

ORGANIC EL DEVICES BASED ON DYE-CONTAINING POLYMERS

Junji Kido

Graduate School of Engineering, Yamagata University

Yonezawa, Yamagata 992, Japan

1. Introduction

Organic electroluminescent (EL) devices are light-emitting devices similar to inorganic semiconductor-based light-emitting diodes. These devices are operated by the injection of carriers, such as electrons (radical anion) and holes (radical cation), into the organic emitter layer and subsequent carrier recombination, resulting in the formation of molecular excitons. Therefore, the component materials should possess carrier-transporting properties as well as fluorescent properties. Various types of device structure have been proposed, which include a double-layer-type having a layered structure composed of the materials with different carrier transport properties: One transporting holes and the other electrons¹⁾. Another type of the device is a single-layer-type which is composed of only one organic layer²⁾. In this case, the emitter layer is designed to transport both electrons and holes so that the recombination can take place in the emitter layer.

A number of polymers have been reported to be useful as active layer in organic EL device³⁾. Compared with low molecular weight materials, polymers have advantages of high mechanical strength and high film-forming properties. In addition, emission color can be tuned with ease by the dye-doping method. In this case, fluorescent dyes are doped to the polymer layer by the solution preparation. This allows us to use various kinds of fluorescent dyes as emitting centers and to obtain white emission as a result of color mixing^{4,5)}. Thus, dye-dispersed polymer systems offer the advantages of the high quantum efficiency of fluorescent dye as well as the mechanical strength of polymer. There are two types of polymers used for electroluminescence application: π -conjugated polymers and charge-transporting polymers. Charge-transporting polymers contain charge-transporting dye units such as hole-transporting aromatic amine and electron-transporting 1,3,4-oxadiazole. In our laboratory, several polymers such as poly(*N*-vinylcarbazole) (PVK)⁴⁻⁶⁾, aromatic amine-containing poly(*N*-substituted methacrylamide)s^{7,8)}, 1,3,4-oxadiazole-containing vinyl polymers⁹⁾, aromatic amine-containing poly(arylene ether)s^{10,11)} have been utilized to fabricate EL devices. In this paper, our recent results using dye-containing polymer systems are summarized.

2. Experimental

Polymers used in this study include PVK, aromatic amine-containing poly(*N*-substituted methacrylamide)s, 1,3,4-oxadiazole-containing vinyl polymers, aromatic amine-containing poly(arylene ether)s, shown in Fig. 1.

Structure of EL device is a glass substrate / indium-tin-oxide (ITO) / organic layer / Mg:Ag.

Polymer layers were formed by dip coating or spin coating method, and organic dyes, such as tris(8-quinolinolato)Al complex (Alq) were vacuum deposited. The total thickness of the organic layer was ca. 1,000 Å. A 2,000-Å-thick magnesium and silver (10:1) was codeposited on the organic layer surface as the top electrode.

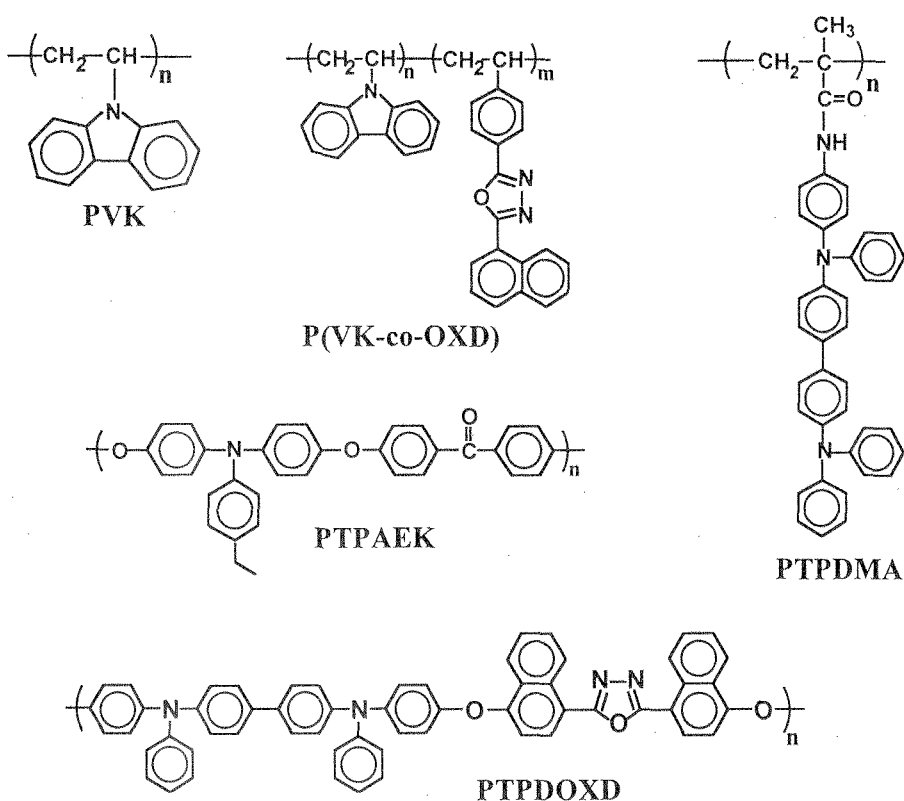


Figure 1. Dye-Containing Polymer Systems.

3. Results and Discussion

One of the typical polymer-based devices is a single-layer-type device, in which the active layer

consists only of one polymer layer that is sandwiched between ITO anode and Mg:Ag cathode. Bipolar carrier-transporting properties required for the single emitter layer are easily archived by molecularly dispersing appropriate additives. Hole-transporting PVK was molecularly dispersed with electron-transporting additives, such as 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) at an appropriate concentration. In addition, several fluorescent dyes, such as 1,1,4,4-tetraphenyl-1,3-butadiene (blue), coumarin 6 (Green), DCM 1 (orange) and Nile Red (red), were dispersed as emitting centers. By adjusting the concentrations of the fluorescent dyes, white light with a maximum luminance of 4,100 cd/m^2 was observed (Figure 2)¹⁾.

Because of the high concentration (30 wt%) of the electron-transporting additive (PBD), this device may not be stable at elevated temperatures due to the segregation of the additive. We have, therefore, synthesized copolymers composed of electron-transporting units and hole-transporting units to prevent such segregation. For example, P(VK-co-OXD) in Figure 1 is a copolymer containing 1,3,4-oxadiazole units and 9-vinylcarbazole units⁹⁾, and PTPDOXD is a poly(arylene ether)

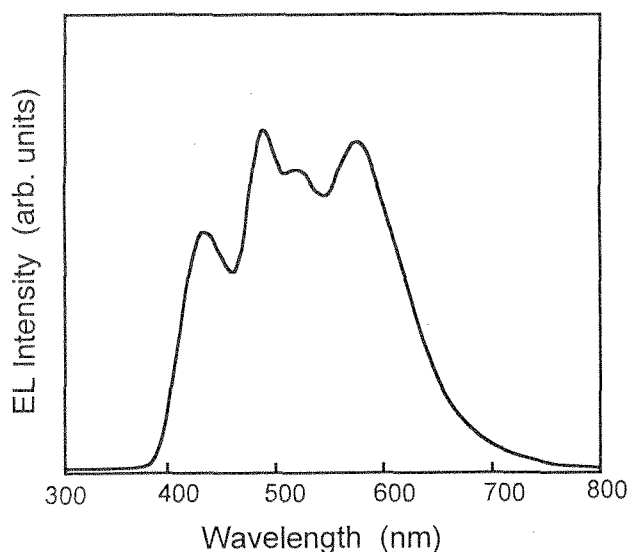
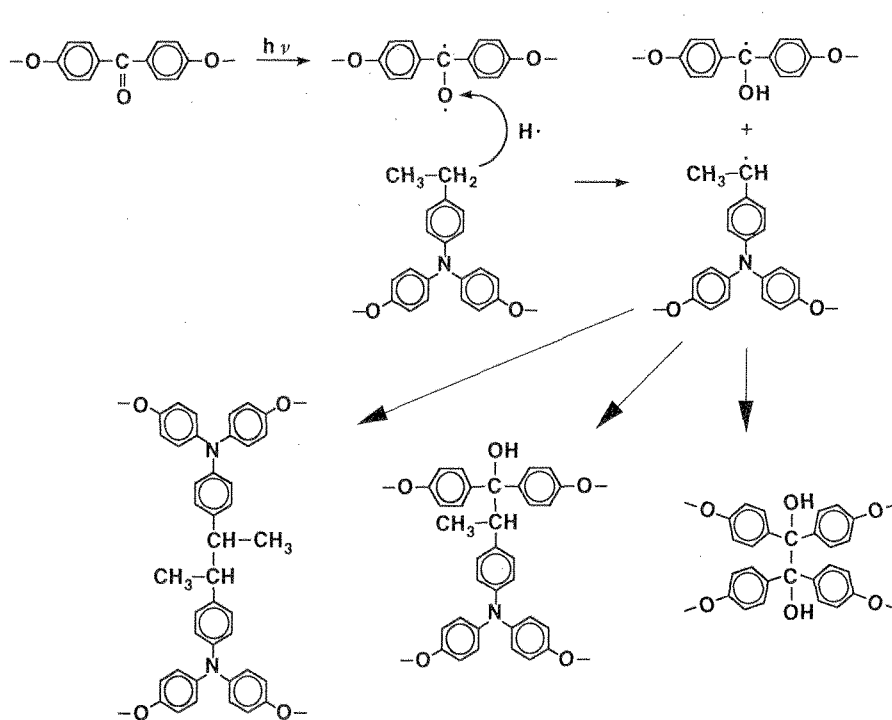


Fig. 2. EL spectrum of white-light-emitting device. Device structure is ITO/dye-dispersed PVK/Mg:Ag.

containing triphenylamine units and 1,3,4-oxadiazole units¹¹). Both polymers have high glass transition temperatures over 180°C and found to serve as an active layer.

Charge-transporting polymers are not only useful in tuning emission color but also useful in patterning emitting surface. One of the poly(arylene ether)s in Figure 1 can be crosslinked by the irradiation of ultraviolet (UV) light. Crosslinking reactions



Scheme 1. Crosslinking mechanism.

such as in scheme 1 are assumed to occur. Even after such reactions, the polymer was found to work as hole transport layer in bilayer structures, polymer/Alq. However, the highest luminance for the device using the crosslinked polymer was lower, ca. 2000 cd/m², than that of the device using non-crosslinked polymer, ca. 4000 cd/m². The driving voltage of the device with crosslinked polymer is also higher than that of the device with non-crosslinked polymer as a hole transport layer. This is partly due to higher ionization potential of the crosslinked polymer compared with the non-crosslinked one, resulting in the lower hole mobility of the crosslinked polymer. It was observed that ionization potential of the polymer increased with the irradiation of UV light from 5.6 to 5.75, depending on the UV irradiation dose. This is probably due to the increase in the glass transition temperature of the polymer, which restricts the local mobility of the triphenylamine moieties which results in hindering the polaron formation.

Taking advantage of this photo-crosslinking method, we can control the ionization potential and subsequently device operation voltages, and fabricated bilayer

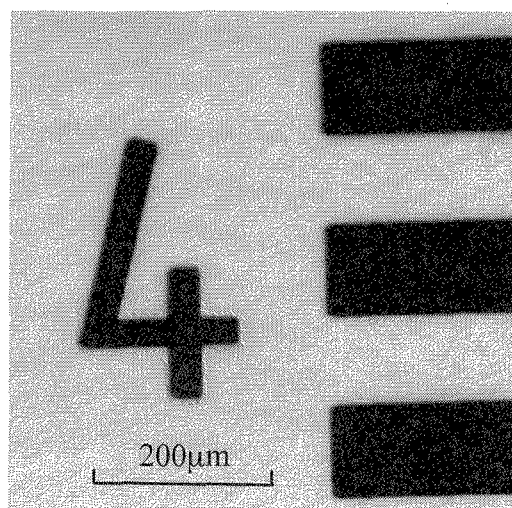


Fig. 3. A photograph of micropatterned polymer-based EL device, ITO / PETPAEK (200Å) / Alq 700 Å / Mg:Ag. PETPAEK layer was partly irradiated with ultraviolet light through metal mask so that the polymer in the irradiated area is cross-linked and has a lower hole-mobility.

devices that have patterned emitting surface. Because the photo-irradiation of hole transport layer causes higher driving voltages, the emitting surface of UV-irradiated part will be darker than the non-irradiated surface. In this case, the contrast depends on the irradiation dose. The photograph of such micropatterned emitting surface is shown in Figure 3. In this device, a photomask was used to partly irradiate polymer layer.

In conclusion, we have shown the suitability of dye-containing polymer systems for the fabrication of organic EL devices. This system is particularly useful in controlling the emission color, and bright white light was successfully obtained. Patterning emitter surface was also demonstrated.

References

- 1) C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, **51**, 913 (1987).
- 2) J. Kido, M. Kohda, K. Okuyama and K. Nagai, *Appl. Phys. Lett.*, **61**, 761 (1992).
- 3) J. Kido, *Trends in Polymer Science*, **10**, 350 (1994).
- 4) J. Kido, K. Hongawa, K. Okuyama and K. Nagai, *Appl. Phys. Lett.*, **64**, 815 (1994).
- 5) J. Kido, H. Shionoya and K. Nagai, *Appl. Phys. Lett.*, **67**, 2281 (1995).
- 6) J. Kido, K. Hongawa, K. Okuyama and K. Nagai, *Appl. Phys. Lett.*, **63**, 2627 (1993).
- 7) J. Kido, G. Harada and K. Nagai, *Kobunshi Ronbunshu*, **52**, 216 (1995).
- 8) J. Kido, M. Komada, G. Harada and K. Nagai, *Polym. Adv. Technol.*, **6**, 703 (1995).
- 9) J. Kido, T. Mochizuki, J. Endo and K. Nagai, *Polymer Preprints, Japan*, **45**, 446 (1996).
- 10) J. Kido, G. Harada and K. Nagai, *Polym. Adv. Technol.*, **7**, 31 (1996).
- 11) J. Kido, G. Harada and K. Nagai, *Chem. Lett.*, 161 (1996).