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

Synthesis of Polymer with Bisstyrylanthracene Chromophore on Polymer Skeleton and Application to Electroluminescent Devices

Dong Uk Kim [a] & Tetsuo Tsutsui [a]

[a] Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, 816, Japan

Version of record first published: 04 Oct 2006.

To cite this article: Dong Uk Kim & Tetsuo Tsutsui (1996): Synthesis of Polymer with Bisstyrylanthracene Chromophore on Polymer Skeleton and Application to Electroluminescent Devices, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 280:1, 325-329

To link to this article: http://dx.doi.org/10.1080/10587259608040351

Mol. Cryst. Liq. Cryst., 1996, Vol. 280, pp. 325–329
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS OF POLYMER WITH BISSTYRYLANTHRACENE CHROMOPHORE ON POLYMER SKELETON AND APPLICATION TO ELECTROLUMINESCENT DEVICES

DONG UK KIM and TETSUO TSUTSUI
Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816, Japan.

Abstract Novel EL polymer, in which 9,10-bis[4-(N,N-diphenylamino)-styryl]anthracene chromophore (polymer-BSA) was synthesized. Two kinds of EL devices were fabricated: One is a single-layer device, ITO/polymer-BSA/MgAg, and the other is a double-layer device, ITO/polymer-BSA/OXD-7/MgAg, in which a vacuum-sublimed 1,3-bis(4-tert-butylphenyl-1,3,4-oxadiazolyl)phenylene (OXD-7) layer plays the roles of electron transport and hole blocking. The quantum efficiency of the double-layer device was observed about 60 times higher than that of the single-layer device. In the double-layer device, the maximum current density of 40 mA/cm^2 was observed at the applied voltage of 23 V and the maximum luminance was about 60 cd/m^2. EL spectra of the single-layer and double-layer devices have peaks at about 595 nm, which coincided with a photoluminescence spectrum of a polymer-BSA film.

INTRODUCTION

Electroluminescent (EL) devices have attracted much attention, since sublimed-dye devices which were composed of multilayer structures demonstrated excellent EL efficiency.[1,2] A lot of studies in recent years have contributed for the better understanding of not only emission mechanisms but also device-design concepts for high EL performance. Studies using fully π-conjugated polymers have also been performed.[3] Polymer materials, in general, have thermal stability and good processibility. In these view points, polymer materials have emerged as one of promising material systems for EL devices. Currently, various classes of polymer materials such as fully π-conjugated polymers, polymers with chromophores on main chains or side chains, and polymer-dispersed dye films have been reported to be useful for fabrication of EL devices.[4-7]

Among various EL material systems, multilayer EL devices made of vacuum-sublimed dye films revealed the most excellent EL performance. Polymers with emissive chromophore units in polymer chains may be one of the most suitable materials containing both high EL performance and intrinsically high durability.

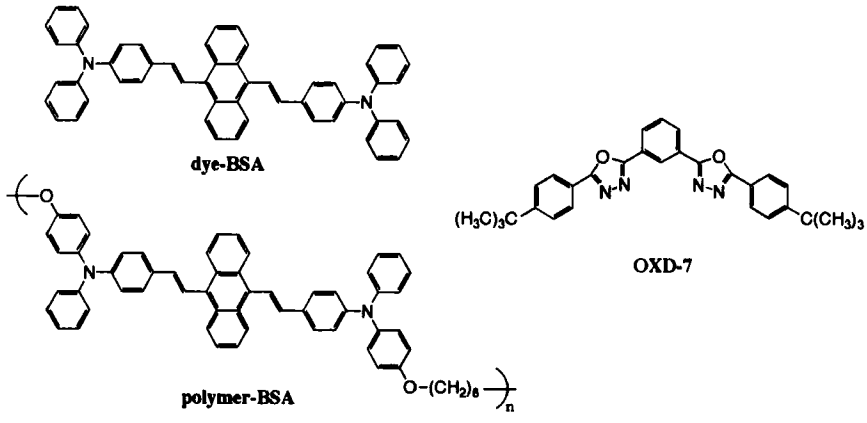


FIGURE 1 Molecular structeres of polymer-BSA and dye-BSA and OXD-7

Additionally, polymers with chromophores reveal more flexibility in molecular design in comparison with the cases in fully π-conjugated polymers. Based on these considerations, we have been trying the extension of our molecular design concepts.[9-10] In this paper, we report the synthesis of one of EL-polymers and its application to EL devices. In our previous report, we demonstrated that 9,10-bis[4-(N,N-diphenylamino)-styryl]anthracene (dye-BSA) is excellent for the use for a vacuum-sublimed single-layer device.[8] Thus we planed the synthesis of polymer-BSA which was composed of the same emissive chromophore as dye-BSA. The molecular structure of polymer-BSA was shown in Figure 1. For the evaluation of this new EL polymer, we fabricated two kinds of EL devices, single-layer and double-layer devices. In the double-layer device, OXD-7 dye was employed as an electron transport layer.

SYNTHESIS OF EL POLYMER

The synthetic route for polymer-BSA was shown in Figure 2. Phosphorousoxychroride (13.2 mmol; 4.18 g) in DMF (30 ml) was stirred at room temperature for 30 minutes. The DMF solution (10 ml) with 1,8-bis(triphenylamine-4-oxy)octane, 1 (6.6 mmol; 4.18 g) which was obtained by the reaction of 1,8-dibromooctane and 4-hydroxytriphenylamine was added to this mixture and stirred for a few minutes. The mixture was heated at 95 ℃ for 24 hours and NaOH solution (20% NaOH; 18 g) was added. 1,8-bis(4'-formyl-triphenylamine-4-oxy)octane, 2 (2.82 g) was obtained as 62% yield. ^{1}H n.m.r. ($CDCl_3$): δ 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), 1655cm^{-1} (C=O, C-O stretching); Elemental analysis: calcd., C 80.21

%, H 6.44 %, N 4.07 %; obsd., C 80.18 %, H 6.51 %, N 4.00 %.

To a mixture (15 ml) of chloroform and ethanol (3/1), 2 (0.38 mmol; 0.26 g) and 9,10-anthracenedimethylbis(diethylphosphonate) (0.38 mmol; 0.18 g) were added at room temperature. A sodium methoxide solution (28% in methanol; 0.13 ml) was added to the mixture and stirred at room temperature for 24 hours. The reaction solution was added slowly into ethanol (250 ml). The precipitates were collected and dried under vacuum. Polymer-BSA (0.16 g) was obtained as 51 % yield. ^{1}H n.m.r. ($CDCl_3$): δ 6.46-8.68 (m, 34H, aromatic H), 6.46-8.68 (m, 4H, -HC=CH-), 4.02 (t, 4H, O-CH_2-), 1.22-2.08 (m, 12H, C-$(CH_2)_6$-C); i.r. (KBr): 950 cm^{-1} (-HC=CH-, trans C-H bending); Elemental analysis: calcd., C 86.68 %, H 6.34 %, N 3.26 %; obsd., C 83.60 %, H 6.26 %, N 3.01 %.

The glass transition temperature of the polymer BSA was found to be 49 °C from a DSC analysis.

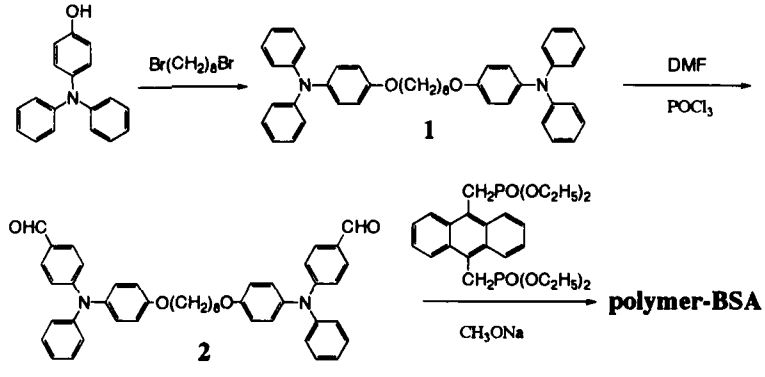


FIGURE 2 Synthetic route of polymer-BSA

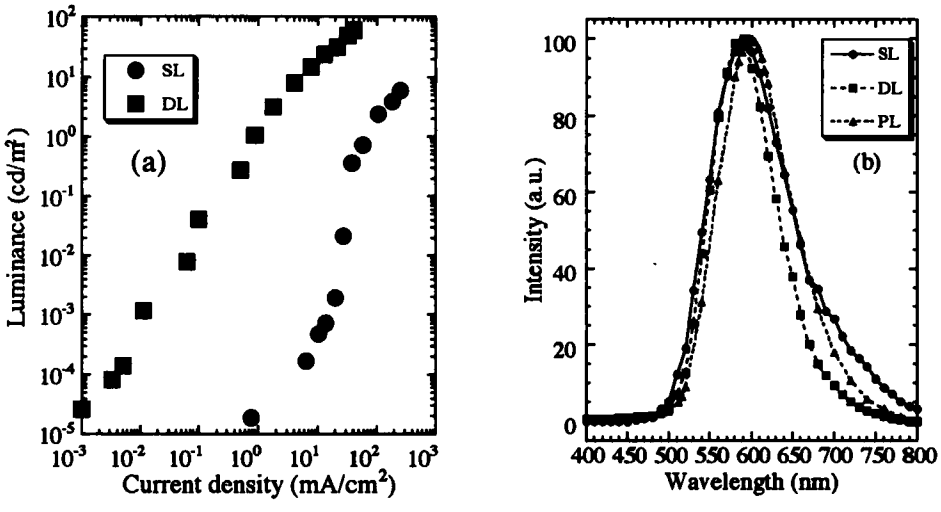
FABRICATION AND EVALUATION OF EL DEVICES

Indium-tin oxide (ITO)-coated glass was etched to give ITO stripes of 2 mm width as an anode.. The patterned ITO-coated glass was cleaned with a detergent, deionized water, acetone and ethanol in sequence, and then dried. On ITO-coated glass, BSA-polymer was deposited by spin-coating from a 2.4 % benzene solution and dried at 45 °C in a vacuum oven. The polymer thin film looked to be homogeneous through an optical microscope and the film thickness was determined to be about 100 nm using a dual-beam interference microscope. On top of polymer layers, stripes of MgAg (weight ratio 9:1) alloy films as a cathode were codeposited from the Mg and Ag sources. The MgAg layer was 200 nm in thickness. In the case of a double-layer device, a 30-nm-thickness OXD-7 layer was deposited before the deposition of a MgAg layer.

Electroluminescent characteristics of the EL devices were measured in a vacuum cryostat with quartz windows for the purpose of avoiding possible degradation due to moisture in air.

RESULTS AND DISCUSSION

In comparison between the i.r. Spectrum of polymer-BSA and that of the compound 2, appearance of the peak of 950 cm^{-1} clearly revealed the formation of phenylene vinylene linkage in the designed polymer, and then the aldehydic characteristic peaks of 2 at 2710 cm^{-1} and 1655 cm^{-1} disappeared perfectly. The molecular structure of polymer-BSA was analyzed through ^1H n.m.r. and elemental analysis, the results of which indicated that the designed polymer was synthesized. Polymer-BSA revealed high solubility in common organic solvents, and thin films obtained through spin-coating appeared homogeneous. We designed polymer-BSA and synthesized it with the view point of the ease of polymer synthesis, good solubility in common organic solvent and high EL efficiency. Figure 3 (a) demonstrates current density-luminance relationships in the single-layer and double-layer devices. In the single-layer device, luminance revealed rapid increase in the current density over 10 mA/cm^2 as the current density increased. In result, about 6 cd/m^2 of luminance was observed at the maximum current density of 250 mA/cm^2, in which the quantum efficiency was calculated to be 0.0008 %. In the



FIGIRE 3 (a) Current density-luminance relationships in the single-layer (SL) and double-layer (DL) devices. (b) EL spectra of the single-layer and double-layer devices, and PL spectrum of the polymer-BSA film.

double-layer device, the maximum luminance, 60 cd/m^2 was observed at 40 mA/cm^2. In comparison between the single-layer device and the double layer device, the quantum efficiency of double-layer device was about 60 times higher than that of the single layer device. This result is due to the improvement of both charge injection-balance and the hole blocking effect by the OXD-7 layer used as an electron transport layer. Figure 3 (b) revealed the EL spectra of the single-layer and double-layer devices. The photoluminescence (PL) spectrum of the BSA-polymer film is also shown. The maximum EL peaks of the two device were detected at about 595nm. These peaks are exactly the same with that of the PL spectrum. It is obvious that EL emission originated from the designed chromophore of BSA-polymer in the both devices.

CONCLUSION

We designed novel EL polymer based on the design concept on low molar dyes, and the polymer was actually synthesized. The designed polymer revealed high luminance even in the single-layer device. When we made a comparison between the single-layer and double-layer devices, the quantum efficiency of the double-layer device was higher than that of the single-layer device, which is indicating the improvement in the balanced injection and transport of holes and electrons.

REFERENCES

1. C. W. Tang and S.A. VanSlyke, Appl. Phys. Lett., 51, 913 (1988).
2. C. Adachi, S. Tokito, T. Tsutsui, and S. Saito, Jpn. J. Appl. Phys., 27, L296 (1988).
3. J. H. Burroughes, D. D. C. Bradley, A. R. Broun, R.N. Marks, K. Mackay, R. H. Friend, P. L. Burn, and A.B. Holmes, Nature, 347, 539, (1990).
4. D. Braun and A. Heeger, Appl.Phys. Lett., 58, 1982 (1990).
5. J. Kido, M. Kohda, K. Okuyama, and K. Nagai, Appl. Phys. Lett., 61, 761 (1992).
6. Z. Yang, I. SokoliK, and F. E. Karasz, Macromolecule, 26, 1188, (1993).
7. T. Tsutsui and S. Saito, in "Intrinsically Conducting Polymers, An Emerging Technology", (M. Aldissi ed., Kluwer Academic Press, The Netherlands, 1993) P. 123.
8. E. Aminaka, T. Tsutsui, and S. Saito, Jpn. J. Appl. Phys., 33, 1061 (1994).
9. D. U. Kim, T. Tsutsui, and S. Saito, Polymer, 36, 2481 (1995).
10. D. U. Kim, T. Tsutsui, and S. Saito, Chem.Lett., 1995, 587 (1995).