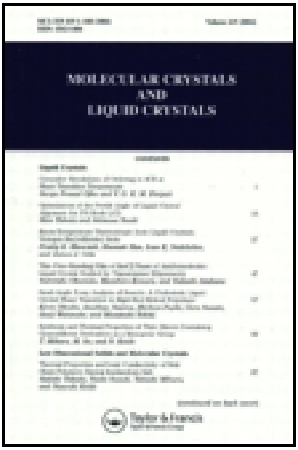

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Electroluminescent Properties of Liquid-Crystalline Polymers Containing Oxadiazole and Carbazole Moieties in the Same Side Chain

Yun Mi Nam [a], Motoi Kinoshita [a], Tomiki Ikeda [a], Masuki Kawamoto [b] & Takeshi Shiono [c]

[a] Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan

[b] Supermolecular Science Laboratory, RIKEN, Saitama, Japan

[c] Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Hiroshima, Japan

Version of record first published: 31 Jan 2007

Mol. Cryst. Liq. Cryst., Vol. 443, pp. 95–104, 2005

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500247318

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Yun Mi Nam
Motoi Kinoshita
Tomiki Ikeda
Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan

Masuki Kawamoto
Supermolecular Science Laboratory, RIKEN, Saitama, Japan

Takeshi Shiono
Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Hiroshima, Japan

Liquid-crystalline polymers containing an oxadiazole moiety as an electron-transporting unit and a carbazole moiety as a hole-transporting unit in the same side chain were designed and synthesized to investigate electroluminescent (EL) properties. The synthesized polymers showed high fluorescence quantum efficiency. Furthermore, it was found that the luminescent polymers possessed bipolar carrier-transporting property. The single-layer organic light-emitting diode was fabricated to demonstrate EL emission. The device, ITO glass/the polymer/MgAg, exhibited intense blue emission with a maximum brightness of 30 cd/m^2 at 30 V.

Keywords: bipolar carrier-transporting; carbazole; electroluminescence; liquid-crystalline polymer; oxadiazole; single-layer organic light-emitting diode

INTRODUCTION

The strong anisotropy of liquid-crystalline polymers (LCPs) and their self-organizing ability allow the preparation of well-oriented thin films

Address correspondence to Tomiki Ikeda, Chemical Resources Laboratory, Tokyo Institute of Technology, R1-11, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan. E-mail: tikeda@res.titech.ac.jp

emitting polarized electroluminescence (EL) [1,2]. Furthermore, liquid crystals (LCs) possess high carrier-transporting ability [3–6]. By using mechanically treated films, LC-aligned films can be prepared by quenching from appropriate fluid phases into solid states [7]. Due to these properties, LCs are well-known as prospective materials to be used not only in display devices but also in various photonic applications [8,9].

Polymeric materials are generally expected to be suitable for organic light-emitting diodes (OLEDs) because of good processability and intrinsically high durability [10]. In general, light-emitting polymers are rarely good conductors for both electrons and holes, whereas LED devices require balanced injection and transport of them. To achieve a high performance single-layer OLED (SLOLED), a chromophore with both electron- and hole-transporting units would be appropriate [11–15]. In relation to the bipolar carrier-transporting LCP, we already reported the carrier mobility of $2 \times 10^{-6} cm^2/Vs$ in an LC-aligned film with an LCP containing an oxadizole (OXD) moiety as an electron-transporting unit and an amine moiety as a hole-transporting unit at 130°C. Furthermore, we observed polarized EL emission in the SLOLED with a dichroic ratio of 1.6 [16].

In this study, we synthesized the polymers possessing a bipolar carrier-transporting chromophore consisting of the OXD moiety as an electron-transporting unit and a carbazole (Cz) moiety as a hole-transporting unit in the same side chain and investigated their EL properties. The Cz is an efficient photoconductive species transporting carriers. Poly(*N*-vinnylcarbazole) (PVK) has an emission band in the blue-violet region and transports holes effectively [17,18]. Therefore, we expected that polymers must show bipolar carrier-transporting ability and emit intense blue light by introducing OXD and Cz moieties. Furthermore, we also predicted that when the polymers show LC behavior, polarized emission could be obtained by SLOLEDs using the polymers.

EXPERIMENTAL

Materials

Figure 1 shows the chemical structures of the luminescent polymers containing OXD and Cz moieties in the same side chain.

Poly{2-[4′-(6-methacryloyloxy-1-hexyloxy)biphenyl-4-yl]-5-(3-*N*-methylcarbazolyl)-1,3,4-oxadiazole} (**PM6-OXD-MCz)** and poly{2-[4′-(6-methacryloyloxy-1-hexyloxy)biphenyl-4-yl]-5-(3-*N*-ethylhexylcarbazolyl)-1,3,4-oxadiazole} (**PM6-OXD-EHCz**) were prepared by radical

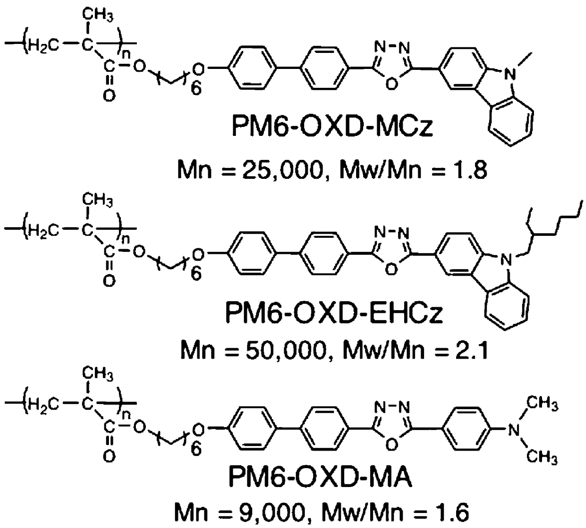

FIGURE 1 Chemical structures of the polymers and their molecular properties.

polymerization of the corresponding monomers, 2-[4′-(6-methacryloyloxy-1-hexyloxy) biphenyl-4-yl]-5-(3-*N*-methylcarbazolyl)-1,3,4-oxadiazole (**M6-OXD-MCz)** and 2-[4′-(6-methacryloyloxy-1-hexyloxy) biphenyl-4-yl]-5-(3-*N*-ethylhexyl-carbazolyl)- 1,3,4-oxadiazole (**M6-OXD-EHCz**). These monomers and poly{2-[4′-(6-methacryloyloxy-1-hexyloxy) biphenyl-4-yl]-5-(4-*N*,*N*-dimethylaminophenyl) 1,3,4-oxadiazole} (**PM6-OXD-MA**) were synthesized according to the literature [16,19].

The number-average molecular weights (Mn) and molecular weight distributions (Mw/Mn) were determined by gel permeation chromatography using polystyrenes as a standard. The Mn's of **PM6-OXD-MCz** and **PM6-OXD-EHCz** were 25,000 and 50,000 and Mw/Mn's were 1.8 and 2.1, respectively.

RESULTS AND DISCUSSION

LC Behavior

Glass transition and phase transition temperatures were determined with a differential scanning calorimeter (Seiko I & E SSC-5200) operated at a heating and cooling rate of 10, 5, and 1°C/min. At least, three scans were performed for each sample to inspect its reproducibility. Phase transition behavior was evaluated by a polarizing optical

TABLE 1 Phase Transition Temperature of the Synthesized Compounds

Compounds	Phase transition temperatures (°C)[a]
M6-OXD-MCz	K 112 N 157 I
M6-OXD-EHCz	N 40 I (cooling)
PM6-OXD-MCz	G 140 N 230 I
PM6-OXD-EHCz	G 40 I

[a]G - glassy; I - isotropic; K - crystalline; N - nematic phase.

microscope (POM; Olympus Model BHSP equipped with Mettler hot stages Models FP-80 and FP-82) and X-ray diffractometry (MAC Science MXP with a thermal controller, model 5301). The phase transition temperatures of the synthesized compounds are given in Table 1.

Comparing two monomers, **M6-OXD-MCz** showed a nematic phase from 112°C and an isotropic phase at 157°C. It was found that the monomer with an ethylhexyl group at the Cz moiety, **M6-OXD-EHCz**, was a monotropic LC. Figure 2 shows textures of the LC monomers observed by POM. X-ray diffraction patterns support these LC phase structures as shown in Figure 3.

Even though both monomers were characterized by LC phase behavior, only the polymer containing a methyl group at the Cz moiety, **PM6-OXD-MCz**, showed LC behavior. The other polymer with an ethylhexyl group, **PM6-OXD-EHCz**, did not exhibit any LC phase.

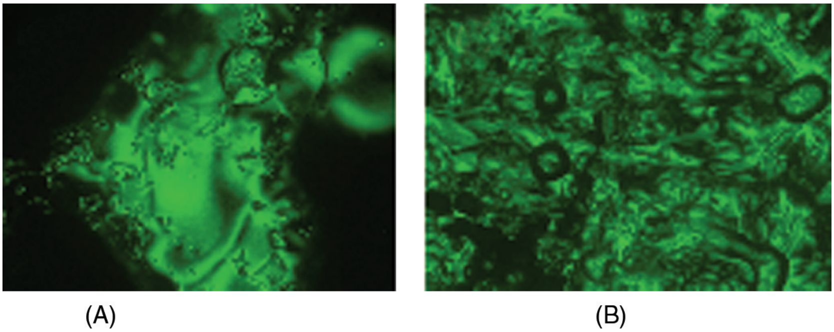

FIGURE 2 Polarizing optical micrographs of the LC textures of **M6-OXD-MCz** at 120°C, (A) and **M6-OXD-EHCz** at 30°C on cooling (B).

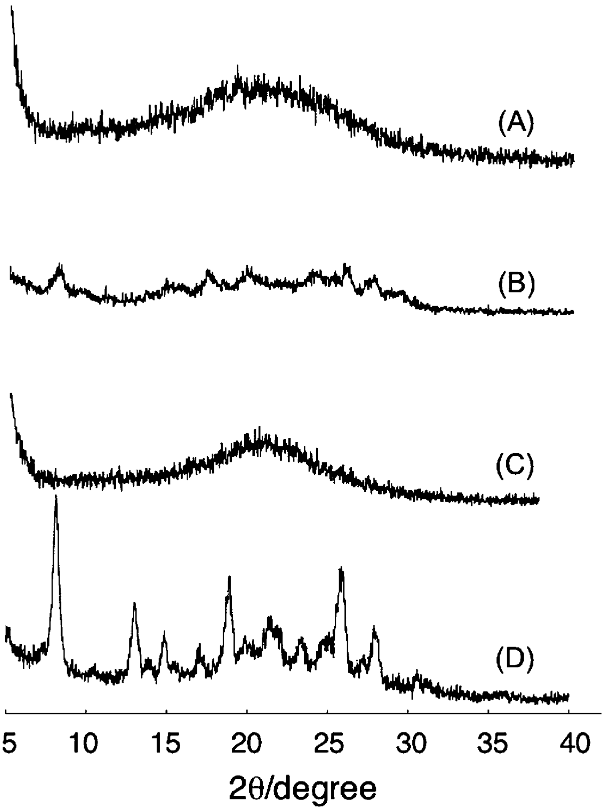

FIGURE 3 X-ray diffraction patterns of the LC monomers: (A) and (B) are N and K phases of **M6-OXD-MCz** at 30°C and 130°C, respectively, (C) and (D) are N and K phases of **M6-OXD-EHCz** at 30°C on cooling and heating, respectively.

It can be assumed that **PM6-OXD-EHCz** has large irregularity or high flexibility of end-groups in the side chain, so that this polymer could not show LC behavior.

Optical Properties

Steady-state absorption and photoluminescence (PL) spectra were measured at room temperature in a 1-cm quartz cell with a spectrophotometer (Jasco, U-550) and a fluorescence spectrophotometer (Hitachi, F-4000), respectively. The concentration of the sample was on the order of 10^{-5} mol/L.

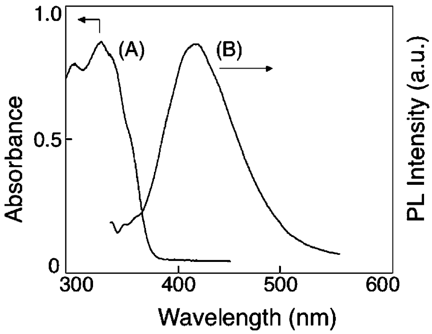

FIGURE 4 Absorption (A) and PL (B) spectra of **PM6-OXD-EHCz** in CH_2Cl_2 at an excitation wavelength of 330 nm.

Figure 4 shows UV absorption and PL spectra of **PM6-OXD-EHCz** in a dichloromethane solution at room temperature. It was found that the polymer exhibited an absorption band with a maximum at 335 nm. Furthermore, **PM6-OXD-EHCz** showed an emission band at around 419 nm when the excitation wavelength was 330 nm. The maximum wavelengths of the absorption and emission bands and the fluorescence quantum yields (Φ_f) of the synthesized polymers are summarized in Table 2. These polymers showed high Φ_f over 0.7.

Electrochemical Properties

To investigate reduction and oxidation behavior of the synthesized polymers, cyclic voltammetry was measured. It was performed on an ALS/chi Model 600 A electrochemical analyzer with tetraethylammonium tetrafluoroborate (10^{-1} mol/L) in an acetonitrile solution at a scan rate of 0.1 V/s. The measurement was carried out using a platinum disk (1.6 mm in diameter) as a working electrode. Platinum wire was used as a counter electrode, and the Ag/$AgNO_3$ solution (10^{-2} mol/L in acetonitrile) was used as an electrolyte. The redox

TABLE 2 Optical Properties of the Synthesized Polymers

	Abs_{max} (nm)	PL_{max} (NM)	Φ_f^a
PM6-OXD-MCz	335	430	0.72
PM6-OXD-EHCz	335	419	0.78

[a]PL spectra were measured in CH_2Cl_2 (10^{-6} M) at an excitation wavelength of 330 nm.

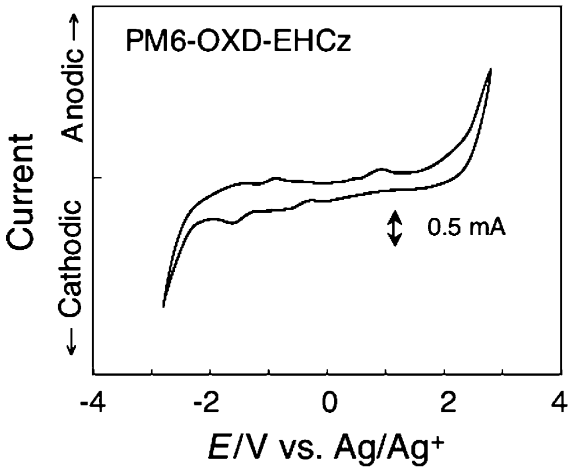

FIGURE 5 CV of the **PM6-OXD-EHCz** coated on a platinum electrode in acetonitrile.

behavior was referenced to $Ag/AgNO_3$ and ferrocene/ferrocenium. Figure 5 shows the cyclic voltammogram (CV) of **PM6-OXD-EHCz**. In the cathodic scan, the CV of the polymer exhibited the reduction peak at –1.6 V. The oxidation peak of **PM6-OXD-EHCz** appeared at 0.94 V. This result indicates that **PM6-OXD-EHCz** possesses bipolar carrier-transporting ability. In this study, the synthesized polymers exhibited intense fluorescence emission and redox behavior. Furthermore, **PM6-OXD-MCz** showed LC behavior. With these results, we expected that it is possible to fabricate SLOLEDs with these polymers.

Fabrication and Performance of the SLOLED

To fabricate a stable SLOLED, a polymer layer with thickness of ~100 nm is needed. Since **PM6-OXD-MCz** showed poor solubility, we used **PM6-OXD-EHCz** to fabricate SLOLED due to its excellent solubility. The device of ITO glass/**PM6-OXD-EHCz**/MgAg was prepared by the following method. The polymer film with thickness of 100 nm was obtained by spin-coating at a rate of 2,500 rpm for 30 s (2 wt% solution in toluene). MgAg as an anode was deposited onto the polymer layer by thermal vacuum evaporation at a vacuum pressure of less than 10^{-6} torr. It was found that the SLOLED with amorphous **PM6-OXD-EHCz** emitted blue light at around 450 nm as shown in Figure 6.

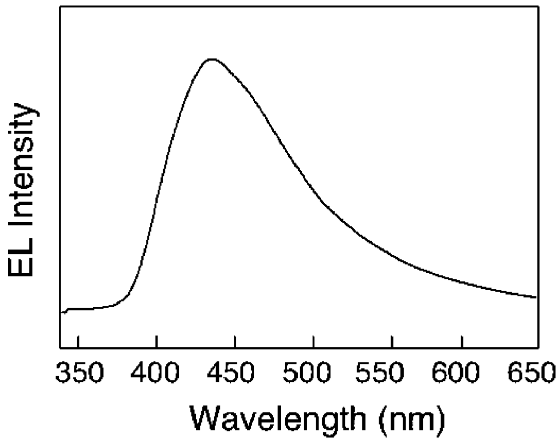

FIGURE 6 EL spectrum of the SLOLED, ITO glass/**PM6-OXD-EHCz**/MgAg.

Figure 7 shows current-voltage and luminance-voltage curves for the device at room temperature. The EL emission started at a driving voltage of 5 V. Similar turn-on voltages for both current density and luminance indicate that charge injection from the cathode and the anode is balanced. The SLOLED exhibited a maximum luminance of

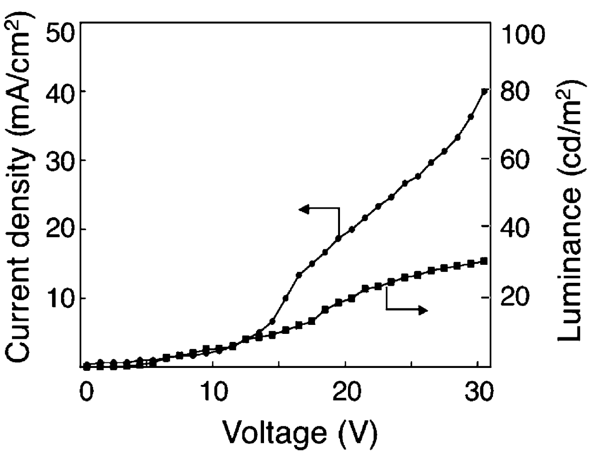

FIGURE 7 Current-voltage (circle) and luminance-voltage (square) curves of the device, ITO glass/**PM6-OXD-EHCz**/MgAg.

30 cd/m^2 at 30 V. It is worth comparing the performance of **PM6-OXD-EHCz** with that of a bipolar LCP with a similar structure, PM6-OXD-MA (Fig. 1). The device of ITO glass/**PM6-OXD-MA**/MgAg exhibited a maximum luminance of 13 cd/m^2 at 26 V [16].

The brightness of emission with **PM6-OXD-EHCz** was much improved in comparison with that of **PM6-OXD-MA**. This is due to the lower LUMO level of **PM6-OXD-EHCz** compared to that of **PM6-OXD-MA,** which facilitates injection of electrons and increases probability of hole-electron recombination.

CONCLUSION

We synthesized a novel class of the polymers, **PM6-OXD-MCz** and **PM6-OXD-EHCz**, containing OXD and Cz moieties in the side chain and investigated their intrinsic properties. Even though both monomers showed LC behavior, only **PM6-OXD-MCz** exhibited a nematic LC phase. Furthermore, these polymers showed high fluorescence quantum efficiency. By measuring cyclic voltammetry, it was found that the polymers possessed bipolar carrier-transporting ability. The fabricated SLOED, ITO glass/**PM6-OXD-EHCz**/MgAg, exhibited blue emission with a maximum brightness of 30 cd/m^2.

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