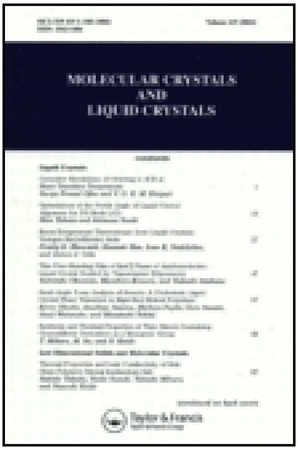

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006.

To cite this article: L. S. Park , S. N. Lee , Y. S. Han & K. S. Shin (1996): Molecularly Doped Liquid Crystalline Polymer as a Hole Transport Layer in Organic Electroluminescence Device, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 280:1, 337-342

To link to this article: http://dx.doi.org/10.1080/10587259608040353

Mol. Cryst. Liq. Cryst., 1996, Vol. 280, pp. 337–342
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MOLECULARLY DOPED LIQUID CRYSTALLINE POLYMER AS A HOLE TRANSPORT LAYER IN ORGANIC ELECTROLUMINESCENCE DEVICE

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Abstract Organic thin film electroluminescence devices were fabricated by molecularly doped method with N,N′-Diphenyl-N,N′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD) as a hole transport agent, tris(8-quinolinolato) aluminium(III) (Alq_3) as an emitting and electron transport agent, and poly(methyl methacrylate) (PMMA), polycarbonate (PC), side chain liquid crystal polymers (SCLCP) and copolymer as matrix for TPD. The effect of polymer matrix and hole transport layer fabrication method on the electroluminescence characteristics were examined. The highest intensity and stability of EL device was obtained by film casting method using dichloroethane as a solvent at a polymer/TPD concentration of 0.005 wt% and evaporation temperature of 30 °C. The electroluminescence intensity increased in the order of PMMA<PC<SCLCP as polymer matrix. The luminance started at voltage as low as 3 V and reached the maximum luminance of 756 cd/m^2 at 11 V in the EL device consisted of ITO/SCLCP:TPD/Alq_3/Mg (SCLCP/TPD=30/70 by wt).

INTRODUCTION

Electroluminescence(EL) devices based on organic materials are of great interest due to their possible application as large-area light-emitting displays which are operative at low drive voltages.[1-3] Generation of light in the cells is the result of combination of holes and electrons injected through the electrodes. A good performance of the EL cell was achieved by the insertion of a hole transport layer and/or an electron transport layer between the electrode and the emitting layer as shown by Tang and VanSlyke[4] and Saito et. al.[5]. One of the problems in the organic EL cell is the short life time compared to the inorganic EL cells.[4] This may be caused by the repeated crystallization of organic materials, destroying the contact between thin layers. A hole transport agent molecularly dispersed in a polymer matrix has been used to improve the life of organic EL cells.[6,7] In this study, we report the use of side chain liquid crystal polymers(SCLCP) as polymer matrix in hole transport layer and their effect on the resulting EL cells.

EXPERIMENTAL

Material

4-Hydroxy-4′-cyanobiphenyl, 6-bromo-1-hexanol, methacryloyl chloride, and triethyl amine (TEA) for the preparation of mesogenic monomer were Aldrich Chemical's regent grade and used as received. Methyl methacrylate (MMA), dichloromethane (DCM), dichloroethane (DCE), and tetrahydrofuran (THF) were distilled with calcium hydride. AIBN initiator from Wako Chemical was purified by recrystallization from methanol. N,N′-Diphenyl-N,N′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD) as a hole transport agent, and tris(8-quinolinolato)aluminium(III) (Alq_3) as a emitting and electron transport agent were from Tokyo Chemical Industry Company and used as received. Magnesium (assay 99.9%) was purchased from High Purity Chemical Company. Polycarbonate (PC) was obtained from General Electric Co. and purified by precifitation.

Synthesis of Polymers

The synthesis of mesogenic monomer(MC) and corresponding side chain liquid crystalline homopolymer(MCH) and copolymer (MCC) are shown in Fig. 1.

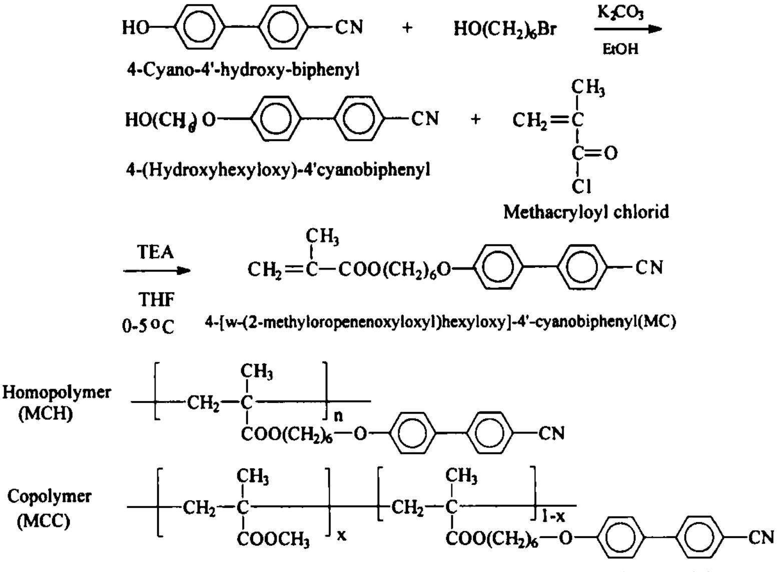


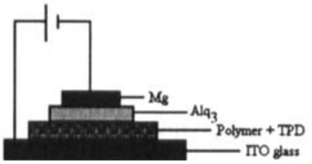
FIGURE 1 Synthesis of mesogenic monomer and side chain liquid crystalline polymers

4-(Hydroxyhexyloxy)-4′-cyanobiphenyl was prepared by refluxing 4-hydroxy-4′-cyanobiphenyl (5.00 g) and K_2CO_3 (5.00 g), and 6-bromo-1-hexanol (5.00 g) in ethanol (90 mL) for 24h. The reaction mixture was filtered hot, and the filtrate was poured into water. The crude product was collected by filtration and recrystallized from benzene.

4-(Hydroxyhexyloxy)-4′-cyanobiphenyl (7.00g) and methacryloyl chloride (3.71g) was reacted in dry THF (160 mL) with triethylamine (3.83g) as catalyst at 5 °C overnight. The resulting mesogenic monomer (MC) was purified by recrystallization from methanol. The mesogenic monomer had T_m = 74-75 °C (by DSC), M^+ (m/e) = 363.2 and elemental analysis data of C(75.51%), H(6.96%), N(3.84%) found and C(76.01), H(6.93), N(3.85%) theoritical. The synthesis of MCH and MCC polymers were conducted by free radical polymerization with 2,2-azoisobutyronitrile (AIBN) initiator in THF solution at 60 °C under N_2 atmosphere. The monomer concentration was 15 % by wt. and initiator (AIBN) was 0.3 mol% based on monomer. The polymers were purified by precipitation twice in methanol and vacuum dried.

Fabrication of EL Device

Indium-tin-oxide coated glass with a sheet resistance of 30 Ω/□ and thickness of 1.08 nm was cut into 2.5 cm×2.5 cm and the electrode area was etched by electrolysis method using NaOH aqueous solution (35 wt%). It was cleaned in a ultrasonic bath in acetone, methanol, and mixture of isopropyl alcohol and water (1:1). Hole transport layer was formed by film casting method, i.e. 0.005 %(wt) DCE solution of polymer/TPD (polymer/TPD=30/70 wt %) was distributed evenly onto an ITO-coated glass, and then solvent was vaporized in a petri dish at 30 °C for 8h. Alq_3 thin film was deposited onto the hole transport layer (size 1cm×1cm) with thickness 500 Å using vacuum evaporator at 3-5 Å/sec rate. Finally Mg was vacuum deposited on the Alq_3 layer (diameter 0.7 cm) with 4,000 Å thickness at 20 Å/sec rate. The completed EL device and structure of TPD and Alq_3 are shown in Fig. 2.



EL device

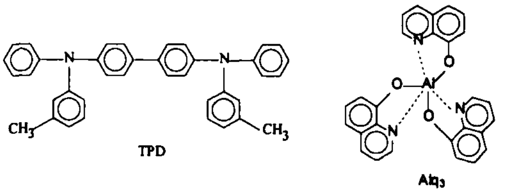


FIGURE 2 EL device and structure of TPD and Alq_3.

Characterization and Measurement

The NMR spectra of monomer and polymers were taken on a Bruker 300 MHz ^{1}H- NMR spectrometer. The molecular weights of the polymers were obtained by

Waters gel permeation chromatograph (GPC) using THF as eluent against polystyrene standards. Current and luminance were measured with Model 8902A Digital Multimeter (Hyun Chang Product Co. Ltd), and Minolta Luminance Meter LS-100 equipped with close-up lens (No. 110, ϕ 40.5mm) at room temperature, respectively. Photoluminescence was measured with fluorospectrophotometer RF-100 (Shimadzu) in DCE solvent. Electroluminescence was measured with Optical Multichannel Analyzer (EG & G, USA) equipped with OMA4 CCD detector.

RESULTS AND DISCUSSION

Synthesis and Molecular Weight of Matrix Polymers

The synthesis of side chain liquid crystal polymers and molecular weights of other two polymers, PMMA and PC also used as matrix for TPD are shown in Table 1. The number average molecular weights of polymers ranged from 8,800 to 62,000 g mol^{-1} with corresponding polydispersity indices of 2.33~5.47. The copolymer compositions of MCC samples were nearly same as those of monomer feed.

EL Cells by Film Casting Method

Hole transport layer containing TPD as hole transport agent was formed on the ITO glass by slow evaporation of solvent at constant temperature. The weight ratio of TPD to polymer was 1:1 and the concentrations of polymer/TPD in different solvents were varied in the range of 0.1~0.005 wt %. When DCM was used as solvent and evaporated at 20 °C, the EL device gave weak luminance with many black dots at 5-10 V. The cell was destroyed above 10 V, indicating pin hole formation due to rapid evaporation of solvent. With DCE as solvent the optimum condition appeared to be 0.005 wt% polymer/TPD concentration and evaporating temperature 30 °C over 8 hr period. EL cells gave consistant electroluminescence over all the area under metal electrode.

TABLE 1 Synthesis and characterization of side chain liquid crystal polymers

Polymer	Feed Ratio	Copolymer	Molecular Weight Data		
Sample	MC:MMA (mol%)	MC:MMA (mol%)	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	PDI
MCH	100 : 0	100 : 0	0.88	2.05	2.33
MCC-1	66.7 : 38.3	68.4 : 31.68	1.80	7.20	4.00
MCC-2	50 : 50	55.3 : 44.7	6.20	33.9	5.47
MCC-3	16.7 : 83.3	11.4 : 88.6	1.51	5.95	3.94
PMMA	-	-	4.88	8.92	1.83
PC	-	-	2.74	5.04	1.84

Effect of Polymer Matrix on the Luminance of EL Device

Fig. 3 shows the luminance-voltage curves of three EL cells with different polymer matrix in the hole transport layer. Luminance started at voltage as low as 3 V. The maximum luminance values of 756 cd/m^2 for MCH, 615 cd/m^2 for PC, and 190 cd/m^2 for PMMA were obtained at 11 V with current density of 81.7 mA/cm^2 for MCH, 290.0 mA/cm^2 for PC, and 387.0 mA/cm^2 for PMMA. The liquid crystalline polymer (MCH) showed hightest luminance at lowest current density.

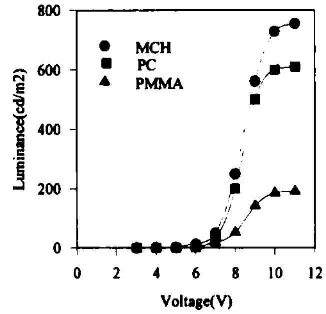


Figure 3 Luminance-voltage characteristics of ITO/TPD:Polymer/Alq$_3$/Mg cells ; ● MCH, ■ PC, ▲ PMMA as polymer matrix in the hole transport layer.

The effect of MCC copolymers on electroluminescence is shown in Fig. 4. As the content of MMA repeat unit increased the luminance decreased, indicating the positive effect of liquid crystalline polymer as matrix in the organic EL device. Kido and coworkers reported that PC gave higher luminance than PMMA as matrix material and suggested that close packing of hole transport agent (TPD) might help high luminance. It seemed that incorporation of well organized liquid crystalline polymer as matrix might allow even favorable configuration of planar hole transport agents and also effective blocking of electrons to the opposite (ITO) electrode.

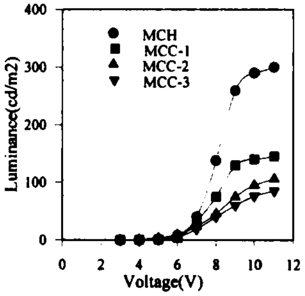


FIGURE 4 Luminance-voltage characteristics of ITO/TPD:Polymer/Alq$_3$/Mg cells ; ● MCH, ■ MCC-1, ▲ MCC-2, ▼ MCC-3 as polymer matrix in the hole transport layer

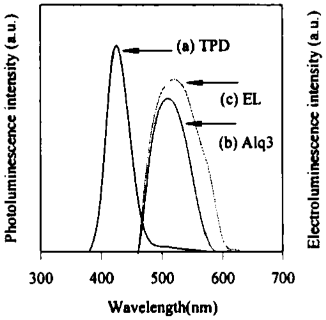


FIGURE 5 Photoluminescence(PL) spectrum of (a) TPD and (b) Alq_3 and electroluminescence(EL) spectrum ITO/PMMA:TPD/Alq_3/Mg EL cell(c).

Fig. 5 shows PL spectra of TPD and Alq_3 in DCE solvent and EL spectrum of EL device(ITO/MCH:TPD/Alq_3/Mg) together. The overlap of photoluminescence peak maximum of Alq_3 with electroluminescence peak maximum at about 514 nm suggests the electroluminenscence originates from Alq_3 layer.

CONCLUSIONS

Fabrication of organic ELD's by film casting method with different polymers as matrix in the hole transport layer gave the following results.

(i) The optimum condition for film casting method was as following ; polymer matrix/TPD = 30/70 (wt%), concentration = 0.005 wt%, solvent : dichloroethane, film casting temperature : 30 C°, (ii) EL intensity was increased in the order of PMMA<PC<SCLCP as matrix polymer in the hole transport layer (iii) In the case of SCLCP's as matrix polymer, EL intensity increased in the order of MCC-3<MCC-2<MCC-1<MCH (iv) From the comparision of EL and PL spectra, luminescence was caused by the Alq_3 layer in the EL device.

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