BUTTERWORTH HEINEMANN

*Polymer* Vol. 36 No. 12, pp. 2481–2483, 1995

0032-3861/95/$10.00+0.00

# Design and synthesis of processable electroluminescent polymer with charge transport capability

**Dong Uk Kim, Tetsuo Tsutsui* and Shogo Saito**
*Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816, Japan*
*(Received 19 December 1994; revised 30 January 1995)*

A polymer with an electroluminescent chromophore on a skeletal chain was designed and synthesized. Homogeneous thin films (~100 nm thick) of the polymer were obtained by spin-coating. Two types of electroluminescent diodes were fabricated, with single-layer and double-layer structures: indium tin oxide (ITO)/polymer/MgAg, and ITO/polymer/electron transport layer/MgAg, respectively. Bright green electroluminescence with a peak at 520 nm, which corresponded to the photoluminescence peak of the polymer, was observed in both types of device. The double-layer device was found to have better electroluminescent efficiency than the single-layer device.

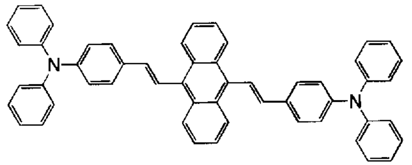
**(Keywords: electroluminescence; polymer diode; charge transport)**

## *Introduction*

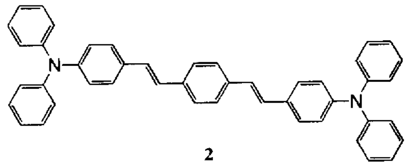
It has been shown that thin-film electroluminescent (EL) diodes with multilayer structures made of sublimed-dye films exhibit excellent properties[1–5]. In the past few years, the origins of high EL efficiencies in multilayer EL diodes have been made clear, and material design concepts for multilayer EL diodes have been well established[6–8]. On the other hand, it has been reported that fully $\pi$-conjugated polymers, such as poly(phenylene vinylene)s, polyphenylenes and polythiophenes, are also useful for thin-film EL diodes. Growing interest has been shown in EL diodes made of conjugated polymers[9–12].

Polymeric materials are generally expected to be suitable for EL diodes because they have good processability and intrinsically high durability. New classes of polymer systems, such as polymers with chromophores on skeletons, polymers with chromophores on side chains, and molecularly dispersed dye–polymer composites, have been reported to be applicable as EL diodes[13–15]. We found very little difference in the working mechanism between sublimed-dye multilayer and fully $\pi$-conjugated polymer systems, and proposed possible molecular designs of a variety of polymers for EL materials[16]. From the standpoint of ease of molecular design and synthesis, polymers with chromophores have advantages over fully $\pi$-conjugated polymers.

Based on the design concept for charge transport and emissive materials which has been established in sublimed-dye systems, we started a systematic study to extend our material design concept to polymeric systems. This paper deals with one of our first experimental results in developing soluble polymers which have both charge transport and emissive characteristics on skeletal chains. 9,10-Bisstyrylanthracene and 1,4-bisstyrylbenzene substituted with diphenylamino groups, structures **1** and **2**, respectively, have been reported to be excellent emissive dyes with both hole and electron transport capabilities. In other words, single-layer EL diodes made of a sublimed-film of **1** or **2** exhibited high EL efficiencies[7,8,17,18].

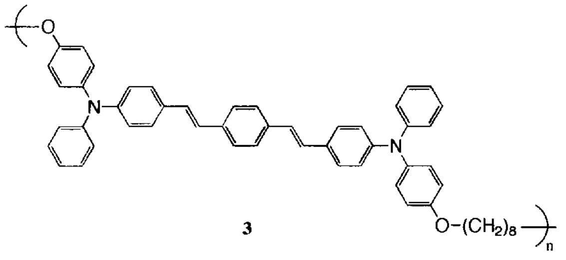


**1**



**2**

Thus we designed a polymer **3** with chromophores of type **2** on the polymer skeleton. Flexible aliphatic connecting groups were introduced for the purpose of increasing the solubility in organic solvents.



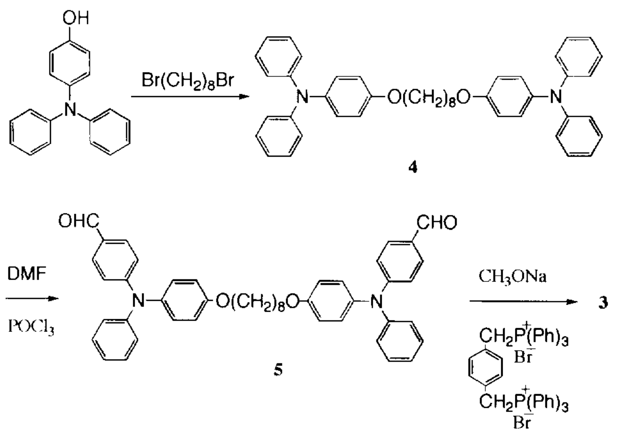
**3**

---

*To whom correspondence should be addressed

### *Experimental*

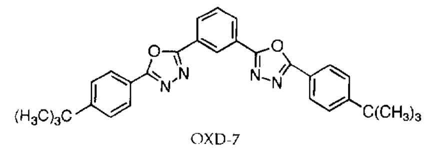
The synthetic route to polymer **3** is shown below.



4-Hydroxytriphenylamine was reacted with 1,8-dibromooctane to produce 1,8-bis(triphenylamine-4-oxy)octane, **4**. Then **4** was reacted with phosphorus oxychloride in dimethylformamide to give 1,8-bis-(4′-formyl-triphenylamine-4-oxy)-octane, monomer **5**, which was purified by column chromatography. $^1$H n.m.r. ($CDCl_3$): $\delta$ 9.80 (s, 2H, H–C=O), 6.70–7.80 (m, 26H, aromatic H), 4.05 (t, 4H, O–$CH_2$), 1.20–2.30 (m, 12H, C–$(CH_2)_6$–C); i.r. (KBr): 2710 cm$^{-1}$ (H–C=O, C–H stretching), 1655 cm$^{-1}$ (C=O, C–O stretching). Elemental analysis: calculated, C 80.21%, H 6.44%, N 4.07%; experimental, C 80.18%, H 6.51%, N 4.00%.

Polymer **3** was obtained by Wittig reaction of monomer **5** with 1,4-xylylene-bis(triphenylphosphoniumbromide). Monomer **5** was mixed with an equal molar amount of 1,4-xylylene-bis(triphenylphosphoniumbromide) in a chloroform/ethanol mixture, and a sodium methoxide solution (28% in methanol) was added to the mixture. The solution was stirred for 24 h at room temperature and neutralized with acetic acid. The reaction mixture was poured into a large amount of ethanol and precipitates were collected and dried under vacuum. The yield of polymer **3** was 65%. $^1$H n.m.r. ($CDCl_3$): $\delta$ 6.75–7.65 (m, 30H, aromatic H), 6.75–7.65 (m, 4H, HC=CH–), 4.05 (t, 4H, O–$CH_2$–), 1.20–2.10 (m, 12H, C–$(CH_2)_6$ C); i.r. (KBr): 950 cm$^{-1}$ ( HC=CH–, *trans* C–H bending). Elemental analysis: calculated, C 85.45%, H 6.64%, N 3.69%; experimental, C 84.36%, H 6.56%, N 3.52%.

We fabricated two types of EL diodes with single-layer and double-layer structures. Patterned indium tin oxide (ITO) coated glass substrates were used as a transparent anode. On an ITO anode, a polymer **3** film was spin-coated from a 1.8 wt% chloroform solution, and the polymer film was dried in a vacuum oven at 45 C. The thickness of the polymer film was 170–200 nm. In the case of the single-layer device, an MgAg (9:1) alloy cathode, with 200 nm in thickness, was directly deposited on the top of the polymer film under a vacuum of $2 \times 10^{-4}$ Pa. In the case of the double-layer device, an oxadiazole derivative (OXD-7), which had the role of an electron injection/transport layer, was deposited by vacuum sublimation[19]. The thickness of the OXD-7 layer was 30 nm. Then an MgAg alloy electrode was attached to the top. The emitting area of the diodes was 2 mm × 2 mm.



OXD-7

Brightness–current density–voltage relationships and EL spectra of the EL diodes were measured under vacuum. Photoluminescence (PL) spectra of spin-coated polymer thin films were obtained by using a conventional fluorescence spectrophotometer.

### *Results and discussion*

Novel EL polymer **3**, which gave homogeneous thin films by a conventional spin-coating method from solution, was synthesized with high yield. Comparison of the i.r. spectrum of polymer **3** with that of monomer **4** evidenced the formation of the designed polymer; the appearance of the peak at 950 cm$^{-1}$ due to *trans*

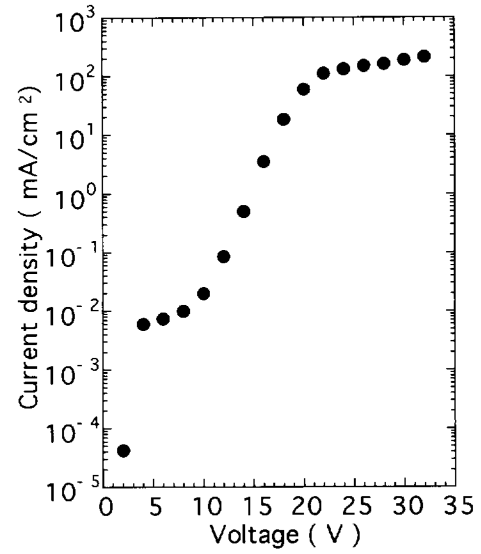


**Figure 1** Current density–voltage relationships for the single-layer device

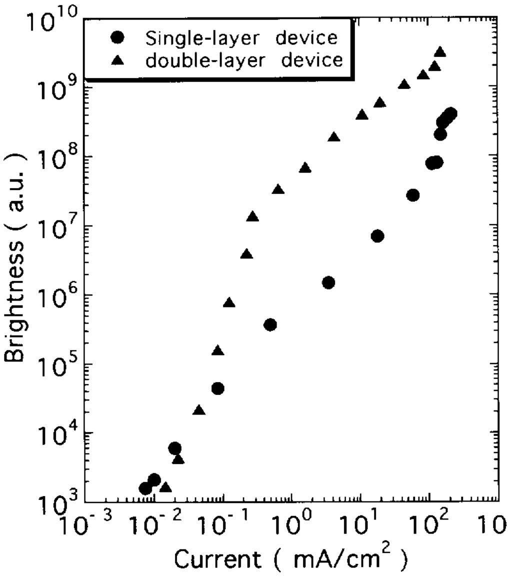


**Figure 2** Brightness–current density relationships for the single-layer and double-layer devices

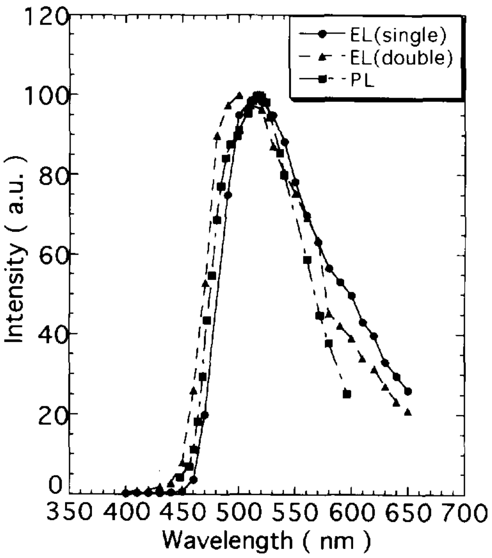


**Figure 3** Photoluminescence spectrum of polymer **3** thin film and electroluminescence spectra for single-layer and double-layer devices

vinylene C–H bending indicates the formation of phenylene vinylene linkage in the polymer. The complete disappearance of the i.r. peaks at 2710 and 1655 $\mathrm{cm}^{-1}$, which indicated the existence of an aldehyde group, suggested a high molar mass for polymer **3** while maintaining good solubility in organic solvents. The molecular structure of polymer **3** was also confirmed from $^1$H n.m.r. spectra and elemental analysis. We stress that the molecular structure of polymer **3** has been designed from the viewpoints of ease of polymer synthesis, good film processability and good EL performance.

In *Figure 1*, current density–voltage relationships in the single-layer device are shown. Current density increased as the applied voltage increased and a maximum current density of 200 $\mathrm{mA\,cm^{-2}}$ was obtained at 32 V. In *Figure 2*, brightness–current density characteristics for both the single-layer and double-layer devices are shown. In the single-layer device, bright green electroluminescence was observed, with luminescence of about 15 $\mathrm{cd\,m^{-2}}$ at a current density of 200 $\mathrm{mA\,cm^{-2}}$. The double-layer device, which included an electron transport layer of OXD-7, was found to exhibit better EL efficiency than the single-layer device owing to the improvement in the balance of charge injections. *Figure 3* compares the EL spectra from both the single-layer and double-layer devices with the PL spectrum of the polymer **3** thin film. The EL peaks were found to be located at 520 nm, which corresponded well with the PL peak. The shapes of the EL spectra are almost the same as that of the PL spectrum, except for a small difference at the longer wavelength region. It is clear that charge recombination and emission occurred on the designed bisstyrylbenzene chromophore of polymer **3**.

At present, little work has been directed towards optimizing the fabrication processes and device structures. We expect that quantitative data on device performances will be reported in the near future after optimization.

## *References*

1 Tang, C. W. and VanSlyke, S. A. *Appl. Phys. Lett.* 1988, **51**, 913
2 Adachi, C., Tokito, S., Tsutsui, T. and Saito, S. *Jpn J. Appl. Phys.* 1988, **27**, L296
3 Adachi, C., Tokito, S., Tsutsui, T. and Saito, S. *Jpn J. Appl. Phys.* 1988, **27**, L712
4 Adachi, C., Tsutsui, T. and Saito, S. *Appl. Phys. Lett.* 1989, **55**, 1489
5 Adachi, C., Tsutsui, T. and Saito, S. *Appl. Phys. Lett.* 1990, **56**, 799
6 Tsutsui, T., Aminaka, E., Fujita, Y., Hamada, Y. and Saito, S. *Synth. Met.* 1993, **55**, 4157
7 Tsutsui, T., Aminaka, E., Hamada, Y., Adachi, C. and Saito, S. *SPIE Proc.* 1993, **1910**, 180
8 Aminaka, E., Tsutsui, T. and Saito, S. *Jpn J. Appl. Phys.* 1994, **33**, 1061
9 Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burn, P. L. and Holmes, A. B. *Nature* 1990, **347**, 539
10 Braun, D. and Heeger, A. *Appl. Phys. Lett.* 1991, **58**, 1982
11 Grem, G., Leditzky, G., Ullrich, B. and Leising, G. *Adv. Mater.* 1992, **4**, 36
12 Ohmori, Y., Uchida, M., Muro, K. and Yoshino, K. *Jpn J. Appl. Phys.* 1991, **30**, L1941
13 Hosokawa, C., Kawasaki, N., Sakamoto, S. and Kusumoto, T. *Appl. Phys. Lett.* 1992, **61**, 2503
14 Yang, Z., Sokolik, I. and Karasz, F. E. *Macromolecules* 1993, **26**, 1188
15 Kido, J., Kohda, M., Okuyama, K. and Nagai, K. *Appl. Phys. Lett.* 1992, **61**, 761
16 Tsutsui, T. and Saito, S. in 'Intrinsically Conducting Polymers, An Emerging Technology' (Ed. M. Aldissi), Kluwer Academic Press, The Netherlands, 1993, p. 123
17 Tokailin, H., Matsuura, M., Higashi, H., Hosokawa, C. and Kusumoto, T. *SPIE Proc.* 1993, **1910**, 38
18 Higashi, H., Hosokawa, C., Tokailin, H. and Kusumoto, T. *J. Chem. Soc., Jpn* 1991, 1162 (in Japanese)
19 Hamada, Y., Adachi, C., Tsutsui, T. and Saito, S. *Jpn J. Appl. Phys.* 1992, **31**, 1812