

## Polymer Light-Emitting Diodes Based on Poly(3-hexyl thiophene)

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**Abstract :** Poly(3-hexyl thiophene)(P3HT) and poly(3-dodecyl thiophene)(P3DT) were polymerized by oxidative coupling with ferric chloride. The P3HT light-emitting device emitted red light and it could be observable in the ordinary indoor light. The device had the turn-on electric field of about  $3 \times 10^7$  V/m. The maximum electroluminescence (EL) intensity was obtained when the thickness of polymer layer was about 130 nm in ITO/P3HT/Al device. The maximum external quantum yield was 0.002%. The maximum luminance was 21 cd/m<sup>2</sup>. The EL intensity decreases with increasing the crystallinity of the polymer layer. By using the oriented poly(3-alkyl thiophene)(PAT) layer as an electroluminescent layer in the ITO/polymer/Al light-emitting devices, the polarized EL light emission was observed. The EL intensity ratio of parallel to perpendicular direction to the stretch direction for P3HT was about 1.40.

### Introduction

Since 1990, polymer light emitting diodes (LED) have been one of the important topics in the organic semiconductor field[1]. Polythiophene can be synthesized chemically or electrochemically and recently by plasma polymerization[2]. In 1979, polythiophene film was synthesized by the electrochemical method and found to be stable at ambient conditions[3]. But the polymer was not used widely because of infusibility and insolubility of the polythiophene.

Some chemists tried to attach alkyl chains to the main polythiophene chains to make them soluble in common solvents. Poly(3-alkyl thiophene) (PAT) was the first thiophene derivative soluble in common solvents, e.g., chloroform(CH<sub>2</sub>Cl), benzene, tetrahydrofuran (THF) etc.

McCullough *et al.*[4] obtained a regioregular PAT having near 100% head-to-tail configuration. They synthesized asymmetric Grignard monomer 2-bromo-5-(bromomagnesium)-3-alkyl thiophene with Ni catalyst .

Wu *et al.*[5] reported a paper entitled head-to-tail regioregular poly(3-(alkylthio)thiophene) prepared by regioselective synthesis using active zinc. This method is easier than McCulloughs method.

Electroluminescence from PAT polymer layer was first reported by Japanese researchers[6].

In this study the optimum processing conditions for the poly(3-hexylthiophene) (P3HT) LED were studied. The optimum thickness was determined for P3HT LED. The effect of thermal annealing on the device performance was investigated. To find the effect of chain orientation on the device performance, the LED with oriented polymer layer was prepared.

### Experimental

#### Materials

##### Polymerization

Polymerizations of P3AT were carried out according to the method of Yoshino *et al.*[7] The monomers, 3-hexylthiophene and 3-dodecylthiophene were purchased from Aldrich and used without further purification. The polymerization was conducted utilizing the oxidative coupling with FeCl<sub>3</sub>.

The monomer(0.04 mol) was added to the solution of ferric chloride(0.16 mol)/chloroform(about 300 ml) with stirring and purging with nitrogen. The mixture was stirred for 2 hours at 30°C. Then the reaction mixture was poured into methanol. The precipitate was filtered with a glass filter and then washed with methanol. The brown solid was obtained and dried under a vacuum at room temperature.

##### Dedoping

The obtained polymer was treated with a concentrated ammonia solution to remove residual Fe compounds (dedoping). Dedoping was made by stirring and refluxing the polymer solution in chloroform and 28% ammonium hydroxide solution for 30 min[7]. The water phase was separated and fresh ammonia solution was added again. This procedure was repeated four times and then the chloroform solution was washed twice with ethylenediaminetetraacetic acid (EDTA) dissolved in water (0.04 M). The chloroform solution was finally washed with distilled water. The solution was poured into methanol and the pure polymer was precipitated.

##### Soxhlet extraction

The low-molecular-weight portion of the synthesized polymer was removed by soxhlet extraction with methanol for one day and then with acetone for 2 days. A reddish solid was obtained. The yield was about 82-89%. After

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extracting the polymer, the 4~5% polymer solution in chloroform was filtered using 1G3 glass-filter to remove the insoluble crosslinked polymer.

### Instruments

#### *FT-IR spectroscopy*

FT-IR spectra were obtained by Nicolet 520<sup>®</sup>FT-IR spectrometer. Samples were 1~2  $\mu\text{m}$  thick films.

#### *<sup>1</sup>H-NMR spectroscopy*

Contents of Head-to-Tail and Head-to-Head coupling were calculated from the spectrum recorded by 200 MHz <sup>1</sup>H-NMR in CDCl<sub>3</sub> solution.

#### *GPC*

The molecular weight and polydispersity index of the polymer were determined by the gel permeation chromatography (Spectra Physics) with THF. Polystyrene was used as a standard and the pore size of columns is in the range of 500~10<sup>4</sup> Å.

#### *UV-vis spectroscopy*

UV-vis spectra of the polymer solution in chloroform/methanol and the film on indium-tin-oxide (ITO)-glass were obtained with a UV/vis spectrophotometer (Shimadzu).

#### *Thermal analysis*

Thermal analysis was carried out using Shimadzu DSC50 and TGA 50. The 2~5  $\mu\text{m}$  thick film was used as a sample, and it was prepared by solution casting from 5% chloroform solution. It was first heated to an indicated crystallization temperature at a rate of 10°C/min and held at that temperature for 30~240 min. Then it was cooled at a rate of 5°C/min to room temperature and scanned again to 250°C with a heating rate of 10°C/min.

#### *X-ray measurements*

Wide angle X-ray diffractogram was obtained by Philips thin film diffractometer at 40 kVx 40 mA with fixed incident beam angle (0.02° from the film plane).

#### *Electrical measurements*

Current was measured with Keithly 617 electrometer. Capacitance of the ITO/polymer/Al devices were measured by Hewlett Packard 4192A LF impedance analyzer at 1 kHz for estimating the thickness of the polymer layer.

#### *Thickness measurements*

The thickness of polymer layer was measured by a stylus method ( $\alpha$ -step 500) and an ellipsometer. The etched side of ITO-glass was used as a substrate for the ellipsometry measurements. Aqua-regia was used to etch out the ITO layer in ITO-glass.

#### *Photoluminescence (PL) and Electroluminescence (EL) spectrum*

Photoluminescence and electroluminescence spectra were obtained with Shimadzu Spectrofluorophotometer RF-540 V-4.0. The direction of detector is at right angle from the excitation beam (wavelength of 320 nm) direction in the instrument. The sample plane was 45° each

from the both direction. The sensitivity was set to 1(High) and the slit was set to 3(10).

### Preparation of the light-emitting devices(LED)

Indium-tin-oxide (ITO) sputtered glass was supplied by Samsung-Corning Company Ltd. It consists of a soda lime glass and a 120 nm thick SiO<sub>2</sub> layer. The polymer solution was spin-coated onto the ITO-glass and then the cathode (aluminum) was vacuum deposited under a 10<sup>-5</sup> torr. vacuum. The electrode area was 2 × 2 mm<sup>2</sup>.

## Results and Discussion

### Characterization of polymers

The molecular structure of the obtained polymer was confirmed by FT-IR and NMR spectroscopy. IR spectrum of the synthesized poly(3-hexylthiophene)(P3HT) and poly(3-dodecylthiophene)(P3DT) were obtained and indicated that the target polymers were successfully synthesized(Figure 1). The I.R. band assignment for the P3HT and P3DT is tabulated in Table 1.

The <sup>1</sup>H-NMR spectrum of P3AT provides sensitive probes for the substituent sequence in the polymer backbone.  $\alpha$ -Methylene protons of the alkyl group could be resolved into two different diads, i.e., head-to-tail(HT) and head-to-head(HH). Also, the proton in the 3-position of the thiophene ring bears four different chemical envi-

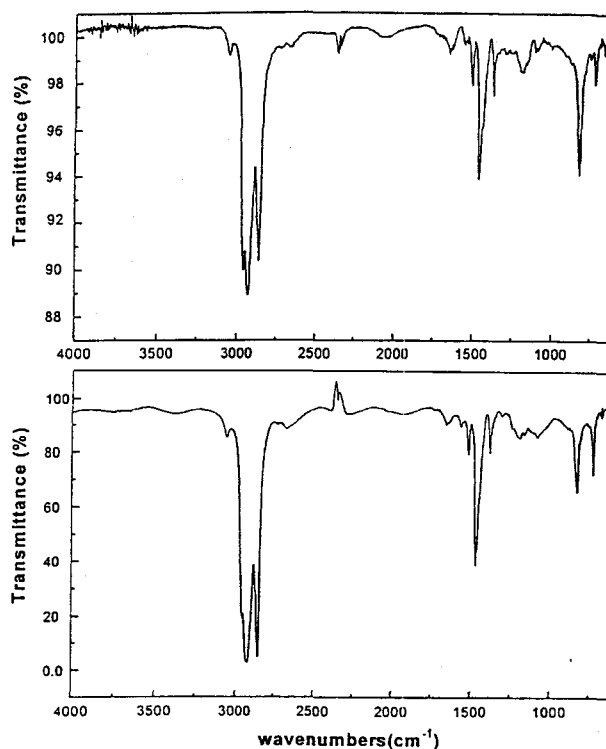


Figure 1. I.R. spectra of P3AT films (See text). Top: P3HT, bottom: P3DT.

**Table1.** I.R. band assignments for P3HT and P3DT

	Aromatic C-H str.	Aliphatic C-H str.	Ring str.	Methyl def.	Aromatic C-H out-of-plane	Methyl rock
P3HT	3062	2960, 2934, 2863	1516, 1470	1383	825	732
P3DT	3059	2954, 2920, 2850	1512, 1468	1377	822	719

ronments in a mixture of the four possible triad regioisomers.

The doublet and quartet can be discernible like the results of other researchers[5,8].  $\alpha$ -Methylene protons of the alkyl group have doublet around 3.0 ppm and the proton in the 3-position of the thiophene ring has quartet at around 7.0 ppm. The contents of triads and diads were calculated from the integral of the corresponding peaks. The calculated configuration of the P3HT and P3DT were shown in Table 2.

HT-HT content was 60~70% and HT content was 76~81%. The thiophene rings in P3DT are expected to have less twisted form and the conjugation length remains less shortened than in P3HT.

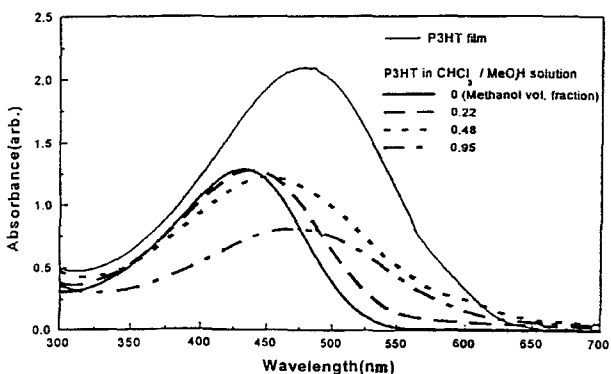
Molecular weight was measured to be  $M_n = 18380$ ,  $M_w = 61717$ , and polydispersity index (PDI) = 3.4 for P3HT and  $M_n = 38,235$ ,  $M_w = 106,658$  and PDI = 2.8 for P3DT.

By thermogravimetric analysis(TGA), we found that P3HT is stable up to 200°C.

As shown in Figure 2, P3HT has absorption peak at 475 nm for the solid film sample and at 420 nm for the chloroform solution. The solvatochromism of the P3HT was confirmed by Figure 2., which exhibits the red shift of

**Table 2.** Relative contents of configuration in the synthesized P3HT and P3DT

	Aromatic proton				$\alpha$ -methylene protons	
	HT-HT	HT-HH	TT-HT	TT-HH	HT/HH	HT/HH
P3HT	59	16.8	15.3	8.9	75/25	76/24
P3DT	69.3	18.2	7.3	5.2	82/18	81/19



**Figure 2.** UV-Vis spectra for P3HT (See text).

absorption peak maximum as the volume fraction of methanol (nonsolvent) increases.

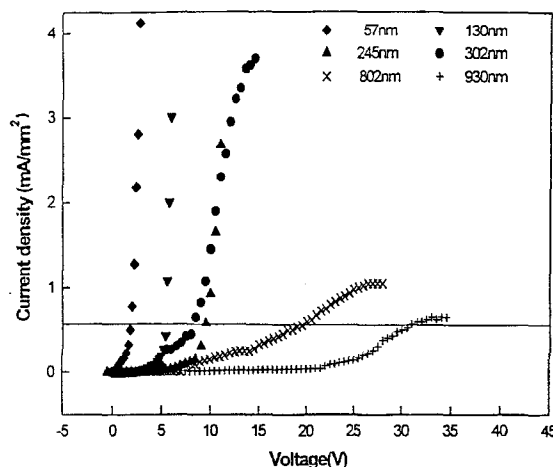
**Optimum polymer layer thickness**

The polymer light-emitting device with P3AT emitted red light when the dedoped polymer was used as the light-emitting layer. This is because Fe compounds in the polymer layer transport charge carriers and obstruct formation of excitons. The surface of spin-coated polymer was macroscopically smooth but microscopically it was not.

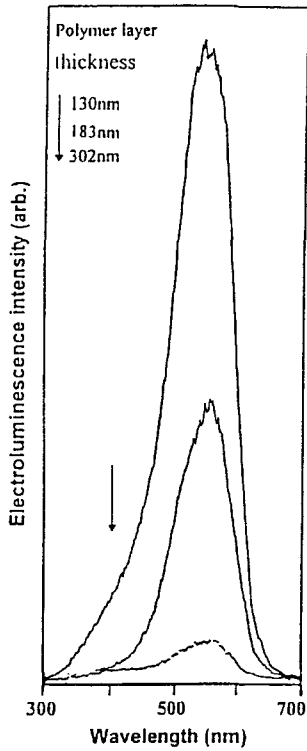
The P3HT layer thickness was controlled by changing the polymer concentration of 0.1~5 wt% in THF solutions and the spinning speed of the substrate in a range of 1000~3000 rpm. The capacitance of the sample device was measured to estimate the thickness of the polymer layer. There is a linear relation between the inverse of capacitance and the thickness.

Figure 3 shows the current density as a function of the applied voltage. If the current density-voltage curve is replotted into the current density-electric field curve, these curves superpose one after another. All devices exhibited steep increase of current density at an electric field of about  $3 \times 10^7$  V/m.

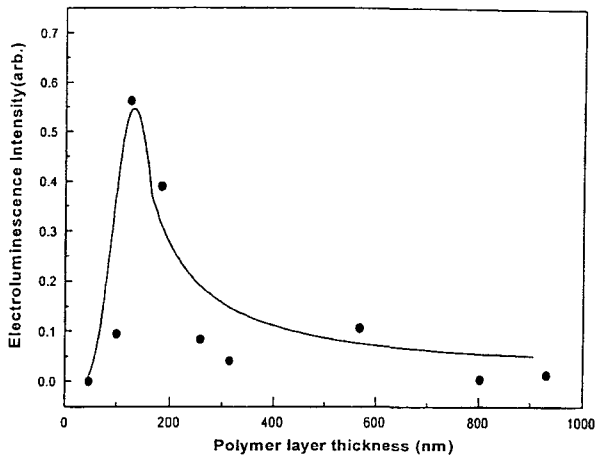
Light emitted from the device was red and it can be seen in the ordinary indoor light. The peak maximum in the EL spectrum was at about 560 nm in Figure 4. The EL intensity of the LED made with P3HT was measured at the constant current density of 0.58 mA/mm<sup>2</sup>.



**Figure 3.** Voltage-current density curves of ITO/P3HT/Al devices with different polymer layer thickness.

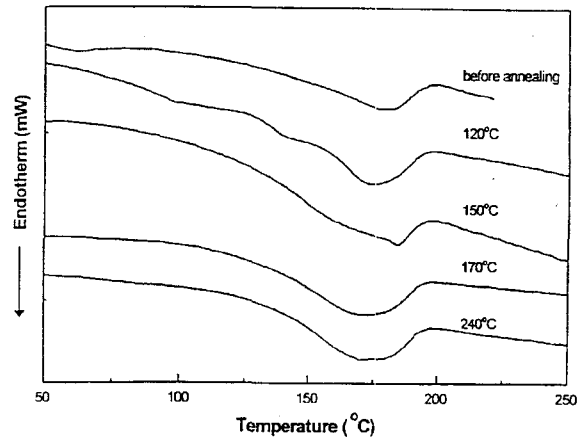


**Figure 4.** Electroluminescence spectrum of the ITO/P3HT/Al devices with different polymer layer thickness.

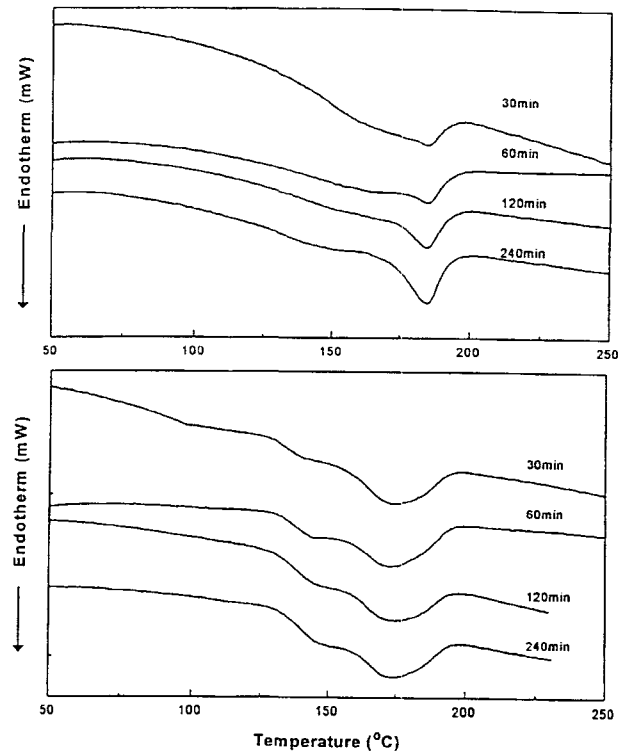


**Figure 5.** EL intensity in ITO/P3HT/Al devices as a function of polymer layer thickness measured under the current density of 0.58 mA/mm<sup>2</sup>.

The EL intensity of devices with different layer thickness is shown in Figure 5. There is a maximum at a thickness of about 130 nm. The thickness of 130 nm is an optimum polymer layer thickness for our ITO/P3HT/Al device. The maximum external quantum yield for the device was 0.002% at 28 V (current density of 4 mA/mm<sup>2</sup>). The maximum luminance was 21 cd/m<sup>2</sup> at this



**Figure 6.** DSC thermogram of P3HT before and after annealing at the indicated temperature for 30 min.



**Figure 7.** Time effects of annealing on the melting thermogram (See text). Top: annealed P3HT at 150°C, Bottom: annealed P3HT at 120°C.

condition.

**Effect of annealing or crystallinity**

Figure 6 shows DSC thermograms of P3HT before and after annealing at 120°C, 150°C, 170°C and 240°C for 30 min. Untreated film shows the melting transition at about 180°C. The melting point of the heat-treated films was observed to be shifted to a higher temperature. The DSC

curves of P3HT film annealed at 120 and 150°C for 30~240 min were shown in Figure 7. The change in the heat of melting was not proportional to the heat-treatment time.

The x-ray diffraction intensity of P3HT film was measured after annealing P3HT film for 30 min. at the predetermined temperature, i.e., 120°C, 150°C, 170°C and 240°C. Then the annealed sample was taken out from the heater and cooled to room temperature. All heat treatments were conducted under nitrogen atmosphere. The heat-treatment led to increase the crystallinity in the amorphous polymer layer as in Figure 8. The diffracted beam intensity of the (110) plane at about  $2\theta = 5.3^\circ$  increases with the annealing temperatures. The thickness of the P3HT film was about 300 nm and the sample was annealed at the indicated temperature for 30 min. under nitrogen atmosphere.

The diffraction peak appearing at a low angle such as  $5.3^\circ$  stands for the distance of 16.36 Å between the

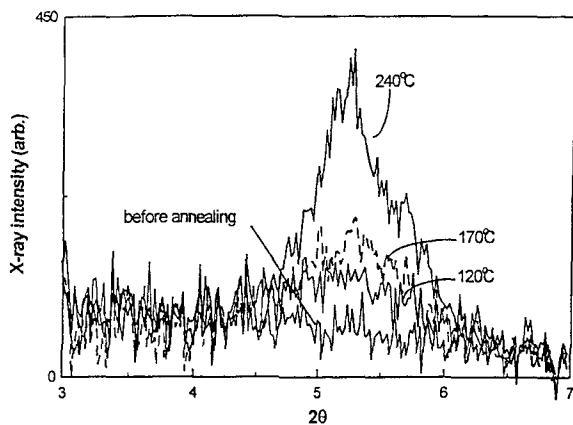


Figure 8. X-ray diffraction intensity profile of the P3HT thin film on the ITO annealed at the indicated temperature for 30 min. under  $N_2$  atmosphere.

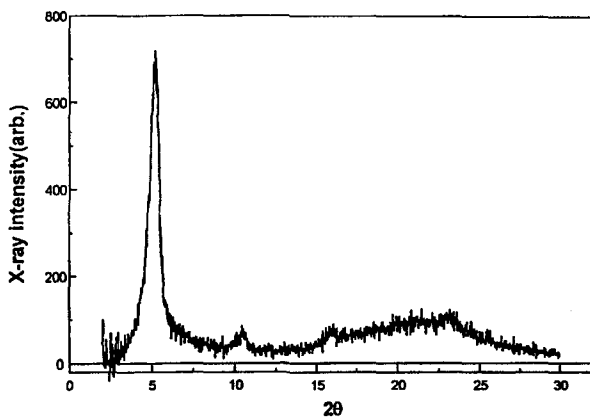


Figure 9. X-ray diffraction peak of (100) plane for the cast P3HT thick film from chloroform solution (See text).

thiophene spines (crystal (100) plane) in the P3HT crystal. The hexyl side chains are more or less disturbed from the thiophene plane, which corresponds to the backbone alternating zigzag conformation plane[16].

The cast thick films (5  $\mu\text{m}$  thick) dried from polymer/chloroform solutions had a semicrystalline structure. The x-ray diffraction pattern for the cast P3HT thick film shows the strong first, second, and third order reflections at  $2\theta$  angles of  $5.4^\circ$ ,  $10.8^\circ$ ,  $16.3^\circ$ , respectively in Figure 9. This corresponds to the (100) d-spacing of 16.36 Å. Another diffraction peak centered at  $2\theta = 23.5^\circ$  for P3HT corresponds to a spacing of 3.79 Å. This spacing is known as side-chain-length-independent and could be attributed to the stacking distance of successive thiophene rings between two polymer chains along crystal b axes[9,10]. The diffraction peaks for the cast P3HT thick film was summarized in Table 3.

The unusual high intensity of the (020) diffraction peak stands for the parallel orientation of the thiophene planes with the substrate plane. The intensity of (100) plane diffraction peak around at  $2\theta$  of  $5.3^\circ$  seems to be proportional to the degree of crystallinity of the polymer layer.

After Al was vacuum deposited, the current density-applied voltage relation was measured with a DC source and an ampere meter. The current density increases rapidly at a certain applied voltage, which stands for the rectification characteristic of the annealed P3HT devices. To determine the effect of the annealing on the device

Table 3. X-ray diffraction data for the cast P3HT thick film from chloroform solution

(hkl) plane	2 theta (degree)	Spacing d(Å)
100	5.3	16.3
200	10.8	8.2
300	16.3	5.4
020	23.5	3.8

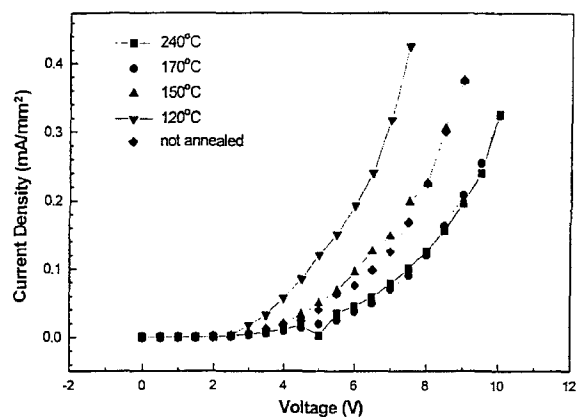
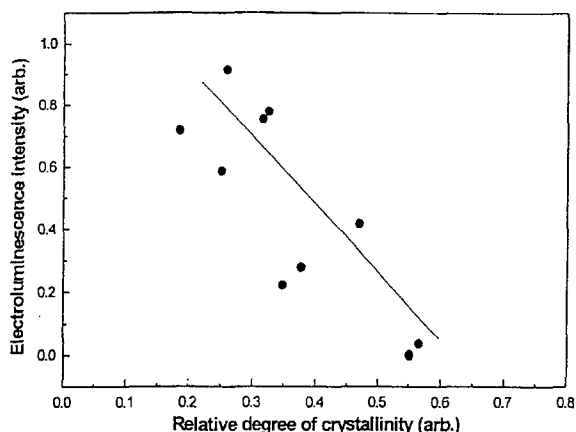


Figure 10. Current density as a function of the applied voltage for the ITO/annealed P3HT/Al devices (See text).

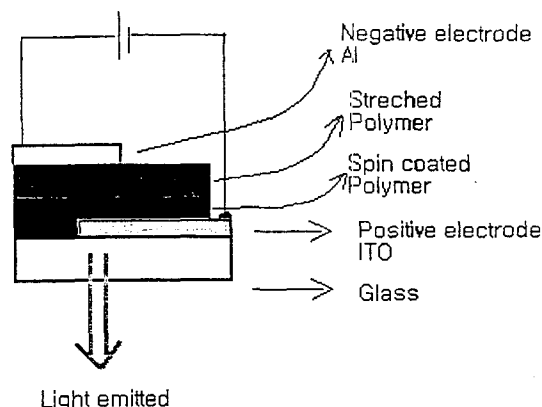


**Figure 11.** Effect of relative crystallinity on the EL intensity. The relative crystallinity values are determined from integrating the (100) plane peak area in the x-ray diffractogram.

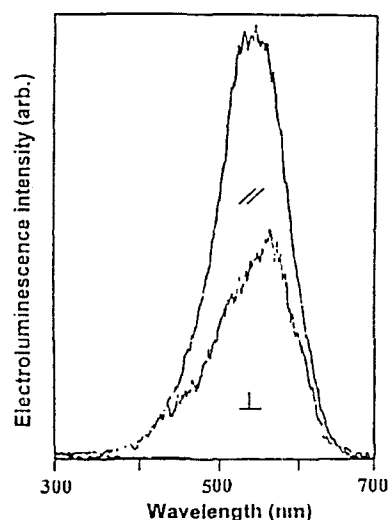
performance, electroluminescence spectrum of the ITO/annealed P3HT/Al device was measured at a constant current density of  $0.58 \text{ mA/mm}^2$  (Figure 10). We assumed that the area under the (100) diffraction peak reflects the relative degree of crystallinity in the polymer layer. The effect of thermal annealing, equivalent to the relative crystallinity on the emitting light intensity is shown in Figure 11. The EL intensity decreases with the increase of crystallinity. This phenomenon probably comes from the lower carrier mobility in the crystalline regions than in the amorphous region.

#### Polarized electroluminescence from an oriented polymer emitting layer

To make a polymer LED emitting a polarized EL along the chain-oriented direction, the uniaxially stretched polythiophene thin film was prepared. Usually the polymer film for the electroluminescent layer was about 100 nm thick, drawing of those thin-film is very difficult. To accomplish the mechanical drawing of the thin P3HT films, we followed the method of Dyreklev *et al.*[13] For the oriented polymer LEDs, P3HT and P3DT solution in chloroform were prepared. From the solution, the polymer was spin coated ( $\sim 50 \text{ nm}$ ) onto a polyethylene(PE) film (household plastic foil with thickness of  $30 \mu\text{m}$ ). The PE/P3HT or PE/P3DT bilayer film was then oriented by mechanical stretching to about twice the initial length. Further elongation caused cracks in the P3HT or P3DT layer. On top of the ITO-glass,  $\sim 50 \text{ nm}$  of P3HT film was spin-coated to enhance the adhesion of the oriented layer onto the ITO surface. The oriented P3HT film was then transferred onto the unoriented P3HT layer by pressing them at  $60^\circ\text{C}$ . The PE foil easily peeled off and the oriented P3HT layer successfully transferred onto the spin-cast P3HT layer. Al was then vacuum deposited onto the oriented P3HT surface. The final structure of the device for



**Figure 12.** Schematic cross-section of the polarized EL device prepared with an oriented polymer layer.



**Figure 13.** Uncorrected EL spectrum for the polarized EL device with the polarizer direction parallel (||) and perpendicular ( $\perp$ ) to the stretching direction. The intensity ratio for the parallel and perpendicular direction was found to be 1.40 by correcting the effect of polarization of the grating system.

the polarized EL is shown in Figure 12.

The EL spectra of the device were measured by rotating the polarizer direction to the parallel or perpendicular direction of the stretch. In Figure 13, the EL spectrum of the oriented P3HT device parallel and perpendicular to the stretching direction is shown. The apparent intensity ratio was about 2.1~2.4. But the light detection system, which uses the grating, has intrinsic detection anisotropy. We measured the intensity ratios for the homogeneous light emitting diodes and found that the  $g$  factor was 1.72. Thus the emission anisotropy ratio for the Al/ oriented poly(hexyl thiophene)/ITO diodes were about 1.40. The intensity ratio for the oriented P3DT device was similar to the oriented P3HT device.

### Conclusions

P3HT and P3DT were polymerized by oxidative coupling with ferric chloride. The resulting polymers had the 2,5-coupled structure and higher contents of head-to-tail (HT) coupling. It was possible to make device showing stable and brighter emission by using the dedoped polymer as a light-emitting material. The P3HT LED emitted red light and it can be observable in the ordinary indoor light.

The maximum EL intensity was obtained when the thickness of polymer layer was about 130 nm in ITO/P3HT/Al device. The maximum external quantum yield was 0.002% and the maximum luminance 21 cd/m<sup>2</sup>.

The EL intensity decreased with the increase of crystallinity in polymer layer. The EL intensity decrease for the annealed P3HT device seems to be due to the low carrier mobility in the crystalline region.

By using the oriented PAT layer as an EL layer in the ITO/polymer/Al light-emitting devices, the polarized EL light emission was observed. The EL intensity ratio of parallel to perpendicular direction to the stretch direction for P3HT was about 1.40.

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