Synthesis of Electroluminescent Polymer Containing Charge Transport and Emissive Chromophores on Polymer Skeleton

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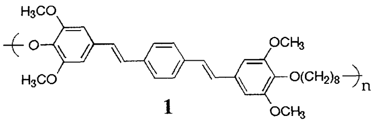
(Received April 7, 1995)

Electroluminescent polymer with a distyrylbenzene unit as an emissive group and a triphenylamine unit as a charge transporting group on polymer backbone was designed and synthesized. A single-layer device was composed of ITO/electroluminescent polymer/MgAg, and the polymer layer was fabricated using a spin-coating method. Greenish blue electroluminescence was observed with an emission maximum at 488 nm. Maximum brightness of 22 cd/m^2 was observed at a current density of 88 mA/cm^2 under drive voltage of 28 V.

Interest in electroluminescent (EL) devices has been on the increase since organic thin-film EL devices composed of sublimed-multilayer dyes were reported to exhibit high performances.[1-4] On the other hand, fully π-conjugated polymers have been intensively investigated and growing concern has been concentrated on the EL devices made of conjugated polymers.[5-8] Generally it has been well known that polymeric materials have good processability and intrinsically high durability. Because of these advantages, polymer materials have been expected to be promising for EL materials. Besides conjugated polymers, varieties of polymer systems, such as polymers containing chromophores on skeleton or side chains and molecularly dispersed dye-polymer composites have been reported to be useful for EL devices.[9-11] Polymers with chromophores on skeleton have the advantage in the ease of molecular design in comparison with fully π-conjugated polymers.[12] In this paper we describe one of our systematic experimental surveys towards the establishment of molecular design concept applicable to polymeric EL materials.



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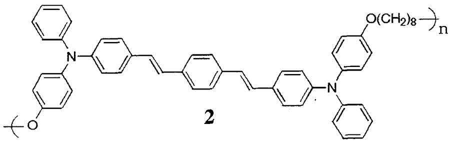

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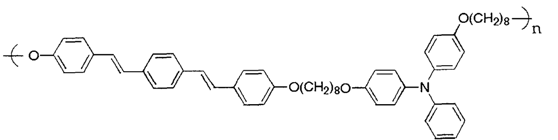

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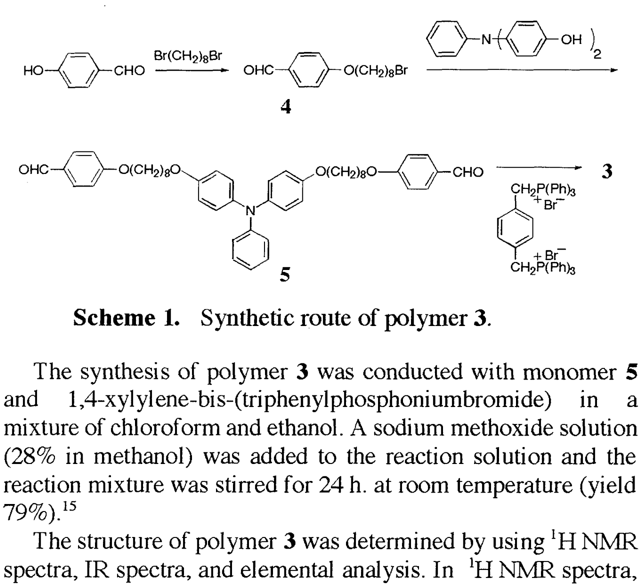
Several reports on the synthesis of EL polymers with emissive and charge transport chromophores in skeletons have been published. Hosokawa and coworkers reported bright blue EL from polycarbonate with a styrylamine chromophore.[9] Also blue EL from the polymer with a phenylene vinylene unit connected by flexible alkylether linkages (polymer **1**) has been reported.[11] We reported the synthesis of the polymer **2** with a diphenylamino-substituted 1,4-bisstyrylbenzene chromophore. As polymer **2** was composed of chromophore with an emissive and charge transporting property, we obtained bright green EL even in single layer device.[13] In this letter, polymer **3** which contained both the 1,4-bisstyrylbenzene group for an emissive and electron transporting functions and the triphenylamine group for hole transporting function on polymer skeleton was synthesized. Functional groups were connected with alkylether chains which were effective for the increase of solubility in organic solvents.

We synthesized the polymer **3** through the route shown in Scheme 1. The reaction of p-hydroxybezaldehyde with 1,8-dibromooctane in DMF was conducted in the presence of K_2CO_3 at reflux temperature to obtain 4-(8-bromooctane-1-oxy)-benzaldehyde, **4** (yield 75%). The mixture of the compound **4** and 4,4'-dihydroxytriphenyl amine was refluxed under the presence of K_2CO_3 in DMF to give 4,4'-bis-[8-(p-formyl-phenoxy)-octane-1-oxy]-triphenylamine, monomer **5**. After purification by column chromatography, we obtained the monomer **5** in 84% yield.[14]



Scheme 1. Synthetic route of polymer **3**.

The synthesis of polymer **3** was conducted with monomer **5** and 1,4-xylylene-bis-(triphenylphosphoniumbromide) in a mixture of chloroform and ethanol. A sodium methoxide solution (28% in methanol) was added to the reaction solution and the reaction mixture was stirred for 24 h. at room temperature (yield 79%).[15]

The structure of polymer **3** was determined by using ^{1}H NMR spectra, IR spectra, and elemental analysis. In ^{1}H NMR spectra, the aldehydic peak, δ 9.90 of monomer **5** disappeared perfectly in polymer **3**. The IR spectrum of polymer **3** showed the perfect disappearance of aldehydic peaks at 2726 cm^{-1} and 1653 cm^{-1} and the appearance of trans vinylic peak at 953 cm^{-1}. The glass transition temperature of polymer **3** was determined to be 47 ℃ from DSC measurements.

We fabricated single-layer device using polymer **3**. As an anode, an indium-tin-oxide (ITO) coated glass substrate was used. Thin film of polymer **3** was spin-coated from a 1.8 wt% hot chloroform solution. The spin-coated film was dried in vacuum at 45 ℃. The thickness of the polymer **3** film was about 130-150 nm. The upper cathode made of MgAg (9:1) alloy was deposited

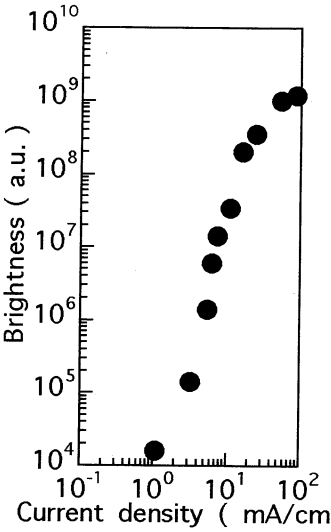


Figure 1. Relationships between brightness and current density in the single-layer device.

on the polymer **3** film. The thickness of the cathode was 200 nm and the size of an emitting area was 2x2 mm^2.

All measurements, such as brightness-current density-voltage relationships and EL spectra were conducted at room temperature under vacuum atmosphere. When dc bias voltage was applied to the device, current increased with the increase of applied voltage and high blue emission was observed. The maximum current density, 87.5 mA/cm^2 was observed at the applied voltage of 28 V. Figure1 shows the brightness-current density relationships in the single-layer device. The maximum luminance of about 22 cd/m^2 at the current of 87.5 mA/cm^2 was observed. These results demonstrate that both holes and electrons were injected well into the polymer **3**.

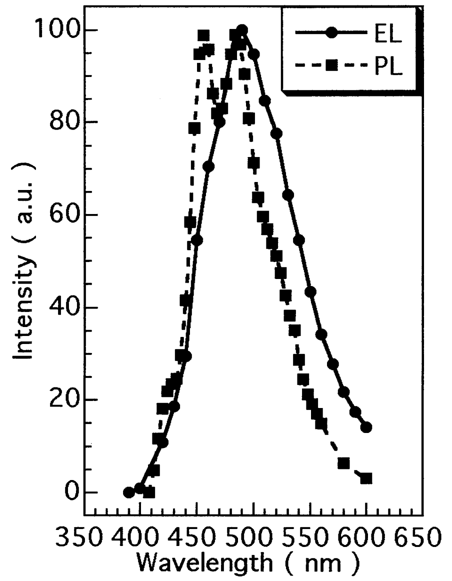


Figure 2. The EL spectrum for the single-layer device and PL spectrum of the polymer **3** thin film.

In Figure 2, the EL spectrum is compared with the photoluminescence (PL) spectrum of the polymer **3** thin film. The EL spectrum showed the maximum peak at 488 nm and well corresponded to the PL spectrum except for small differences arising from the difference in vibronic structures. Evidently EL emission is due to the excitation of the distyrylbenzene chromophore on the skeleton of the polymer **3**.

In conclusion, we successfully synthesized EL polymer **3** which had both charge transport and emissive capabilities. The experimental efforts to modify the molecular structures in polymer **3** are in progress.

References and Notes

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14 Monomer **5**: ^{1}H NMR (CDCl$_3$): δ9.90 (s., 2H, H-C=O), 6.75-8.25 (m., 21H, aromatic H), 4.17 (t., 8H, O-CH$_2$), 1.25-2.35 (m., 24H, C-(CH$_2$)$_6$-C); IR (KBr): 2726 cm^{-1} (H-C=O, C-H stretching), 1653 cm^{-1} (C=O, C-O stretching); Found: C 77.44%; H 7.50%; N 1.84%. Calcd. for molecular formula: C 77.70%; H 7.47%; N 1.89%.
15 Polymer **3**: ^{1}H NMR (CDCl$_3$): δ6.45-7.90 (m., 29H, aromatic H and -CH=CH-), 4.05 (t., 8H, O-CH$_2$), 1.10-2.35 (m., 24H, C-(CH$_2$)$_6$-C); IR (KBr): 953 cm^{-1}(-CH=CH-, trans C-H bending); Found: C 82.82%; H 7.57%; N 1.73%; Calcd. for molecular formula: C 82.08%; H 7.60%; N 1.71%.