

Electroluminescent Properties of Poly(10-octylphenothiazine-co-2',3',6',7'-tertrakis-octyloxy-9-spirobifluorene) of as an Emitting Material

Ji-Soung Kang and Jong-Wook Park*

Dept. of Chemistry / Display Research Center, The Catholic University of Korea,
Puchon, Kyonggi, Korea
Phone:+82-(0)2-2164-4821 ; E-mail: hahapark@catholic.ac.kr

Ji-Hoon Lee

Dept. of Polymer Engineering / Chung-Ju National University
Chung-Ju, Chungbuk, Korea

Kyung-Soo Kim, Cheol-Kyu Choi, Sang-Do Lee, Sang-Wook Kim
OLED Team/ Electro-Materials BG, Doosan Corporation, Yongin, 449-795, Korea

Abstract

We report synthesis and properties of new phenothiazyl polymer derivatives, Poly(10-octyl-10H-phenothiazine-3,7-diyl)(POP), Poly(2',3',6',7'-tertrakis-octyloxy-9-spirobifluorene-2,7-diyl)(PTOSF), and their random copolymers, Poly(10-octylphenothiazine-co-2',3',6',7'-tertrakis-octyloxy-9-spirobifluorene) (POTOSF).

PL emission of POP, PTOSF and POTOSF copolymer were found to be 480, 434 and 484nm, respectively. EL emission peak of double-layer EL device of POTOSF was at 494nm (bluish green).

1. Introduction

Polymer light-emitting diodes (PLEDs) have attracted much attention from academia and industry because of their applications in large area flat-panel displays[1,2]. In particular, interest in PLEDs fabricated from conjugated Polymers[3,4] has augmented because such PLEDs have properties that are well-suited to flat panel displays: good processability, low operating voltages, fast response times, and facile color tunability over the full visible range.

On the other hand, a number of issues, such as low electroluminescent(EL) efficiencies and luminescent stability, which need to be resolved, currently spoil their commercial applications, although many light-emitting polymers have been

synthesized and investigated, and the performance of PLEDs has been improved greatly in recent years. Therefore, investigation for new π -conjugated polymers with higher luminescent performance remains one of the major challenges in the area. Among the many kinds of conjugated polymers, PPV and its derivatives are the most extensively investigated polymers employed as emitting layers in PLEDs[5,6]. Recently, dendrimer-type Ir complexes, having large molecular weight, have been investigated so that the thin film of these materials can be fabricated by the solution process[7]. Phenothiazine is a well-known heterocyclic compound with electron-rich sulfur and nitrogen heteroatoms. Molecules and polymers[10,11] containing phenothiazine moieties have recently attracted much research interest because of their unique electro-optical properties and their resulting potential in diverse applications such as light-emitting diodes[9,11].

It has been suggested that inclusion of phenothiazine into a polyfluorene should improve the hole-transporting properties of the polyfluorene and thus improve the EL device efficiency. recently synthesized an alternating copolymer of phenothiazine and fluorene by the

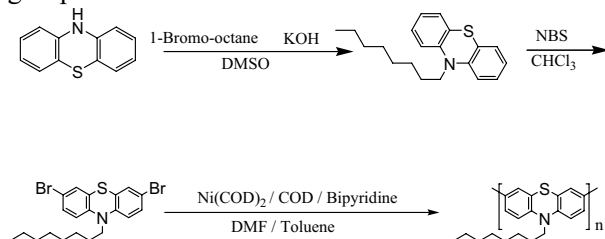
Suzuki coupling reaction and characterized its properties[11].

In this paper, we have synthesized phenothiazine homopolymer and spriobifluorene copolymer. Poly(10-octyl-10H-phenothiazine-3,7-diyl) (POP), Poly(2',3',6',7'-tertrakis-octyloxy-9-spirobifluorene-2,7-diyl)(PTOSF), and their random copolymers, Poly(10-octylphenothiazine-co-2',3',6',7'-tertrakis-octyloxy-9-spirobifluorene) (POTOSF), were synthesized through Yamamoto polymerization. Optical properties of these polymers were characterized by UV-visible and photoluminescence (PL) spectra. Moreover, double-layer EL device was fabricated using POTOSF as emitting materials.

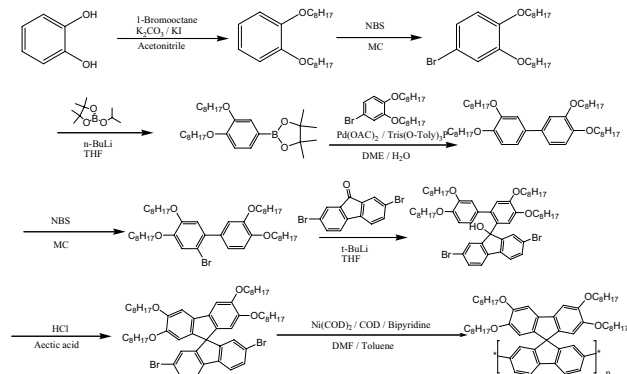
2. Results

Synthesized polymer structures are shown in Scheme I-III. The number average molecular weights (Mn) of POP, PTOSF and POTOSF copolymer were determined by gel-permeation chromatography (GPC) using a polystyrene standard with THF solvent and found to be range from 17,000 to 300,000 with polydispersity indices of 1.6 ~ 6.5. Although molecular weights of synthesized polymers were high, their polydispersity was wide. These results are summarized in table 1.

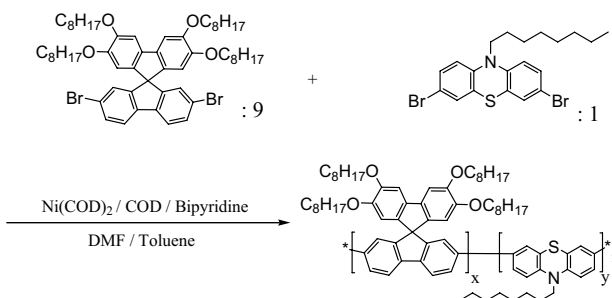
POP homopolymer showed low molecular weight with good polydispersity value. POTOSF copolymer exhibited high molecular weight of 300,000(Mn) and 1,440,000(Mw). The reason why phenothiazine moiety of 10% was introduced into spirobifluorene moiety is that phenothiazine could be working as charge carrier moiety to emitter of spirobifluorene group.



Scheme I Synthetic route of POP.



Scheme II Synthetic route of PTOSF.



Scheme III Synthetic route of POTOSF.

	Feed mole ratio of spirobifluorene unit (%)	Feed mole ratio of phenothiazine unit (%)	Mn	Mw	polydispersity
POP	-	100	17,000	28,000	1.63
PTOSF	100	-	71,000	460,000	6.48
POTOSF	90	10	300,000	1,440,000	4.78

Table 1. Average molecular weight and polydispersity indices of synthesized polymer.

UV-visible absorption spectra of thin films of POP, PTOSF and POTOSF copolymer are depicted in figure 1. Each spectrum was normalized to the peak maximum for more accurate comparison of wavelength. The maximum UV-visible absorption and absorption onset of POP, PTOSF and POTOSF copolymer exhibited at around 370, 391, 403nm and 466 , 434, 436nm, respectively, which are originated from π - π^* transition of conjugated polymer backbone. The optical band gaps of the polymers were determined from the analysis of absorption edge with a plot of (hv) vs. $(ahv)^2$, where a , h , and v are absorbance, Plank's constant, and the frequency of light. The optical band gap of POP, PTOSF and POTOSF copolymer were found to be 2.76, 2.91 and 2.90 eV.

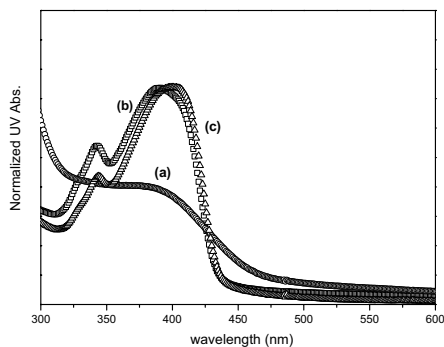


Figure 1. UV-visible spectra of POP(a, circle), PTOSF(b, square), and POTOSF(c, triangle) copolymer films on glass.

Figure 2. shows the PL emission spectra of polymer thin films. Two homopolymer of POP and PTOSF showed its own characteristic PL maximum value as 480nm and 434nm including 454nm shoulder peak. Copolymer POTOSF which contained POP(10%) and PTOSF(90%) exhibited PL maximum value of 484nm, which means that the exciton energy of PTOSF unit in POTOSF might be transferred to POP unit. As shown in scheme III, the feed ratio of POP moiety and PTOSF moiety in synthesis of POTOSF was 9:1 and polymerization yield was always more than 50%. It means that POTOSF contains PTOSF moiety and POP moiety together. Therefore the reason why figure 2(c) of POTOSF is similar with figure 2(a) of POP is that exciton energy in copolymer can be transferred from PTOSF moiety having relatively wide band gap energy to POP moiety.

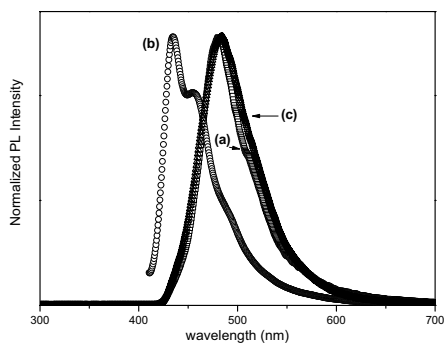


Figure 2. PL spectra of POP(a, square), PTOSF(b, circle), and POTOSF(c, triangle) copolymer films on glass.

The electrochemical characteristics of the polymers were investigated by using cyclic voltammetric analysis. The first oxidation potential was used to determine the HOMO energy level. Ferrocene was used as an internal standard for calibrating the potential. This data accounts that we could get HOMO level. Based on UV-visible data and CV data, all electronic levels of HOMO, LUMO and band gaps are summarized in table 2.

	HOMO	LUMO	Optical band gap
POP	5.26	2.50	2.76
PTOSF	5.63	2.72	2.91
POTOSF	5.64	2.74	2.90

Table 2. Electronic levels of POP, PTOSF and POTOSF copolymer.

Even though POP has smaller band gap than PTOSF and POTOSF, it shows higher LUMO level of 2.5eV. We believe that there is energy barrier to inject electron from cathode compared to PTOSF and POTOSF in device. Also PTOSF and POTOSF showed similar band gap value and HOMO and LUMO level values, but they showed quite different PL spectrum because of energy transfer as shown in figure 2.

Double-layer EL device was fabricated using POTOSF copolymer such as ITO/PEDOT:PSS(50nm)/POTOSF(70nm)/LiF(1nm)/Al(200nm) device. EL spectrum of POTOSF device is shown in figure 3. Emission peak of copolymer POTOSF device exhibited EL maximum value of 494nm, which matched with its PL emission peak of 484nm.

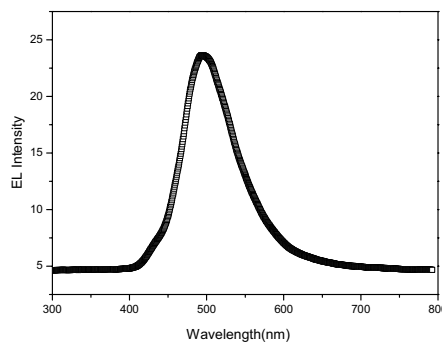


Figure 3. EL spectrum of ITO/PEDOT:PSS(50nm)/POTOSF(70nm)/LiF(1nm)/Al(200nm) device at 20mA/cm².

Further studies of synthetic compounds devices optimization are under way. We will report the EL efficiency and life time data in other paper.

3. Conclusion

Weight average molecular weights (Mw) of PTOSF ranged 1,440,000 with polydispersity index of 4.78. And emission peak of copolymer POTOSF device exhibited EL maximum value of 494nm. These materials could be applied to emitting material in PLED device.

5. References

- [1] C. W. Tang, S. A. Vanslyke, *Appl. Phys. Lett.*, **54**, 913, (1987).
- [2] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund, W. R. Salaneck, *Nature (London)*, **397**, 121, (1999).
- [3] P. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend, R. W. Gymer, *Nature*, **356**, 47, (1992).
- [4] A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem., Int. Ed.*, **37**, 402, (1998).
- [5] H. Spreitzer, H. Becker, E. Kluge, W. Kreuder, H. Schenk, R. Demandt, H. Schoo, *Adv. Mater.*, **10**, 1340, (1998).
- [6] Z. K. Chen, N. H. S. Lee, W. Huang, Y. S. Xu, Y. Cao, *Macromolecules*, **36**, 1009, (2003).
- [7] J. P. J. Markham, S. C. Lo, S.W. Magennis, P.L. Burn, I. D. W Samuel. *Appl. Phys. Lett.*, **80**, 2645, (2002)
- [8] S. A. Jenekhe, L. Lu, M. M. Alam, *Macromolecules*, **34**, 7315, (2001).
- [9] S. K. Kim, C. J. Lee, J. H. Lee, I. N. Kang, J. W. Park, *Thin Solid film*, in press.
- [10] J. W. Park, S. E. Lee, H. C. Park, T. G. Chung, H. j. Seo, *Materials Science and Engineering*, **24**, 103, (2004).
- [11] X. Kong, A. P. Kulkarni, S. A. Jenekhe, *Macromolecules*, **36**, 8992, (2003)
- [12] D. H. Hwang, S. K. Kim, M. J. Park, J. H. Lee, B. W. Koo, I. N. Kang, S. H. Kim, T. Zyung, *Chem. Mater.*, **16**, 1298, (2004).