

Synthesis and Characterization of Poly(aryl ether) Containing Diphenylanthracene and Benzoxazolyl-phenylene as Emitting Chromophore

Soon-Ki Kwon, Yun-Hi Kim, and Sung Chul Shin^{†,*}

Dept. of Polymer Science & Engineering and Research Institute of Industrial Technology

[†]Dept. of Chemistry, Gyeongsang National University, Chinju 660-701, Korea

Received July 25, 2001

Keywords : Diphenylanthracene, Benzoxazole, Light-emitting diode, Electron injection, Poly(aryl ether).

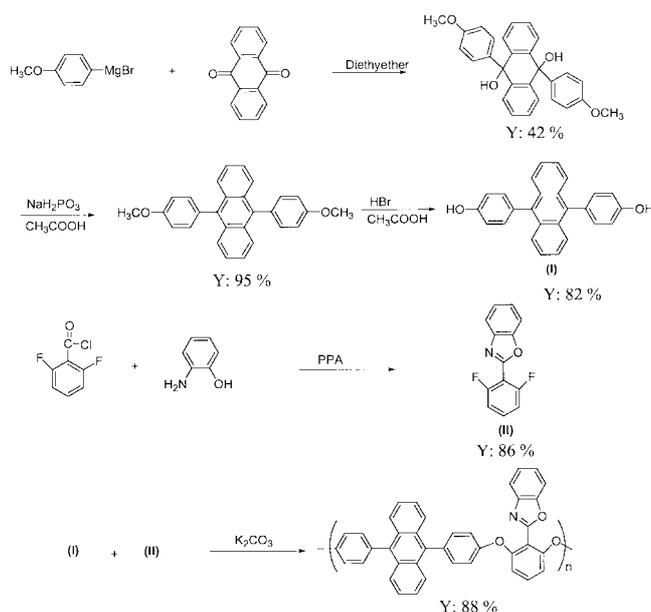
Since the first report of polymer light-emitting diodes based on poly(*p*-phenylenevinylene) (PPV) by the Cambridge group,¹ a great deal of effort have been devoted to the synthesis of light emitting polymers because of several advantages over small organic molecules, such as excellent mechanical properties and simple fabrication method of spin casting etc.^{2,3} Many conjugated polymers including PPV, poly(2-methoxy-5,2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV)⁴ poly(*p*-phenylene) derivatives (PPPs),⁵ polyfluorene derivatives (PFs),⁶ and polythiophene derivatives (PThs)⁷ have been synthesized for as emissive and/or charge-transporting materials in polymer light-emitting diodes (PLED). However some important issues such as balancing of charge injection, device stability, and color tunability remain to be addressed.

To improve the device efficiency of PLEDs, it is necessary to balance the rate of injection of electrons and holes from opposite electrodes into the device. For the most of conjugated polymers including PPV derivatives, the barrier of electron injection is much higher than that of hole injection. Therefore, many substituents including cyano, oxadiazole, triazole, pyridine, quinoxaline, thiadiazole etc. which have a high electron affinity have been introduced.^{8,9}

It is known that diphenylanthracene has PL quantum yield of unity, good electrochemical property and orthogonal structure between anthracene and substituted phenyl ring.^{10,11,12} Therefore, LED's containing diphenylanthracene as emitting unit are expected to have higher EL quantum yield, long lifetime and blue color.

In this study, we designed new blue emitting polymer, poly(aryl ether), which is composed efficient diphenyl anthracene moiety and benzoxazolyl phenylene moiety with high electron affinity for charge balancing. The linkages in the backbone improve both the solubility and the processability. Further, this oxygen linkage limits the conjugation length. Confinement of the effective conjugation has proved to be an efficient means for blue shifting the spectrum, because the conjugated emitters can allow charge carriers to form, but not to diffuse along the main chain. This electronic localization results in a large band gap, which decreases with conjugation length.

A new poly(diphenylanthracene-benzoxazolyl phenylene), poly(DPB), was prepared by nucleophilic displacement of 9,10-bis(4'-hydroxyphenyl)-2-alkylanthracene and 1-(2-benzoxazolyl)-2',6'-difluorobenzene as shown in Scheme 1.



Scheme 1

Nucleophilic displacement reaction of aryl halide with phenol usually needs catalyst to enhance reactivity and yield. However, aryl halide become more susceptible toward nucleophilic aromatic substitution when it was activated by a substituent that can also accept the negative charge developed through the formation of a stabilized transition state. Benzoxazolyl benzene has the electron withdrawing ability so that it can activate nucleophilic displacement reaction. The number average molecular weight of polymer was controlled by the ratio of the two bifunctional monomer. After polymerization was completed, excess 1-(2'-benzoxazolyl)-2',6'-difluorobenzene was added for end-capping of hydroxy group, because it was known that hydroxy group could quench photoluminescence of polymer.

The elemental analysis result and spectroscopic analysis of polymer agreed with its chemical composition. The solubility of the polymer is very good in common organic solvents such as chloroform, toluene, or tetrahydrofuran. The GPC measurement of the obtained polymer with polystyrene as the calibration standard shows the weight average molecular weight (Mw) was 16000 with the polydispersity index of 1.3. Thermal transition property of the polymer was investi-

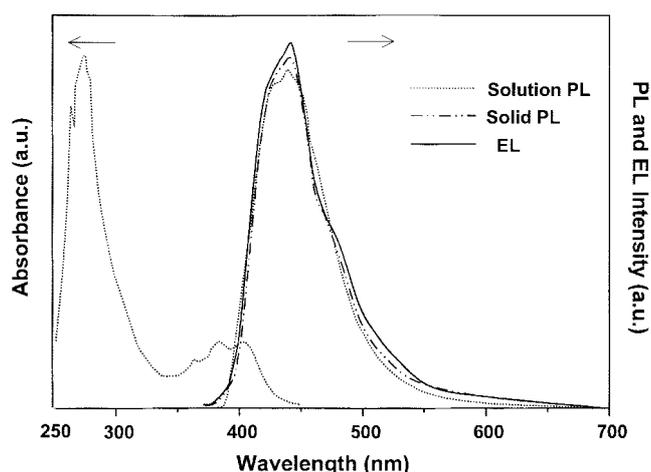


Figure 1. UV-absorption (---) and photoluminescence spectra of poly(DPB) in chloroform solution (---), and the solid photoluminescence spectrum (- · - ·) and electroluminescence spectrum (—) of poly(DPB).

gated using a DSC. The polymer exhibit glass transition temperature (T_g) at 129 °C. The decomposition temperature in nitrogen was estimated by a TGA thermogram. The polymer has good thermal stability up to 400 °C. The excellent thermal properties promise that the polymer could endure the high temperature in the process of fabrication and operation.

The UV-vis absorption spectra of the obtained polymer in CHCl_3 solution has maxima at 270, 332, 378 and 399 nm, which are characteristic diphenylanthracene peaks (Figure 1). Upon UV excitation, solutions of the polymer exhibit the very intense fluorescence with a maxima at 430 and 440 nm (Figure 1). The fact that the emission band is much narrower than the absorption band and shows well resolved vibronic bands is consistent with the emission from localized excited states, most likely after a migration of the excitons along the polymer main chain to segments that represent low energy states. The photoluminescence quantum yield of the polymer in chloroform solution was measured to be around $\Phi = 0.72 \pm 10\%$ upon excitation at 365 nm.^{10,13}

Homogeneous and pinhole-free thin film could be obtained by spin-casting from CHCl_3 solution. The solid PL spectrum is almost same PL spectrum of the solution (Figure 1). The polymer film with 130-150 nm thickness was prepared by spin-casting on a glass substrate covered with on ITO conducting layer (anode). The aluminum electrode (cathode) was then evaporated on to it *in vacuo*. The electroluminescence from the ITO/Poly(DPB)/Al device shows the maximum at 440 nm (Figure 1). The electroluminescence spectrum is similar to the PL spectrum of poly(DPB). It indicates that the same excited states are involved in the two processes. Figure 2 represents typical current-voltage and luminescence-voltage measurements in a device. Current and light arise at almost the same voltage, which increases with the film thickness. The polymer has turn-on voltage at 20 V in a 130 nm thick film. The light emitted from the device

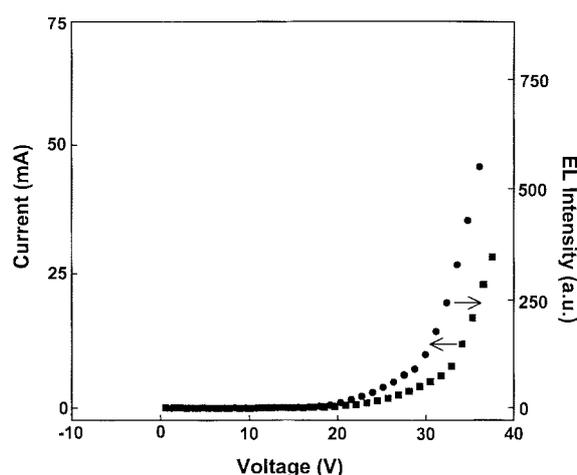


Figure 2. Light-voltage and current-voltage plots of ITO/poly(DPB)/Al device.

appears blue in color and is clearly visible in daylight.

Now we are pursuing the study of the devices with present polymer and hole transporting polymer by using Ca electrode, which we expect to be more efficient devices with lower turn-on voltage.

Acknowledgment. This study was financially supported by the Brain Korea 21 program of the Ministry of Education and Korea Research Foundation Grant (KRF-2000-005-E00005).

References

- Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
- Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem. Int. Ed.* **1998**, *37*, 402.
- Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121.
- (a) Braun, D.; Heeger, A. *J. Appl. Phys. Lett.* **1991**, *58*(10), 1982. (b) Spreitzer, H. *et al. Adv. Mater.* **1998**, *10*, 1340.
- (a) Fukuda, M.; Sawada, K.; Yoshino, K. *J. Polym. Sci. Polym. Chem.* **1993**, *31*, 2465. (b) Ohmori, Y.; Uchida, M.; Morishima, C.; Fujii, A.; Yoshino, K. *Jpn. J. Appl. Phys.* **1993**, *32*, 1663. (c) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1991**, *30*, L1941.
- Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628.
- Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. *J. Science* **1995**, *267*, 1969.
- Gill, R. E.; Malliaras, G. G.; Wildeman, J.; Hadziioannou, G. *Adv. Mater.* **1994**, *6*(2), 132.
- Shin, D. C.; Ahn, J. H.; Kim, Y. H.; Kwon, S. K. *J. Polym. Sci. Polym. Chem.* **2000**, *38*, 3086.
- Kim, Y. H.; Kwon, S. K.; You, D. S.; Rubner, M. F.; Wrigton, M. *Chem. Mater.* **1997**, *9*, 2699.
- Kim, Y. H.; Park, K. M.; Kwon, S. K. *Bull. Korean Chem. Soc.* **2001**, *22*, 975.
- Kim, Y. H.; Shin, D. C.; Kim, S. H.; Ko, C. H.; Yu, H. S.; Chae, Y. S.; Kwon, S. K. *Adv. Mater.* **2001**, *13*, 1690.
- Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.