

# Synthesis and Light-Emitting Properties of Cyanofluorenylvinylene and Cyanophenylenevinylene-Based Alternating Copolymers by Heck Reaction

*Sung-Ho Jin, Mi-Yeon Kim, and Seung-Yun Kang*

Department of Chemistry Education Pusan National University, Busan 609-735, Korea

*Yeong-Soon Gal*

Polymer Chemistry Lab, College of General Education, Kyungil University, Hayang 712-701, Korea

Phone : +82-51-510-2727, e-mail: shjin@pusan.ac.kr

## Abstract

A new series of statistical alternating EL copolymer, poly[bis{2-(4-phenylenevinylene)-2-cyanoethyl}-9,9-dihexyl-9H-fluorene-2,7-yl-alt-1,4-phenylene vinylene] (polymer-1) was synthesized by the modified Heck coupling reaction, and their EL characteristics were also investigated. Double layer polymer light-emitting display (PLED) with the configuration of ITO/PEDOT/polymer/Al devices show maximum brightness and luminous efficiency up to 3000 cd/m<sup>2</sup> at 30 V and 0.07 lm/W at 21 V, respectively.

## 1. Introduction

Since the discovery of polymer light-emitting display (PLED) based on poly(*p*-phenylenevinylene) (PPV) [1], many research group have been explored electroluminescence (EL) polymers including PPV [2], poly(9,9-dialkylfluorene) (PF) [3] and their derivatives, which are the most promising materials for LED applications. Most of red-emitting polymers are composed with poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), polythiophenes (PThs), 4-(dicyanomethylene)-2-methyl-6-[*p*-(dimethylamino) styryl]-4H-pyran (DCM), and their derivatives or newly synthesized chromophores with electron withdrawing substituents into the main chain or side chain along the polymer backbone. The copolymerization method has been widely used in the preparation of EL polymers to achieve easy tuning the emission colors by intramolecular energy transfer and physical properties. A number of PF derivatives are suitable wide-band gap materials because of facile substitution at carbon 9 position in fluorene unit to improve the processability and their high photoluminescence (PL) and EL efficiency. They also offer the possibility of

varying the emission colors via energy transfer process. A variety of fluorene-based alternating and random copolymers were synthesized by using fluorenes and other aromatic compounds, which covered fully red, green, and blue emission color in visible spectrum.

In our continuous studies on PLEDs, we have reported a novel EL polymers such as alkylsilylphenyl and alkyloxyphenoxy substituted PPVs, blending systems with oxadiazole containing electron transfer polymer, and alternating copolymers composed with PPV segments and aromatic amine blocks to improve the device performance [4-7]. In this article, we report the synthesis of a novel chromophore containing bis(phenylenylvinylene) fluorene moiety with electron withdrawing cyano substituent into the vinylene unit and a statistical light-emitting alternating copolymers series composed with bis(cyanophenylenevinylene) fluorenyl and phenylenevinylene or biphenylene vinylene repeating units along the polymer backbone and the characteristics of their electro-optical properties.

## 2. Experimental

**2,7-Bis(bromomethyl)-9,9-dihexylfluorene (1).** 9,9-Dihexylfluorene was synthesized according to the procedure from the literature. A three-necked flask containing 10.5 g (31.4 mmol) of 9,9-dihexylfluorene, 9.43 g (314 mmol) of paraformaldehyde, 9.7 g (94.2 mmol) of sodium bromide, and acetic acid (50 mL) was placed in an ice bath. To this flask, 10 mL of 50% sulfuric acid solution in acetic acid was added carefully, and the mixture was stirred for 24 h at 60-70 °C. The resulting mixture was extracted with methylene chloride and the organic portion was concentrated. Finally, the viscous liquid was obtained by column chromatography with the yield of 37 %

(6.05 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm) : 7.61 (d, 2H, ArH), 7.34 (d, 4H, ArH), 4.58 (s, 4H,  $-\text{CH}_2\text{Br}$ ), 1.92 (m, 4H;  $\alpha$ - $\text{CH}_2$  of hexyl group at 9-position of fluorene), 1.06 (12H;  $\beta$ - $\delta$ - $\text{CH}_2$ ), 0.76-0.75 (10H,  $\text{CH}_2$  and  $\text{CH}_3$ ).

**[7-(Acetyloxymethyl)-9,9-dihexylfluorene-2-yl]methyl Acetate (2)**. A mixture of 6.0 g (11.5 mmol) of 2,7-Bis(bromomethyl)-9,9-dihexylfluorene, anhydrous sodium acetate (4.73 g, 57.6 mmol), acetic anhydride (3.29 mL, 34.6 mmol), and acetic acid (50 mL) was stirred at 90 °C for 18 h. The reaction mixture was cooled and extracted with methylene chloride. After evaporation of the solvent under reduced pressure, the yellow liquid was obtained (4.5 g, 82 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm) : 7.65 (d, 2H, ArH), 7.34 (d, 4H, ArH), 5.15 (s, 4H,  $-\text{CH}_2\text{O}-$ ), 2.12 (s, 6H,  $-\text{OCOCH}_3$ ), 1.93 (m, 4H;  $\alpha$ - $\text{CH}_2$ - of hexyl group at 9-position of fluorene), 1.02 (12H;  $\beta$ - $\delta$ - $\text{CH}_2$ -), 0.76-0.70 (10H,  $\varepsilon$ - $\text{CH}_2$ - and  $\text{CH}_3$ ).

**[9,9-Dihexyl-7-(hydroxymethyl)fluorene-2-yl]methanol (3)**. A mixture of compound 2 (4.5 g, 9.5 mmol) and sodium hydroxide (1.9 g, 47 mmol) in 70 mL of ethanol was stirred at 40 °C for 1 h. After cooling, the mixture was poured into the dilute HCl solution by dropwise until the pH of the suspension was changed to 7. This solution was extracted with methylene chloride and the organic portion was concentrated. Finally, the viscous liquid was obtained by column chromatography with the yield of 65 % (2.5 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm) : 7.64 (d, 2H, ArH), 7.3 (d, 4H, ArH), 4.8 (s, 4H,  $-\text{CH}_2\text{OH}$ ), 1.93 (m, 4H;  $\alpha$ - $\text{CH}_2$ - of hexyl group at 9-position of fluorene), 1.10 (12H;  $\beta$ - $\delta$ - $\text{CH}_2$ -), 0.80-0.70 (10H,  $\varepsilon$ - $\text{CH}_2$ - and  $\text{CH}_3$ ).

**9,9-Dihexylfluorene-2,7-dicarbaldehyde (4)**. A solution of diol compound 3 (2.45 g, 6.2 mmol) in 100 mL of anhydrous methylene chloride was stirred and cooled with an ice bath while pyridinium chlorochromate (4.02 g, 18.6 mmol) was added in a portion wise manner over a period of 20 min. The oxidation reaction was monitored by TLC and stirred for 2 h at room temperature. After a dark brown suspension had formed, it was diluted with 150 mL of diethyl ether and stirred for further 30 min. The mixture was then filtered through silica gel to remove inorganic salt. The solution was washed with 100 mL of 1N HCl and then with water and dried over  $\text{MgSO}_4$ . The ether solution was filtered and concentrated and the remaining yellow viscous liquid was purified by column chromatography (eluent; *n*-hexane:ethyl acetate=10:1). The pure yellow liquid

was obtained with the yield of 63% (1.53g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 10.20 (s, 2H,  $-\text{CHO}$ ), 7.8 (s, 6H, ArH), 2.05 (m, 4H;  $\alpha$ - $\text{CH}_2$ - of hexyl group at 9-position of fluorene), 1.05 (12H;  $\beta$ - $\delta$ - $\text{CH}_2$ -), 0.75-0.60 (10H,  $\varepsilon$ - $\text{CH}_2$ - and  $\text{CH}_3$ ).

**2,7-Bis[2-(4-bromophenyl)-2-cyanoethenyl]-9,9-dihexyl-9H-fluorene (5)**. A mixture of compound 4 (3.0 g, 5.12 mmol) and 4-bromophenylacetonitrile (2.0 g, 10.24 mmol) was dissolved in 50 mL of dry ethanol under nitrogen atmosphere in 250 mL three-necked round-bottom flask. A mixture of sodium hydroxide (51.2 mg, 1.28 mmol) and 30 mL of dry ethanol was added slowly and then the crude product was precipitated in the reaction mixture. The reaction mixture was stirred for 10 h at room temperature and the precipitate was filtered and washed with water. A yellow powder was obtained.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 7.9-7.4 (16H, vinylic proton and ArH), 2.05 (m, 4H;  $\alpha$ - $\text{CH}_2$ - of hexyl group at 9-position of fluorene), 1.10 (12H;  $\beta$ - $\delta$ - $\text{CH}_2$ -), 0.80-0.70 (10H,  $\varepsilon$ - $\text{CH}_2$ - and  $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{43}\text{H}_{42}\text{Br}_2\text{N}_2$ : C 69.17, H 5.67, N, 3.75. Found: C 69.84, H 6.48, N 3.56.

**Poly[bis{2-(4-phenylenevinylene)-2-cyanoethenyl}-9,9-dihexyl-9H-fluorene-2,7-yl-*alt*-1,4-phenylene vinylene] (polymer-I)**. The polymer was prepared by Heck coupling reaction between 2,7-bis[2-(4-bromophenyl)-2-cyanoethenyl]-9,9-dihexyl-9H-fluorene (5) and 1,4-divinylbenzene. A mixture of compound 5 (1.0 g, 1.34 mmol), 1,4-divinylbenzene (0.172 mg, 1.34 mmol),  $\text{Pd}(\text{OAc})_2$  (1.5 mg, 0.068 mmol), tri-*o*-tolylphosphine (0.164 mg, 0.54 mmol), and tributylamine (2 mL) in 8 mL of DMF was stirred at 80 °C in 50 mL Schlenk flask. To this flask, 4 mL of NMP was added and the mixture was stirred for 3 days at 120 °C. The hot reaction mixture was poured into 500 mL of hexane to precipitate the polymer. The collected polymer was redissolved in 100 mL of chloroform and then washed with 400 mL of deionized water. The water layer was decanted. The catalyst particles in the polymer solution were removed by filtration followed by evaporation of the solvent using a rotary evaporator. The polymer was dissolved in a small amount of chloroform and then poured into hexane. The polymer was collected by filtration and dried under vacuum. (0.5 g, 52 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 8.0-7.3 (br, 20H, vinylic proton and ArH), 7.2-7.0 (br, 4H, vinylic proton), 2.1-1.8 (br, 4H;  $\alpha$ - $\text{CH}_2$  of hexyl group at 9-position of fluorene), 1.2-0.9 (br, 12H;  $\beta$ - $\delta$ - $\text{CH}_2$ -), 0.8-0.6 (10H,  $\varepsilon$ - $\text{CH}_2$ - and

CH<sub>3</sub>). Anal. Calcd for C<sub>53</sub>H<sub>50</sub>N<sub>2</sub>: C 88.82, H 6.98, N 3.91; Found: C 83.75, H 7.33, N 4.35.

### 3. Results and Discussion

The synthetic route of newly designed monomer, 2,7-bis[2-(4-bromophenyl)-2-cyanoethenyl]-9,9-dihexyl-9H-fluorene and its corresponding alternating copolymer with divinylbenzene are outlined in Scheme 1. The modified Heck polymerization condition, DMF and NMP as cosolvent and tributylamine instead of triethylamine, was used to increase the molecular weight of the EL polymer compared to DMF solvent in conventional Heck coupling reaction. The resulting EL polymer was purified by successive Soxhlet extraction with different solvents including methanol, hexane, and finally dissolved in CHCl<sub>3</sub> and reprecipitation into methanol. Molecular structures and purity of the monomer and the corresponding EL polymer was identified by <sup>1</sup>H NMR spectroscopy and elemental analysis.

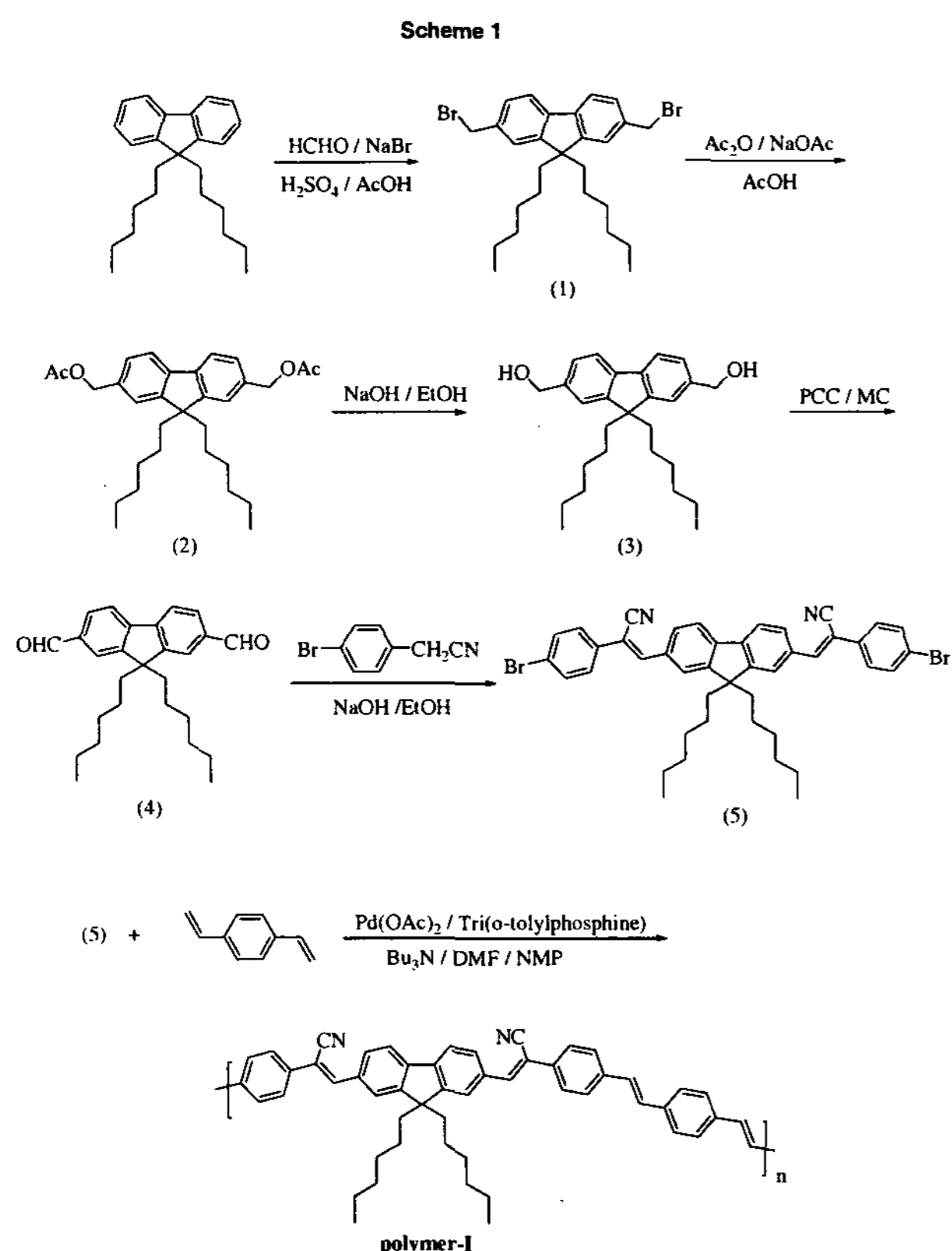


Figure 1 displays the absorption and emission spectra of polymer-I in thin film state. The maximum absorption peak of polymer-I has a sharp peak at 419 nm with an onset absorption peak at 514 nm. From

onset of the absorption spectrum, the band gap of polymer-I is 2.41 eV

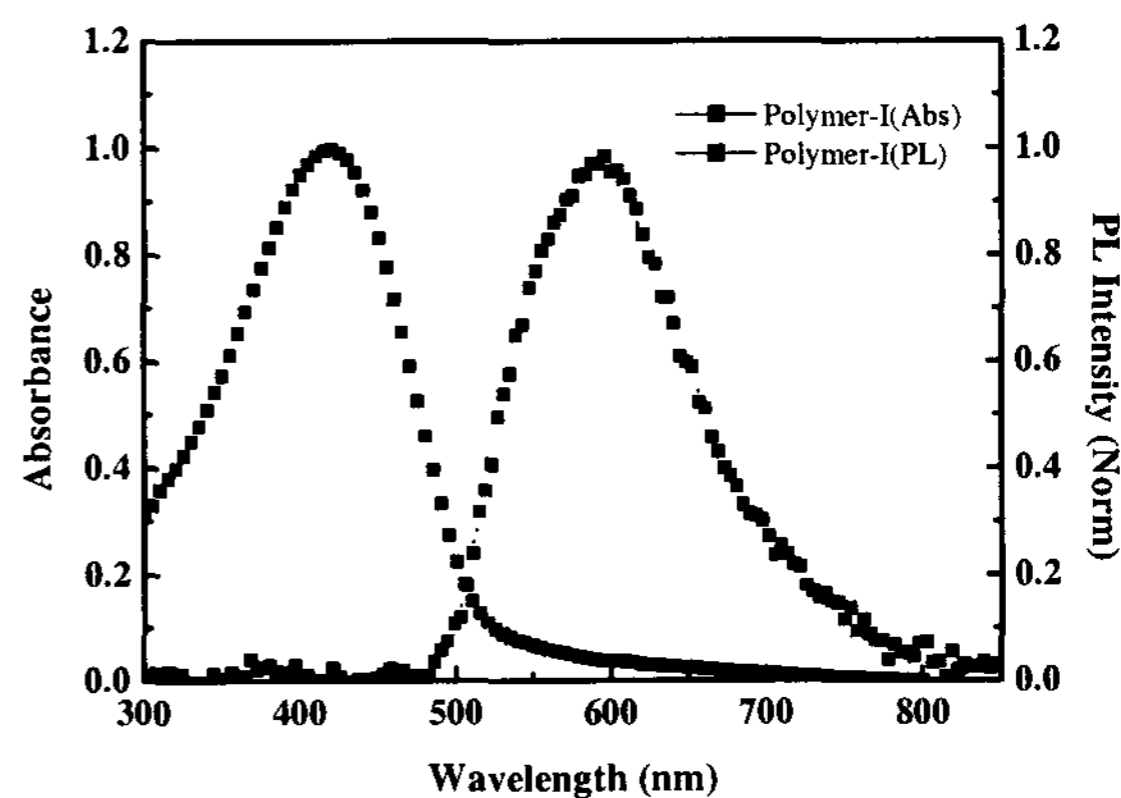


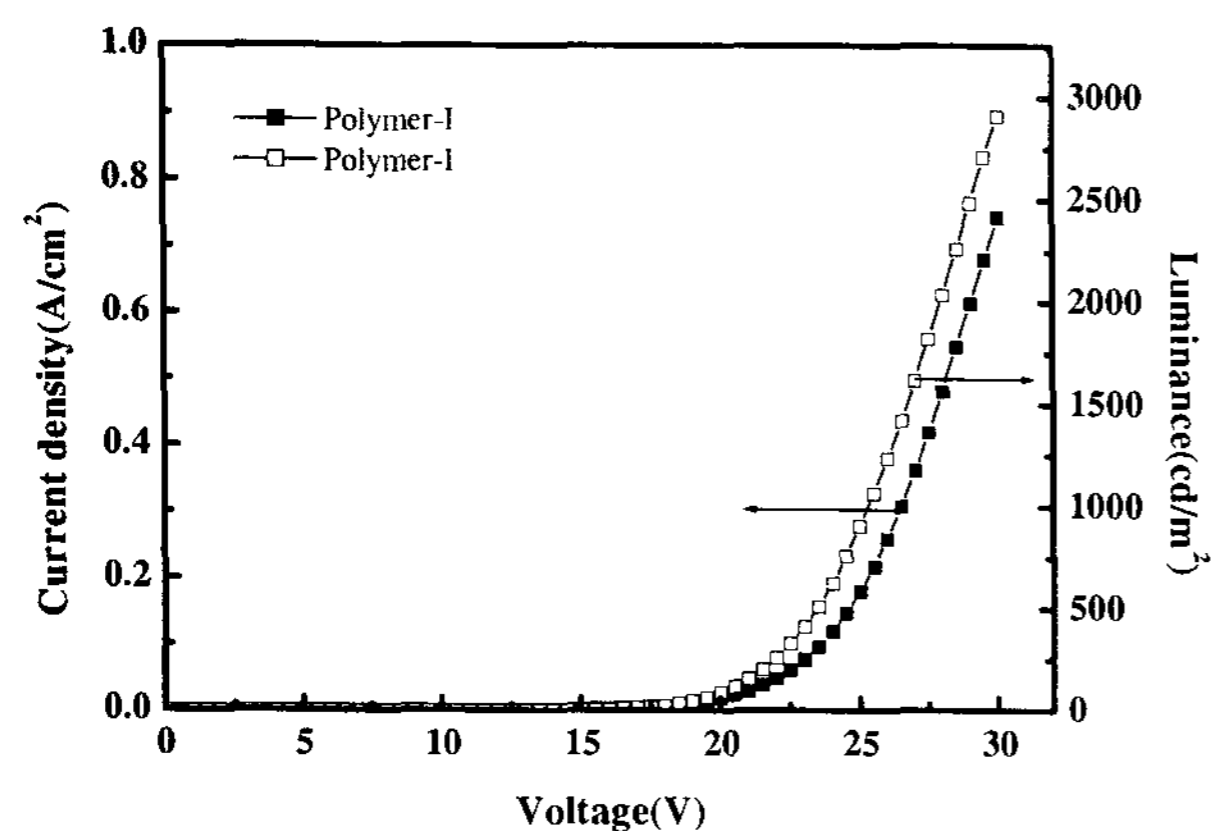
Figure 1. UV-visible absorption and PL spectra of polymer-I in solid state.

The measurement of external PL quantum efficiency ( $\Phi$ ) is an important factor in designing the molecular structure of the emitting materials and determining the efficiency of the PLED. The  $\Phi$  values of polymer-I and MEH-PPV for comparison were measured by using an integrating sphere method. Spin-coated thin films of the polymer-I and MEH-PPV gave  $\Phi$  values of 5.7 and 10 %, respectively.

To get information on the charge injection and device performance, it is very important to calculate the energy band diagram from electrochemical measurements using cyclic voltammetry (CV) for HOMO binding energy as ferrocene standard and band gap from optical absorption spectrum. From CV measurement, the HOMO energy level of polymer-I was 5.59 eV. The LUMO level was approximated by subtracting the optical band gap from the HOMO binding energy. The barrier heights were found to be 0.89 eV at the interface of ITO/HOMO state for hole injection and 1.12 eV at the interface of Al/LUMO state for electron injection of the polymer-I. Based on this energy level, it is expected that the major carrier is holes than electrons.

To evaluate the device performance, we fabricated the double layer PLED with the configuration of ITO/PEDOT/polymer/Al devices. Figure 2 shows the current density-voltage-luminescence (*J-V-L*) characteristics of ITO/PEDOT/polymer/Al devices. The turn-on voltage of polymer-I is 15 V for current and luminance, respectively. The emission color of

polymer-I at the CIE coordinates of  $x=0.48$ ,  $y=0.48$  exhibits yellow.



**Figure 2.** Current density-voltage-luminescence-characteristics of ITO/PEDOT/polymer-I/Al devices.

The maximum brightness of polymer-I was about  $3000 \text{ cd/m}^2$  with a current density of  $0.75 \text{ A/cm}^2$  at 30 V. Further optimization of EL device such as introduction of electron-transport layer (ETL) or

lower work function metal, as a cathode electrode will show the better EL performance.

#### 4. References

- [1] Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature*, 347, 539 (1990).
- [2] Johansson, M. D.; Wang, X.; Johansson, T.; Inganäs, O.; Yu, G.; Srdanov, G.; Andersson, M. R. *Macromolecules*, 35, 4997 (2002).
- [3] Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. S. *Adv. Mater.* 12, 1737 (2000).
- [4] Jin, S. H.; Jang, M. S.; Suh, H. S.; Cho, H. N.; Lee, J. H.; Gal, Y. S. *Chem. Mater.* 14, 643 (2002).
- [5] Jin, S. H.; Park, H. J.; Kim, J. Y.; Lee, K.; Lee, S. P.; Moon, D. K.; Lee, H. J.; Gal, Y. S. *Macromolecules* 35, 7532 (2002).
- [6] Jin, S. H.; Jung, J. E.; Park, D. K.; Jeon, B. C.; Kwon, S. K.; Kim, Y. H.; Moon, D. K.; Gal, Y. S. *Eur. Polym. J.* 37, 921 (2001).
- [7] Lee, J. H.; Yu, H. S.; Kim, W.; Gal, Y. S.; Park, J. H.; Jin, S. H. *J. Polym. Sci., Part A: Polym. Chem.* 38, 4185 (2000).