Macromol. Symp. ***125****, 133–142 (1997)*

SYNTHESIS AND CHARACTERIZATION OF A SOLUBLE BLUE LIGHT EMITTING ALTERNATING COPOLYMER

Hyun Nam Cho, Jai Kyeong Kim, Dong Young Kim and Chung Yup Kim*

Polymer Materials Laboratory, KIST, P.O. Box 131, Cheongryang,
Seoul 130-650, Korea.

Abstract: An alternating copolymer with monomer units of fluorene and phenylenedivinylene was synthesized by reaction between n-hexyl fluorene phosphonium salt and isophthalic aldehyde based on the Wittig reaction. The polymer solution in chloroform was made into a film with a very fine surface by spin-casting on indium-tin oxide (ITO) coated glass to fabricate a light emitting diode (LED) with an aluminum negative electrode. The optical absorption spectrum of the solid film shows a peak at 370 nm while the PL spectrum has the main peak at 560 nm with a secondary peak at 440 nm and the EL spectrum has a single peak at 560 nm showing the Stokes shift of 190 nm. The peak in the PL spectrum shifts to 420 nm with a vibronic structure at 440 nm on either dilution by chloroform or blending with polyvinylcarbazole (PVK). The emissive polymer bulk seemed to generate sites for excimers and molecular aggregates which were diminished on the dilution or blending. The peak in the EL spectrum also shifts to 440 nm on blending of 20% of the copolymer with PVK. Further dilution to 10% of the copolymer shifts the EL peak to 420 nm with the onset potential of 15 V and the highest quantum efficiency of 0.01% in this series. The concentrated channels were developed in the blends with severe phase separation to show a lower onset potential but poor quantum efficiency.

INTRODUCTION

Light emitting diodes(LEDs) fabricated with organic materials attracted much attention since their handling and color tuning were easier than inorganic semiconductors (Ref. 1). The discovery of a light-emissive polymer intensified studies on polymer-based LEDs(Ref. 2). The basic polymer has been modified to enhance processibility as well as to tune emissive color. Attaching alkoxy groups on the main chain or as pendant groups in poly(*p*-phenylenevinylene)(PPV) makes the polymer soluble in organic solvents (Ref. 3-5).

CCC 1022-1360/97/$ 04.00

Polymers such as poly(*p*-phenylene), polyalkylthiophene and polyalkylfluorene were also introduced as emissive polymers(Ref. 6-8). A few copolymers were synthesized as emissive polymers (Ref. 9-11). Polymer blends between two emissive polymers demonstrated a significant enhancement of quantum efficiency of LEDs fabricated with the blends as an emissive layer (Ref. 12-14).

In this work we have synthesized an alternating copolymer whose monomers form light emissive homopolymers and are connected covalently developing conjugation bonds between the monomers. The copolymer consists of only carbon and hydrogen to reduce ill effects such as adsorption of oxygen or moisture. The copolymer is soluble in organic solvents to result in a good processibility. A high quantum efficiency as well as a pure color are obtained by an LED fabricated with the copolymer blended with another light-emissive polymer.

EXPERIMENTAL

9-n-hexylfluorene (**1**) was synthesized by the reaction of fluorene and n-hexyl bromide using n-butyl litium in THF according to the literature procedure(Ref. 15). The light emissive polymer was synthesized as shown in Fig. 1.

Synthesis of 2.7-bis(bromomethyl)-9-n-hexylfluorene(2). A mixture of 50.0 g(0.2 mol) of 9-n-hexylfluorene, 60 g(2.0 mol) of paraformaldehyde and 500 g of 30% HBr solution in acetic acid was stirred in a 1-L three-neck flask for 24 h at 60 °C. The reaction mixture was cooled to room temperature to be precipitated as pale yellow solid powder. The powder was filtered and then extracted three times with 200 mL of dichloromethane and was washed sequentially with water and saturated aqueous solutions of $NaHCO_3$ and NaCl. The powder was dried in a vacuum oven at 40 °C to afford 74.0 g(85% yield) of white solid having a melting point of 143 ~ 145°C. ^{1}H-NMR($CDCl_3$), δ:0.88(t, 3H, CH_3), 1.25(m, 8H, CH_2), 2.01(m, 2H, CH_2), 3.98 (t, H, CH), 4.63(s, 4H, CH_2Br), 7.39-7.72(m, 6H, fluorenyl aromatic).

Synthesis of 2.7-bis(bromomethyl)-9-n-hexylfluorene triphenylphosphonium salt(3). A mixture of 43.6g(0.1 mol) of **2**, 78.7g(0.3 mol) of triphenylphosphine and 500 mL of dimethylformamide was heated to reflux in a 1-L three-neck flask on stirring for 12 h. The reactant was cooled to room temperature and added slowly to a flask with 3 L of ether while stirring. White solid precipitated was filtered, washed with ether three times and dried in a vacuum oven at 40 °C. Yield: 92.2 g(96% yield) ^{1}H-NMR($CDCl_3$), δ:0.25(br, 3H, CH_3), 1.60-1.24 (m,10H, CH_2), 2.83(t,H,CH) 5.66-5.76 (d, 4H, CH_2Br), 6.76-7.11(m, 6H, fluorenyl aromatic), 7.49-7.81(m, 30H, aromatic).

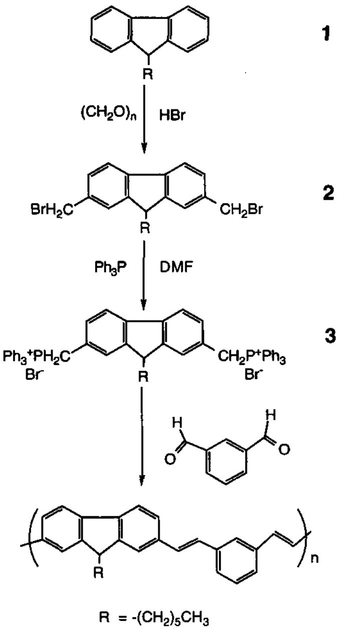

Fig. 1. Synthesis route to PHFMPV.

Synthesis of poly(9-n-hexyl-2,7-fluorenediylvinylene-alt-1,3-Phenylenevinylene)(PHFMVP). 1.92 g(2 mmol) of **3** and 0.27 g(2 mmol) of isophthalaldehyde were dissolved in a mixture of 60mL of anhydrous ethyl alcohol and 20 mL of chloroform, and 2.3 g of 5% sodium solution in anhydrous ethyl alcohol was added dropwise through syringe. The mixture was kept at room temperature for 12 h and 1 mL of 0.1 N HCl aqueous solution was added to it to end the reaction. The precipitated yellow solid was washed thoroughly with water and methyl alcohol and dried in a vacuum oven at 40 °C. Yield: 0.6g. ^{1}H-NMR(CDCl$_3$), δ:0.6-2.2 (br, m,aliphatic) 3.4-4.0(br, s, fluorene-CH), 6.4-7.8 (br, m, vinyl and aromatic). Weight average molecular weight(M_w) and molecular weight distribution(MWD) measured by gel permeation chromatography(GPC) based on polystyrene as standards were 12,700 g/mol and 5.01, respectively. THF was used as the solvent as well as the effluent.

LED device fabrication and instruments. 100 mg of PHFMPV was dissolved in 5 mL of chloroform and the solution was filtered with a pore size of 0.2 μm. The LED structure consists of an aluminum rectifying contact on the surface of the polymer which was spin-cast on ITO coated glass. The spin-cast film with a thickness of 100 nm was formed by controlling a spin rate of 1000 rpm. Aluminum was deposited onto the surface of the spin-cast film by vacuum evaporation at pressure below 10^6 torr, yielding an active layer of a circle with a diameter of 5 mm. All processing steps were carried out in air.

Optical absorption(AB) spectra were recorded with a H/P 8452A diode array spectrophotometer. Photoluminescence(PL) and electroluminescence spectra were recorded with an ISS K-2 fluorometer. The polymer was excited with ultraviolet light at 365nm for PL. I-V-L characteristics were recorded by a Keithley 236 source/measure unit for voltage-current relationship and by a Newport 818-SL photodiode for voltage-electroluminescence intensity. Surface morphology of the blends was studied using PSI Autoprobe CP atomic force microscopy.

RESULTS AND DISCUSSION

The polymer shows glass transition temperature (Tg) at 120 °C and little weight change on heating to 380 °C in N_2 as shown in Fig. 2. About 3% of weight loss on heating to 380 °C is probably attributed to evaporation of oligomers.

The AB and PL spectra of a PHFMPV film spin-cast from 2%-w/v solution in chloroform are shown in Fig. 3 along the EL spectrum of an LED fabricated with the polymer as an emissive layer sandwiched between ITO coated glass and aluminum. The AB spectrum due to a π–π^* transition rises rapidly at a wavelength of 450 nm and shows the absorption peak at 370 nm.

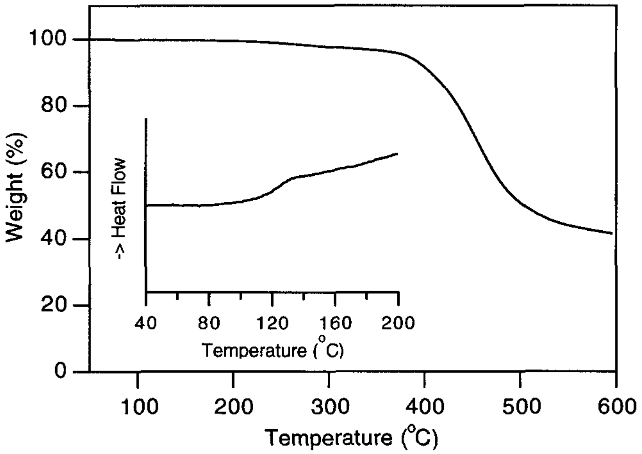

Fig. 2. TGA and DSC(inset) thermograms of PHFMPV.

The PL spectrum shows a multiple structure with a main peak at 560 nm and another one at 440 nm with Stokes shifts of 190 and 70 nm, respectively. There must be a strong absorption of PL by the emissive polymer to reduce the PL intensity around 400 nm. It is difficult to assign the emissive centers for the peaks at 440 and 560 nm. Since the excitation wavelength for PL was 365 nm, the emission peak at 440 nm was not due to the reflection of the ITO glass. The peak at 560 nm may be assigned as the radiative decay of excitons which generate the peak at 440 nm but migrate from a high energy state to a delocalized interchain state. However, there is also a possibility that PHFMPV has two chromophores to emit actively two colors. The EL spectrum is simple to have a sharp peak at 560 nm with a very weak shoulder around 500 nm. The light absorption by the emissive polymer around 450 nm is rather small since the EL spectrum overlaps only slightly the AB spectrum at the region. The radiative decay center for EL seems to be basically the same as that for PL except the site for the PL peak at 440 nm.

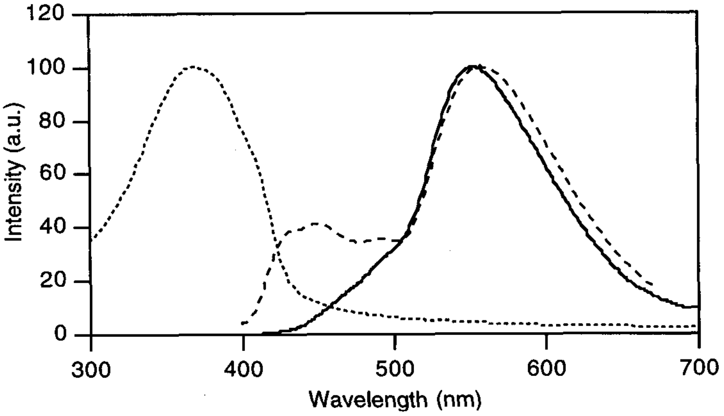

Fig. 3. AB (······), PL(- - -), and EL (—) spectra of PHFMPV.

Fig. 4 shows the effect of dilution of PHFMPV by a solvent as well as a polymer on the PL spectra. The PL spectra of a PHFMPV solution in chloroform and a blend with polyvinylcarbazole (PVK) with a blending ratio of 10/90 for PHFMPV are very different from the PL spectrum of the polymer film. The main peak at 560 nm almost disappeared while a peak at 420 nm with a fine vibronic structure at 440 nm was intensified when the emissive polymer was diluted by the solvent or the polymer. A weak PL is observed around 560 nm in the polymer/PVK blend but the polymer solution has a negligible intensity in the same region. The band width of the PL peak of the solution or the blend is rather narrow to show saturated blue color.

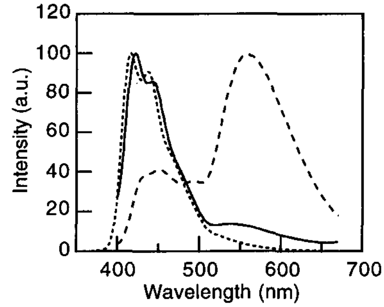

Fig. 4. PL spectra of PHFMPV in chloroform solution (10^{-6} mol/L)(- - -), solid film (——), and PHFMPV/PVK =10/90 blend film (······).

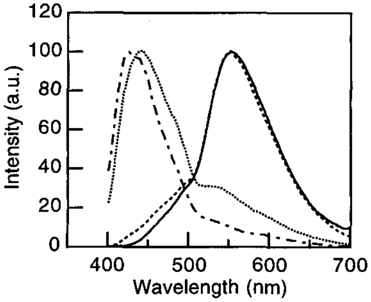

Fig. 5. EL spectra of PHFPPV/PVK blends; 100/0 (—), 50/50 (- - -), 20/80 (·······), and 10/90 (- · - ·).

The strong PL peak at 560 nm which disappeared on dilution by either the solvent or the polymer might be generated by excitons which migrated to the aromatic pairs to form excimers or aggregate states developed by interchain interactions(Ref. 16). The PL side peak at 440 nm, however, indicates existance of a high-energy gap state in the polymer bulk which traps charge carriers or excitons to result in a radiative decay with the high energy while most of the radiative decay for 560 nm are generated at the lower states.

Changes in EL spectra of PHFMPV/PVK blends with different blending ratios are shown in Fig. 5. When the two polymers have a 50/50 ratio in the blend, the EL spectrum is identical to that of the polymer alone with the emission peak at 560 nm except a slight increase in the intensity below 510 nm. However, the peak position shifts to 440 nm from 560 nm and a weak emission is observed around 560 nm when the blend has the emissive polymer of 20%. The blend with 10% of the emissive polymer shows the emissive peak at 430 nm and the emission around 560 nm shrinks further. It is apparent that the molecular arrangements for excimer formations or aggregate states were disturbed on dilution. The blend with a concentration of the emissive polymer by 10 or 20% still has enough molecular contacts between each other to generate the sites for the excimer formations and molecular aggregates and to display the emission tail in the region of 560 nm. It needs more work to clarify the mechanism of changes in the peak position of the EL spectra of the blends. It is, however, possible to tune emissive color and to enhance the EL intensity by lowering the blending ratio of the emissive polymer.

Fig. 6 shows atomic force micrographs(AFM) of blends of PHFMPV with PVK. Phase separation is clearly observed for the blends with ratios of 75/25 and 50/50 between PHFMPV and PVK. The black spots were identified as PHFMPV-rich domains. The blend with a ratio of 20/80 between the two polymers also showed phase separation morphology although the size of the black domains is much smaller than that of the blends with higher concentrations of PHFMPV. The separation is not clear in the blend with a ratio of 10/90. The AFM with phase separation information is well correlated with the PL and EL spectra. Large domains of PHFMPV in the blends seem to generate the PL and EL emission peaks at 560 nm. The delocalized interchain state is present in the blends with a concentration of PHFMPV of 50% or higher. When the emissive polymer molecules with a concentration of 20% or lower in a blend are dispersed homogeneously in a matrix, there are less aggregates of the emissive polymer to result in radiative decay of excitons at a high energy state and to show the EL peak shifted to the lower wavelength.

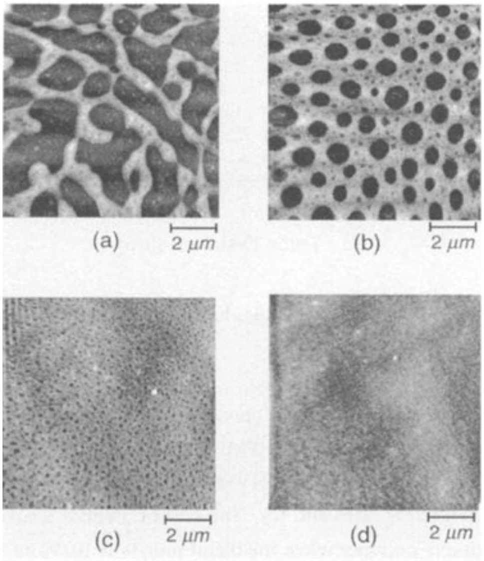

Fig. 6. AFM images of PHFMPV/PVK blend films. (a) 75/25, (b) 50/50, (c) 20/80, and (d) 10/90.

It was found that the role of PVK in the blend was not only a diluent but a charge transporter. When PHFMPV was blended with polymethylmethacrylate (PMMA) or polystyrene(PS), the PL peak shifted from 560 nm to 440 nm as was observed for the blends with PVK and the PL intensity was enhanced to prove to be used as a diluent. However, an LED with the blend of PMMA or PS with the emissive polymer showed no rectifying effect and emitted no light before breakdown on applying higher than 20 V.

The indentation profiles of the surface morphology of the spin-cast films were deduced from AFMs as shown in Fig. 7. The surface of the blend with the ratio of 75/25 or 50/50 between PHFMPV and PVK is very rough and becomes smoother with a low concentration of PVK in the blend. It was cleared that the PVK-rich domains protruded above the PHFMPV-rich domain surface when a PVK concentration in the blend was 25 or 50%. The severe surface roughness might be caused by the difference in the evaporation rate of chloroform from the two polymers.

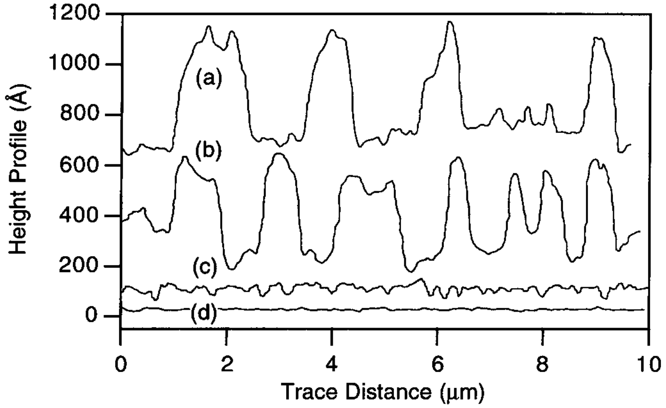

Fig. 7. Height profiles of PHFMPV/PVK blends in AFM imges. (a) 75/25, (b) 50/50, (c) 20/80, and (d) 10/90.

Fig. 8(a) shows current through LEDs on various bias potentials. The onset potential of an LED with a single component of PHFMPV for light-emitting is 15V. The onset potential decreased to less than 10V when PHVMPV was blended with PVK with ratios of 75/25 or 50/50 as shown in Fig. 7(b) and (c). The onset potential recovered to that of the LED with the pure emissive polymer when the blend ratio was 10/90 as shown in Fig. 7(d). Quantum efficiency was calculated as 0.01% photons/electron for the LED with the blend of 10/90 while all others showed poor results by one order.

A high current was observed at a low bias potential when the polymer blends have the morphology of distinctive phase separation. The indentation profiles of the surface morphology of the spin-cast films [Fig. 6(a) and (b)] show a possibility of thinning effect of the emissive layer at the PHFMPV-rich domains. The emissive layer experiences effects of both film-thinning and higher bias potential in a smaller surface area. The blend with 10% of PHFMPV makes a much smoother surface [Fig. 6(d)] causing no narrow channel for the current flow shows a high onset potential of 15 V.

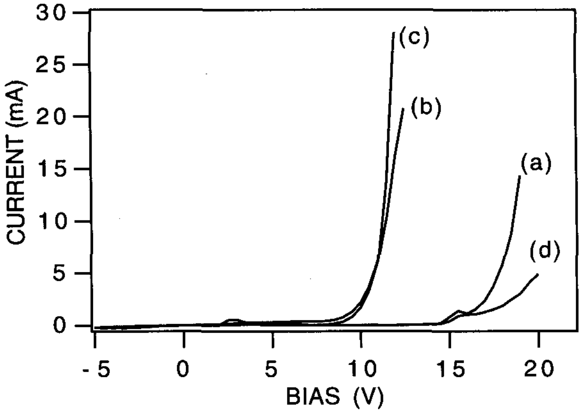

Fig. 8. I-V characteristics of PHFMPV/PVK blends with LED structure of ITO/polymer/Al layers. (a) 100/0, (b) 75/25, (c) 50/50, and (d) 10/90.

SUMMARY

A light emissive alternating copolymer whose homopolymers are both light emissive was synthesized by the Wittig reaction. The polymer is thermally stable with high Tg and degradation temperature. The soluble polymer was spin-cast on the anode for fabrication of an LED. The PL and EL spectra showed a high Stokes shift from the AB spectrum but dilution of the polymer by chloroform or blending with PVK shifted the emission peak of green color to a higher energy for blue color. The interchain interactions seemed to develop excimers and molecular aggregates whose sites were diminshed on the blending with PVK or removed almost on dilution in chlorofom. The emissive polymer made a poor blend with PVK and the phase separation disappeared finally with the concentration of 10%. The emission peak of EL shifted to blue color by 140 nm on blending with the PVK concentration of 80% or higher. The poor blends showed a low onset potential for emissive current due to the concentrated channels developed on the phase separation. The highest quatum efficiency of 0.01% was calculated on the LED fabricated with the emissive polymer of 10% in the blend.

REFERENCES

(1) C.W. Tang and S.A. Vanslyke, *Appl. Phys. Lett.* **51**, 913 (1987).

(2) J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns, and A.B. Holmes, *Nature* **347**, 539 (1990).

(3) D. Braun and A.J. Heeger, *Appl. Phys. Lett.* **58**, 1982 (1991).

(4) N.C. Greenham, S.c. Moratti, D.D.C Bradley, R.H. Friend, and A.B. Holmes, *Nature* **356**, 628 (1993).

(5) Z. Yang, I. Sokolik, and F.E. Karasz, *Macromolecules* **26**, 1188 (1993).

(6) G. Grem, G. Leditzky, B. Ulrich, and G. Leising, *Adv. Mater.* **4**, 36 (1992).

(7) Y. Ohmori, M. Uchida, K. Muro, and K. Yoshino, *Jpn. J. Appl. Phys.* **30**, L1938 (1991).

(8) Y. Ohmori, M. Uchida, K. Muro, and K. Yoshino, *Jpn. J. Appl. Phys.* **30**, L1941 (1991).

(9) R.M. Tarkka, X. Zhang, and S.A. Jenekhe, *J. Am. Chem. Soc.* **118**, 9438 (1996).

(10) H.L. Wang, J.W. Park, M.J. Marsella, D.K. Fu, T.M. Swager, A.G. MacDiarmid, Y.Z. Wang, D.D. Gebler, and A.J. Epstein, *Polym. Prep.* **36**, 45 (1995).

(11) J.K. Kim, S.I. Hong, H.N. Cho, D.Y. Kim, and C.Y. Kim, *Polym. Bull.* **38**, 169 (1997).

(12) J.I. Lee, I.N. Kang, D.H. Hwang, H.K. Shim, S.C. Jeoung, and D.H. Kim, *Chem. Mat.* **8**, 1925 (1996).

(13) M. Berggren, M. Grandström, O. Inganäs, and M. Andersson, *Adv. Mater.* **7**, 900 (1995).

(14) J.Y. Park, H.M. Le, G.T. Kim, H. Park, Y.W. Park, I.N. Kang, D.H. Hwang, and H.K. Shim, *Synth. Met.* **79**, 177 (1996).

(15) H.N. Cho, D.Y. Kim, Y.C. Kim, J.Y. Lee, and C.Y. Kim, *Adv. Mater. in press.*

(16) D.R. Baigent, A.B. Holmes, S.C. Moratti, and R.H. Friend, *Synth. Met.* **80**, 119 (1996).