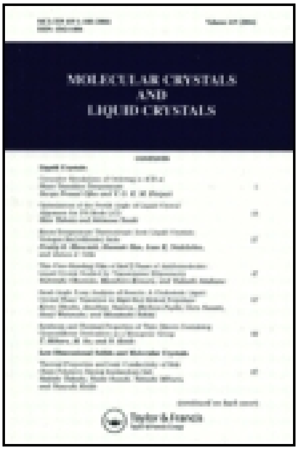

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Synthesis of Polyazomethine Type Conjugated Polymers as Light Emitting Materials

Lee Soon Park [a], Yoon Soo Han [a], Sang Dae Kim [a] & Jin Sang Hwang [a]

[a] Department of Polymer Science, Kyungpook National University, Taegu, 702-701, Korea

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Synthesis of Polyazomethine Type Conjugated Polymers as Light Emitting Materials

LEE SOON PARK, YOON SOO HAN, SANG DAE KIM
and JIN SANG HWANG

*Department of Polymer Science, Kyungpook National University,
Taegu, 702-701, Korea*

Aromatic dialdehyde based on phenothiazine and aromatic diamine were used to synthesize polyazomethine type conjugated polymer, poly(PZ-PI) which had good solubility in common organic solvents. The UV absorption maximum($\lambda_{max,UV}$) and edge($\lambda_{edg,UV}$) of poly(PZ-PI) were observed at 415 and 510 nm, respectively. The threshold voltage of ITO/polymer/Mg and ITO/polymer/Alq3(100Å)/Mg device was at 10 V and 7 V, respectively. Besides double layer LED with Alq3 exhibited both enhanced emission intensity and efficiency compared to the single layer LED.

Keywords light-emitting diode; conjugated polymer; polyazomethine

INTRODUCTION

Recently conjugated polymers have received considerable attention due to their application in LED, since R. H. Friend et al.[1] reported green color emission utilizing poly(p-phenylene vinylene) (PPV). A number of polymers with basic structure similar to PPV have been synthesized as light emitting materials in LED. Weaver and Bradley fabricated organic LED with chemical vapour deposited polyazomethine films [2]. They reported that the polyazomethine had a large ionization potential and acted as a hole-blocking electron transporting polymer. W. Fisher et al. introduced a successive deposition of aromatic diamine and dialdehyde monomers under high vacuum conditions to make a thin film of oligoazomethines[3]. They also reported that oligoazomethines acted as electron-transporting layers in light-emitting diodes. Polyazomethines are, however, difficult to dissolve in organic solvent and thus require vapour deposition technique to make thin films.

In this work, we used an aromatic dialdehyde based on phenothiazine and aromatic diamine to get polyazomethine type conjugated polymer which had good solubility in common organic solvents. We also examined the charge transport property of this polymer by making double layer LEDs utilizing vapour deposited Alq3.

EXPERIMENTAL

The synthetic scheme of polyazomethine type conjugated polymer is shown in Figure 1. N-(2-ethylhexyl)phenothiazine(EHPZ) was obtained from phenothiazine and 2-ethylhexyl bromide in dimethyl sulfoxide solvent with sodium hydroxide. EHPZ was reacted with $POCl_3$ and dimethylformamide(DMF) in dichloroethane solvent to give aromatic dialdehyde monomer, N-(2-ethylhexyl)-3,6-diformylphenothiazine (DFPZ). DFPZ monomer was reacted with 1,4-phenylenediamine in benzene to give a conjugated polymer with azomethine linkage, poly(N-(2-ethylhexyl)-3,6-phenothiazinylenemethylidynenitrilo-1,4-phenylene-nitrilomethylidyne)[poly(PZ-PI)]. The synthesized polymer was characterized with ^{1}H-NMR and FT-IR. The molecular weight was measured by Waters GPC with THF as eluent.

Single layer light-emitting diodes were fabricated with the poly(PZ-PI) as light-emitting layer. Double layer LEDs were made by spin coating of poly(PZ-PI) on ITO glass and then thermal deposition of Alq3 to a varying thickness. UV-visible absorption spectra of polymer films were obtained by Schimadzu UV-2000, and electroluminescence (EL) spectra and CIE coordinates were measured by Spectroscan PR 704(Photoresearch Inc.). The EL intensity was measured by using Minolta luminance meter LS-100 at room temperature.

RESULTS AND DISCUSSION

The synthesized polyazomethine type conjugated polymers were characterized by FT-IR, UV and GPC. In the FT-IR spectrum poly(PZ-

PI) exhibited new strong absorption peaks at 1616 $cm^{-1}$and 1467 cm^{-1} (C=N stretching) which were consistent with the formation of azomethine linkages. The molecular weight of conjugated polymer was about 13,200 g/mol as determined by GPC. The poly(PZ-PI) had good solubility in common organic solvents such as chloroform, benzene and THF due to the presence of long alkyl chain in the phenothiazine units. The UV absorption maximum($\lambda_{max,UV}$) and edge($\lambda_{edg,UV}$) of poly(PZ-PI) were observed at 415 and 510 nm, respectively.

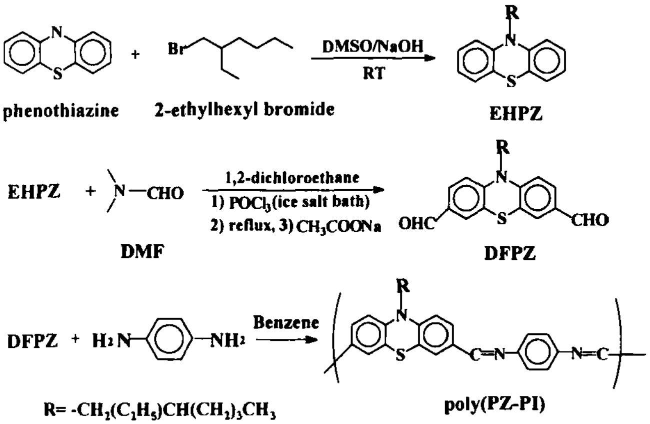

FIGURE 1. Synthetic route to EL polymer.

Figure 2(a) shows the luminance vs. voltage profile of single and double layer LEDs made with poly(PZ-PI). The threshold voltage of ITO/polymer/Mg and ITO/polymer/Alq3(100 Å)/Mg devices was at 10 V and 7 V, respectively. Besides double layer LED with Alq3 exhibited both enhanced emission intensity and efficiency compared to the single layer LED. Therefore, on the contrary to the previous reports the polyazomethine type conjugated polymers synthesized acted like a hole transport agent. This may be due to the presence of alkyl substituted phenothiazine units in the poly(PZ-PI) since the aromatic amines are well known to be a hole transport agent in the EL devices.

EL emissions of double layer LEDs with different thickness of Alq3 are shown in Figure 2(b) in the NTSC chromaticity diagram. The double layer LEDs with Alq3 exhibited gradual shift to the single layer LED characteristics as the thickness of Alq3 increased. This result indicates that recombinations of holes and electrons occur close to the Alq3 layer as the thickness of Alq3 increases. The emission maximum ($\lambda_{max,EL}$) and color coordinates determined from the Kelly's map in CIE 1931 chromaticity diagram of single and double layer LED's are summarized in TABLE 1.

TABLE 1. $\lambda_{max,EL}$ and color coordinates of single and double layer LEDs

	$\lambda_{max,EL}$ (nm)	Color coordinates		Color[1]
		x	y	
Single	576	0.5230	0.4712	yO
Alq3-100 Å	572	0.4790	0.4930	Y
Alq3-200 Å	562	0.4323	0.5108	Yg
Alq3-400 Å	528	0.3901	0.5535	yG

[1] yO ; yellowish orange, Y ; yellow, Yg ; yellow green, yG ; yellowish green

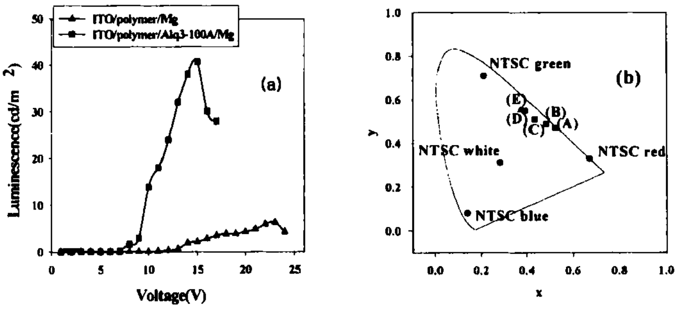

FIGURE 2. (a) Luminance versus voltage profile of single and double layer LED's (b) effect of thickness of Alq3 layer in the CIE chromaticity diagram of LED ; (A) single LED, (B) bilayer (100Å), (C) bilayer (200Å), (D) bilayer (400Å), and (E) single Alq3 LED.

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