can we prepare PLED within 3 or 4 processing stages? This is the aim of our research. We tried to find the simple and short way to PLED based on PPV.

## 2.EXPERIMENTAL

### 2.1 PPV Preparation

We followed the general synthetic procedure of Karasz et al.[8] and Schwoerer et al.[9]

#### 2.1.1 Monomer synthesis

#### 2.1.2 Precursor polymer synthesis

## 2.2 Preparation of PPV light-emitting diode

Indium-tin oxide (ITO)-coated glass was supplied by Samsung-Corning Co. The sheet resistivity was  $20 \Omega / \square$  and the ITO layer thickness 285 Å.

Indium-tin oxide (ITO)-coated glass substrates were cleaned with acetone and subsequently with propan-2-ol, both in an ultrasonic bath. In some cases a part of ITO layer was etched off using 10 wt% NaOH at 65 °C in 5 minutes. The precursor film was formed on the ITO glass by spin-coating with adjustment in both spin-speed and solution concentration.

The precursor-coated ITO glass was then thermally converted at several temperatures in dry nitrogen stream (50 ml/min) to convert the precursor polymers into PPV. Al electrodes were vacuum deposited on the PPV layer. Sample areas were about 5mm x 5mm.

The devices were driven by applying a positive bias to the ITO with a Heung-Chang voltage source and electric currents were monitored with a Keithley 617 programmable Electrometer. Emitting light was observed through the ITO substrate.

## 2.3 Characterization

### 2.3.1 Intrinsic viscosity measurement

### 2.3.2 Infra-red spectroscopy

### 2.3.3 UV/VIS spectroscopy

### 2.3.4 Thickness measurement

### 2.3.5 The I(current)-V(voltage) measurement

### 2.3.6 DC conductivity

### 2.4.7 Fluorescence spectra

## 3.RESULTS AND DISCUSSION

The polymerized polyelectrolyte solution was highly viscous. The intrinsic viscosity of the solution was found to be about 5.1 dl/g. Figure 1 shows the IR-spectra of the precursor film and partially converted and fully converted PPV films. The precursors were heated to the indicated temperature with a rate of 10 °C /min and kept at that temperature for 40 minutes.

Infra-red spectroscopy of the fully eliminated PPV showed a strong absorbance at  $3030\text{cm}^{-1}$ , consistent with the trans-CH stretching mode of the vinylene group, while small absorbance was observed near  $2950\text{cm}^{-1}$ , which arises from aliphatic CH stretching mode. The absorbance ratio  $A_{3030}/A_{2950}$  must be dependent

on the degree of conversion to vinylene moiety. Fig.2 shows the absorbance ratio  $A_{3030}/A_{2950}$  as a function of heat-treatment temperature.

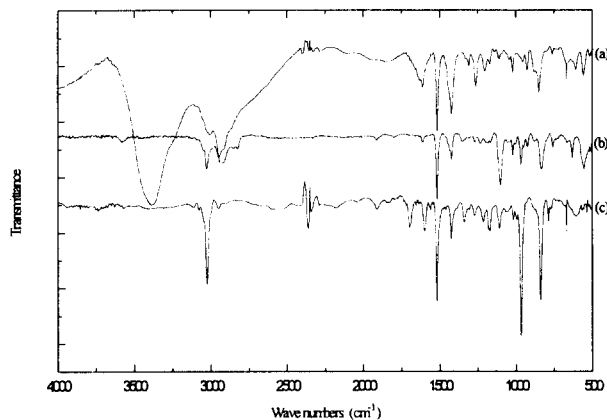


Fig.1. IR-spectra of the precursor film(a), film heat treated at 100 °C for 40 min.(b), and fully converted PPV film(c).

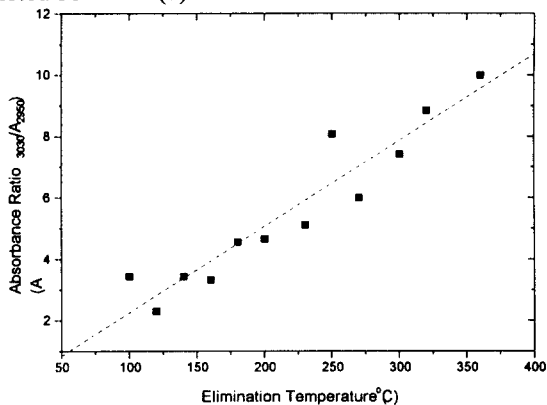


Fig.2. The absorbance ratio as a function of heat treatment temperature.

All samples were heat to hat temperature with a rate of 10 °C /min and heat-treated for 40 min. at that temperature.

Our ITO/partially converted PPV/Al devices emit yellow-greenlight from the turn-on voltage of 4 V. The light intensity increases with the applied current density. From 8V the device emitted bright stable light. At about 14 V the devices show sparks due to the short circuit and died away. In this case the devices were very hot.

DC conductivity of the precursor films as a fuction of the heat treatment temperature is shown in Fig.3. With increasing the heat-treatment temperature, the conductivity increases.

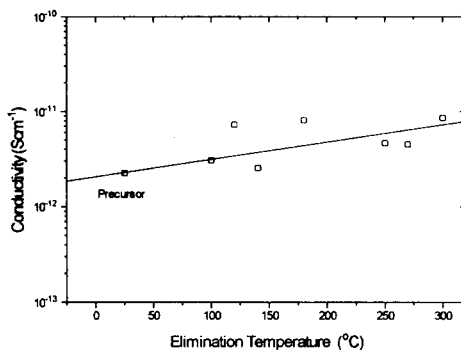


Fig. 3. D.C. conductivity of the heat-treated precursor films as a function of the heat treatment temperature.

The electroluminescent spectrum of our PPV LED is shown in Fig.4. The device was heat-treated at 230°C for 5 min. and postannealed at 160°C for 2 hrs.

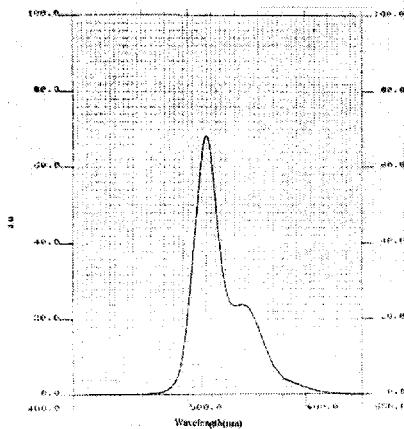


Fig.4. Electroluminescence spectrum of the light emitted from the partially converted PPV, heated at 230 °C for 5 min. under nitrogen gas flow of 50 ml/min., and followed by subsequent annealing at 160 °C for 2 hrs.

#### 4. CONCLUSIONS

The PPV precursor is a good material for fiber and film formation. The material can be easily drawn to yield a highly oriented crystalline fiber, which is tough and flexible.

The optimal method for fabricating PLED based on PPV was set up as follows.

To get pure polymer solution, fine filtering of the dialyzed polymer solution is needed.

For 230 °C heat treatment for elimination of precursor film, heating time does not longer than 5 min. For 160 °C, heating time of 30 min. is good for the elimination reaction.

The optimum thickness of PPV layer for the single-layer type PLED is around 50 nm.

The post annealing at a lower temperature is effective for stable observation of the emitting light.

## **Acknowledgment**

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