Macromol. Symp. ***143***, *221–230 (1999)*

Electroluminescence in Alternating Copolymers with the Acetylene Unit

Dong Young Kim, Jae Min Hong, Jai Kyeong Kim, Hyun Nam Cho, and Chung Yup Kim

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

SUMMARY: 2,7-diethynyl-9,9'-di-n-hexylfluorene and 2,7-dibromo-9,9'-di-n-hexylfluorene were alternately bonded with each other by a Heck reaction to produce poly(9,9'-di-n-hexyl-2,7-fluorenyleneethynylene). The alternating copolymer emitted blue color with the peak maximum at 475 nm on excitation either at 340, 365 or 400 nm. The principal emission maximum shifted to 425 nm on excitation at 340 nm when the polymer was blended with polyvinylcarbazole(PVK). Light-emitting diodes (LEDs) fabricated with the alternating copolymer sandwiched between indium-tin oxide glass and Al emitted a light with the peak maximum at 550 nm. The peak maximum shifted to 425 nm when the copolymer was blended with PVK with the blending ratios between 5 to 20% of the emissive copolymer.

Introduction

Light-emitting diodes (LEDs) fabricated with light emissive polymers showed a significant progress since its introduction.1) Prototypes of LEDs emitting green, yellow, orange and red colors have been displayed at several occasions indicating that the fabrication of LEDs was almost perfected.2)

There were many attempts to design polymer molecules which emitted blue color. Polydihexylfluorene3) and polyparaphenylene4) were introduced in the early stage of the development. A polythiophene derivative5) and derivatives of polyparaphenylene with a ladder structure6,7) were also known to emit blue color. Copolymers based on fluorene8,9) or pyridine10) were introduced as emissive polymers for blue color. These polymers have either aromatic or heterocyclic units in the main chain and some of them are interconnected with vinylene or acetylene units. Most of the polymers described here have conjugation throughout the individual molecules but there are some exceptions.11,12) The emissive

CCC 1022-1360/99/$ 17.50+.50/0

polymers give a big advantage on processing if the polymers or their precusors are soluble. The emissive polymers are spin-cast to make very homogeneous films on a substrate such as indium-tin oxide (ITO) glass or a charge transporting layer

The present work designs to synthesize a copolymer which emits blue color on photoexcitation and is soluble in organic solvents for a good processibility. An alternating copolymer with units of fluorene and acetylene was synthesized by a Heck reaction and its photoluminescence and electroluminescence properties are examined.

Experimental

Materials

Fluorene, tetrakis(phenylphosphine)palladium [$(PPh_3)_4Pd$], bis(triphenylphosphine) palladium dichloride [$(PPh_3)_2PdCl_2$], trimethylsilyl acetylene, polymethylmetacrylate (PMMA) and polyvinylcarbazole(PVK) were supplied by Aldrich and used as received. The rest of chemicals used were a reagent grade. Synthesis of 2,7-dibromo-9,9'-di-n-hexylfluorene (I) was introduced previously.[13)]

Synthesis of 2,7-bis[(trimethylsilyl)ethynyl]-9,9'-di-n-hexylfluorene

In a 1 L three-neck flask equipped with a stirrer, a thermometer and a reflux condenser, 49.2g (0.1 mol) of 2,7-dibromo-9,9'-di-n-hexylfluorene, 3.95 g (5 mmol) of bis (triphenyl-phosphine) palladium dichloride [$(PPh_3)_2PdCl_2$], and 0.95 g (5 mmol) of copper iodide were mixed with 400 mL of piperidine. 21.6 g (0.22 mol) of trimethylsilyl acetylene was slowly dropped in the flask at room temperature. The reaction temperature was then slowly increased and the reactant was refluxed for three hours. The solvent was stripped off from the reactant under a reduced pressure followed by extraction three times with benzene and washing with distilled water several times. The reactant was dried by anhydrous magnesium sulfate and then bleached by active carbon. Thereafter, the product was filtered and stripped off solvent to obtain milky solid material. It was recrystallized twice using ethanol to get crystalline granules. The granules were fully dehydrated in a vacuum oven at 30 °C. The product was weighed 42g with a yield of 80% and the melting temperature was 126-128 °C. ^{1}H-NMR ($CDCl_3$), δ 0.28 (s, 18H, $SiCH_3$), 0.52 (br, s 6H, CH_3), 0.73-1.12

(m, 16H, CH_2), 1.89-1.97 (m, 4H, CCH_2), 7.42-7.61 (m, 6H, aromatic group). IR (KBr) : 2156 ($C\equiv C$), 852 ($SiCH_3$).

Synthesis of 2,7-diethynyl-9,9'-di-n-hexylfluorene

27.4g (52 mmol) of 2,7-bis[(trimethylsilyl) ethynyl]-9,9'-di-n-hexyl fluorene and 4.53g (78 mmol) of potassium fluoride were dissolved into a mixture of 5 mL water and 150 mL dimethyl formamide in a 250 mL flask equipped with a stirrer and a thermometer. The reactant was left at room temperature for 6 hours. The reactant was then poured into 500 mL of ice water and the resultant material was extracted three times with ethyl ether. The extracted solution was dried over magnesium sulfate. After filtering, the solvent was stripped off to obtain viscous liquid, which was then refined using a silica gel column (ethylacetate/hexane = 1/10 of solvent mixture) followed by recrystallization in ethanol. Soft yellow solid material of 17.1 (86%) was obtained and the melting point was 36-37 °C. ^{1}H-NMR ($CDCl_3$), δ 0.58 (br, 6H, CH_3), 0.76-1.13 (m, 16H, CH_2), 1.93-1.96 (m, 4H, CCH_2), 3.14 (s, 2H, CH), 7.46-7.65 (m, 6H, aromatic group), ^{13}C-NMR ($CDCl_3$), δ 13.90 (CH_3), 22.34, 23.68, 29.62, 31.47, 40.22 (CH_2), 55.23 (quaternary), 77.28 ($\equiv CH$), 84.54 ($C\equiv$), 119.95, 120.92, 126.58, 131.26, 141.01, 151.09 (aromatic group), IR (KBr) : 3296 ($\equiv CH$).

Synthesis of poly(9,9'-di-hexyl-2,7-fluorenyleneethynylene)(PDHFA)

Under nitrogen atmosphere, 0.76g (2 mmol) of 2,7-diethynyl-9,9'-di-n-hexyl fluorene, 0.89 g (1.8 mmol) of 2,7-dibromo-9,9'-di-n-hexyl fluorene, 62.8mg (0.4 mmol) of bromobenzene, 92.4 mg (0.08 mmol) of tetrakis(triphenylphosphine)palladium [$(PPh_3)_4Pd$] and 15.2 mg (0.08 mmol) of cuprous iodide were dissolved in a mixture of 50 mL of toluene and 20 mL of diisopropylamine in a 100 mL flask equipped with a stirrer and then polymerized at 70 °C for 2 hours. 0.16g (1.0 mmol) of bromobenzene was then mixed with the reactant for end-capping the polymer for 2 more hours. The reaction temperature was lowered to a room temperature and the reactant was dropped into 1 L of methanol to precipitate the polymer. The precipitated solid was filtered, disssolved in chloroform and precipitated again with methanol to obtain refined solid, the resultant solid was washed with methanol and dried in a vacuum oven at 40 °C. As a result, 1.42 g of the polymer as yellow solid was obtained. The weight average molecular weight and molecular weight distribution measured by gel permeation chromatography using THF as an eluent based on polystyrene standards were 16,800 and 2.97, respectively. ^{1}H-NMR ($CDCl_3$), δ 0.5-1.2 (br, m, CH_3, and CH_2), 1.9-2.1 (br, m, CCH_2), 7.3-7.7 (br, m, aromatic). The polymer synthesis was illustrated in Fig. 1.

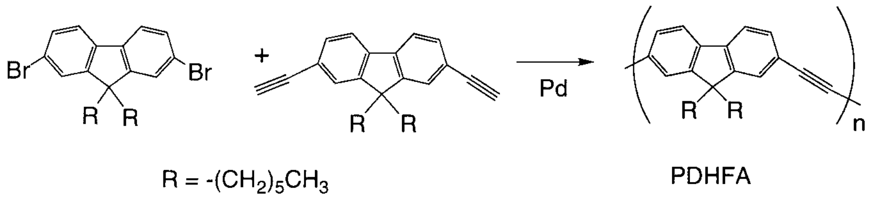


Fig. 1: Synthesis Route to PDHFA.

Measurement

Ultraviolet-visible (UV-VIS) spectra were recorded with a HP 8452 Diode Array Spectrophotometer. Photoluminescence (PL) spectra were recorded from the films or the polymer solution cells with the concentration of 10^{-5} mol/L and the spacer of a 100 μm-thick film cells with an ISS K-2 Fluorometer. The LEDs were fabaricated by sandwiching the emissive polymer between ITO glass and Al. The copolymers was spin-cast in air on the ITO glass from a 2% solution in chlorobenzene with a spin rate of 2,000 rpm to give the film thickness of 100 nm. Al was deposited on the surface of the spin-cast film by vacuum evaporation at pressure below 10^{-6} torr, yielding an active layer of a 2 mm x 10 mm rectangular spot. Electroluminescence (EL) spectra of the LEDs were reproduced by employing the fluorometer used in the PL measurement. 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 the voltange-electroluminescence intensity.

Results and Discussion

The spectra of UV-visible absorption (AB) and PL of the copolymer film along that of the solution were shown in Fig. 2. The π-π^* ($^1B \leftarrow {}^1A$) electronic transition was observed at 380 nm with two shoulders at 365 and 415 nm. The PL spectrum of the copolymer excited at 365 nm showed the emission peak at 475 nm with a broad shoulder at 545 nm and a weak one at 425 nm. The fluorophore generating the emission maximum at 475 nm may have the same electronic structure of the alternating copolymer between fluorene and vinylene units.[8] The shoulder at 545 nm might be assigned as an excimer or an interchain aggregate emission peak.[9]

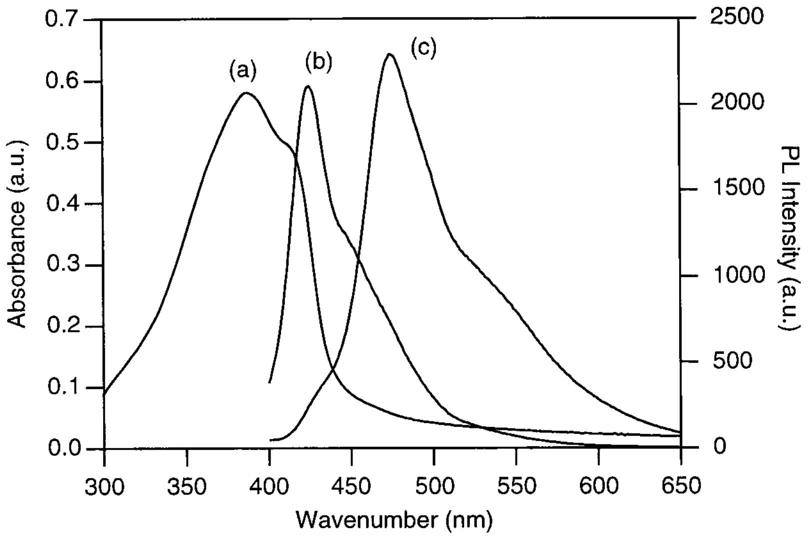


Fig. 2: AB (a) and PL spectra of PDHFA in dilute solution (10^{-5} M) (b) and solid film (c).

When the copolymer was diluted to 10^{-5} mol/L in chloroform, the emission peak shifted to higher energy by 50 nm. It is generally known that a PL emission peak shows a blue-shift when the polymer is diluted in a solvent.[14] The shift, however, was too large and might not be due to the solvent effect. It seems that the weak shoulder at 425 nm in the PL spectrum from the solid copolymer was intensified on dilution in chloroform. The peak might be assigned as the PL emission of the fluorene unit in the polymer.[15] The PL spectrum of the film has the full width at half maximum(FWHM) less than 100 nm giving clean prussian blue color. There is a strong possibility of the energy transfer between two fluorophores to enhance the PL emission generated by the lower energy fluorophore for 475 nm on an expense of the higher one for 425 nm.[16] The solution brought more kinks to the polymer main chain to reduce the molecular coplanarity by isolating the fluorene unit from the acetylene unit and to confine the excitons in the higher energy fluorophore.[17] The PL emission maximum from the solid film at 475 nm might be reduced to the shoulder of the PL maximum in the solution. The distinct shoulder at 545 nm from the solid film almost disappeared on dilution to prove the existence of excimers in the solid film.

The dilution effect of PDHAF was examined again by blending the copolymer with PMMA which was inactive on photoexcitation. The excitation and the emission spectra of the blend were shown in Fig. 3. The emission maximum at 475 nm was delivered by excitation of the fluorophore either at 365 or 400 nm. The emission intensity is higher on excitation at 400 nm than at 365 nm. The contribution of the excitation energy at 365 and 400 nm to the emission maximum at 475 nm on the photoexcitation decreased monotonically on the dilution of the polymer in PMMA as shown in the inset of Fig. 3. The PL intensity on excitation at 340 nm also decreased monotonically with a decrease of the PDHFA concentration in the blend. The bump at 520 nm shrank with a decrease of the PDHFA concentration. It is interesting to observe that the weak peak at 425 nm increased with an increase of the PMMA concentration. It seems that the low concentration of PDHFA in PMMA might experience a decrease of the coplanarity by the dilution effect to cause a kink between the units of fluorene and acetylene.

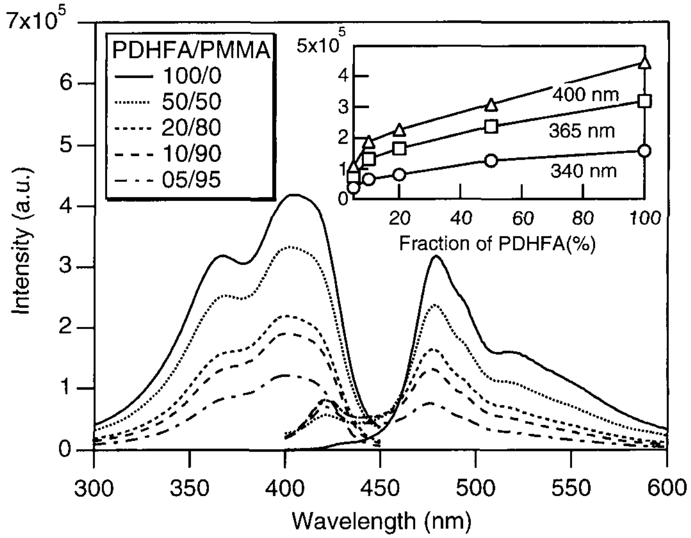
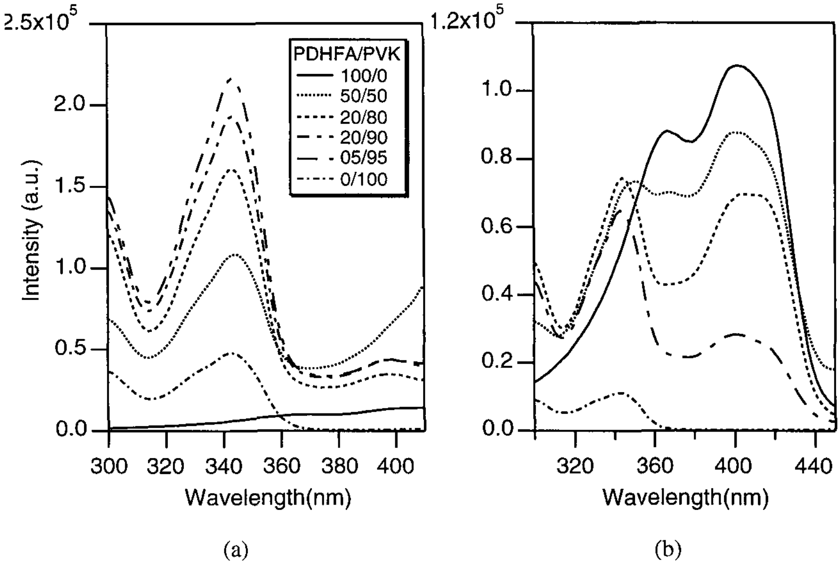


Fig. 3: PL spectra excited at 365 nm (right) and excitation spectra at 475 nm (left) of PDHFA/PMMA blends. Inset shows the PL intensity changes at 475 nm with different excitation wavelengths.

The excitation spectra of the blends of PDHFA with PVK at 425 and 475 nm were different from each other as shown in Fig. 4. The emission at 425 nm failed to be detected on excitation of PDHFA alone at any excitation energy as shown in Fig. 4 (a) (the solid spectrum). However, the polymer emitted blue color at 425 nm when the blends with PVK were excited at 340 nm. The highest emission intensity at 425 nm was observed from the blend with only 5% of the emissive polymer. The emission intensity decreased with an increase of the emissive polymer concentration in the blend. It was noticed that PVK also emitted blue color at 425 nm on excitation at 340 nm but with a much lower intensity.



(a) (b)

Fig. 4: Excitation spectra of PDHFA/PVK blends contributed to the PL emission at 425 nm (a) and 475 nm (b).

The highest contribution of the excitation energy to the emission intensity at 475 nm was 400 nm followed by 365 nm for PDHFA as shown in Fig. 5(b). The blends, however, displayed that the emission intensity at 475 nm decreased with a decrease of the emissive polymer concentration on excitation at either 365 or 400 nm. The emissive contribution of the excitation at 340 nm to the emission at 475 nm was also detected in PVK. It is clear that the emission intensities at 425 and 475 nm were enhanced with an increase of the PVK concentration in the blends. It seems that PVK with a poor extinction coefficient is capable of transfering effectively the absorbed energy on the π-π* transition to the fluorophores for the emissions at 425 and 475 nm.

A strong excimer emission was observed from LEDs fabricated with the blends as shown in Fig. 5. The EL emission spectrum of the LED with 100% PDHFA as the emission layer showed the broad structured band with two relative maxima at about 550 and 480 nm. The peak at 480 nm might be assigned as the fluorophore emitting the light at 475 nm in PL. Since the LEDs fabricated with the blends show that the emission maximum at 565 nm shrank as the PVK concentration was increased in the blends, the majority of the photo responsive chemical moieties disappeared to prove the broad structured band as the excimer emission. The further increase of the PVK ratio in the blends developed the new band maximum at 425 nm with a negligible emission at 565 nm.

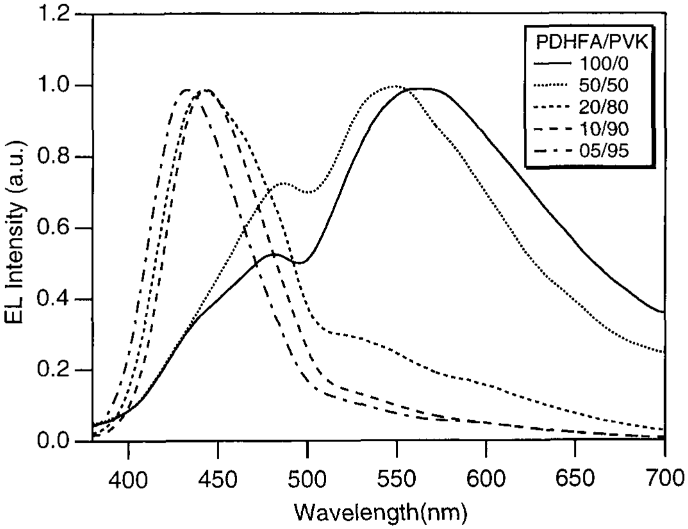


Fig. 5: EL spectra of PDHFA/PVK blends.

When the first π-π* (^1B <– ^1A) electronic transition was imposed on excitation of the solid film, there should be a high concentration of the coplanar unit formed on the sequential chemical structure of fluorene and acetylene units. With dilution of PDHFA with PVK, a kink might be developed between the two units of fluorene and acetylene to inhibit formation of the dimer moiety either by dilution of the fluorophores or by stearic hinderance of the PVK molecules. The secondary broad structured maximum at 475 nm might be assigned as the peak maximum due to the fluorophore developed between fluorene and acetylene units in 100% PDHFA. When the emissive polymer was blended with PVK with the ratio of 1:1, some of the dimer moiety was distrupted to show the higher intensity at 475 nm. The intensity of the excimer emission decreased much with an increase of PVK in the blend and only a trace of the PVK emission was recorded with the PVK concentration over 90% in the blend. The major emission maximum on excitation of the polymer blends with less than 10% of the emissive polymer appeared at 425 nm, of which fluorophore should be assigned as the fluorene unit.16) It is probable that the aromatic element in the fluorene unit fails to develop a coplanarity with the acetylene unit in the diluted system as observed previously (Fig. 3). Neither π plane in the acetylene unit develops a structure to give the most stable electronic arrangement to the covalently-bonded coplanar fluorene-acetylene unit.

Conclusion

The alternating copolymer with the units of fluorene and acetylene emitted light with the PL peak maximum at 475 nm on excitation at 340, 365 or 400 nm while the EL peak maximum appeared at 565 nm. When the copolymer was dissolved in an organic solvent or blended with either PMMA or PVK, the PL peak maximum shifted to 425 nm. The EL peak maximum also shifted to 425 nm when the blend with PVK was used as the emissive layer. It seems that a high concentration of the fluorene unit formed a coplanarity with the acetylene unit in the bulk to emit the light with the peak maximum at 475 nm. Excitons generated in LEDs found more dimeric moieties than in the open film to transfer energy for excimer emission. The coplanarity was disturbed when the emissive copolymer was blended with PVK. A kink seems to develop between the fluorene and the acetylene units. It was apparent that the π–π* electronic transition energy might transfer from PVK to the fluorene unit with a high efficiency to give a high emission intensity at 425 nm.

Refeences

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

2) A. Kraft, A.C. Grimsdale, A.B. Holmes, *Angev. Chem. Int. Ed.* **37**, 402 (1998)

3) Y. Ohmori, M. Uchida, K. Muro, K. Yoshino, *Jap. J. Appl. Phys.* **30**, L1941 (1991)

4) G. Leising, G, Grem, G. Leditzky, B. Ullrich, *Adv. Mater.* **4**, 36 (1992)

5) M. Berggren, O. Inganäs, G. Gustafsson, M.R. Anderson, T. Hjertberg, O. Wennerström, *Synth. Met.* **71**, 2185 (1995)

6) J. Grüner, P.J. Hamer, R.H. Friend, H.-J. Huber, U. Scherf, A.B. Holmes, *Adv. Mater.* **6**, 748 (1994)

7) J. Stampfl, S. Tarch, G. Leising, U. Scherf, *Synth. Met.* **71**, 2125 (1995)

8) H.N. Cho, D.Y. Kim, Y.C. Kim, J.Y. Lee, C.Y. Kim, *Adv. Meter.* **9**, 326 (1997)

9) H. Kreyenschmidt, G. Kaerner, T. Fuhrer, J. Ashenhurst, S. Karg, W.D. Chen, V.Y. Lee, J.C. Scott, R.D. Miller, *Macromolecules* **31**, 1099 (1998)

10) H.L. Wang, J.W. Park, D.K. Fu, M.J. Marsella, T.M. Swager, A.G. MacDirmid, Y.Z. Wang, D.G. Gebler, A.J. Epstein, *Polym. Prep.* **36(2)**, 45 (1995)

11) M. Hay, F.L. Klavetter, *J. Am. Chem. Soc.* **117**, 7112 (1995)

12) G.G. Malliaras, J.K. Herrema, J. Wildeman, R.H. Weiringa, R.E. Gill, S.S. Lampoura, G. Hadziioannou, *Adv. Mater.* **5**, 721 (1993)

13) M. Fukuda, K. Sawada, K. Yoshino, *J. Polym. Sci.: Part A, Polym. Chem.* **31**, 2465 (1993)

14) S.A. Jenekhe, J.A. Osaheni, *Science* **265**, 765 (1994)

15) Q. Pei, Y. Yang, *Macromolecules* **118**, 7416 (1996)

16) D.Y. Kim, J.K. Kim, H.N. Cho, C.Y. Kim, *Proc. SPIE Int. Soc. Opt. Eng.* **3148**, 151 (1997)

17) A. Hilberer, H.-J. Brouwer, B.-J. Scheer, J. Wildeman, G. Hadziioannou, *Macromolecules* **28**, 4525 (1995)