JOURNAL OF
Materials
CHEMISTRY

Synthesis and characterization of novel blue light emitting poly[4,4′-biphenylylene(α-phenylvinylene)]

Yun-Hi Kim,[a] Dong-Cheol Shin,[a] Soon-Ki Kwon*[a] and Jeong-Hyun Lee[b]

[a]*Department of Polymer Science & Engineering and Research Institute of Industrial Technology, Gyeongsang National University, Chinju 660-701, Korea*
[b]*Display Lab. Technology Division, Samsung SDI Co., LTD, Korea*

Received 4th January 2002, Accepted 27th February 2002
First published as an Advance Article on the web 28th March 2002

Novel blue light emitting poly[4,4′-biphenylylene(α-phenylvinylene)] (PBPPV) was synthesized using the well-known nickel coupling reaction. PBPPV containing an asymmetric monophenyl group at the vinylene of the main chain was highly soluble in common organic solvents and was found to be thermally stable. The polymer containing suitable electron a donating monophenyl substituent gives rise to bright blue fluorescence both in solution and thin solid films. The solid photoluminescence quantum efficiency of the PBPPV was 0. 43(±10%). The EL spectra of PBPPV and the blend with PVK had similar maxima at about 460 nm in the blue region. The maximum brightness of devices of structure ITO/PBPPV/Al–Li and ITO/PBPPV : PVK (3 : 7)/Al–Li were 250 cd m^{-2} and 2700 cd m^{-2}, respectively.

Introduction

Since light-emitting devices (LED) using conjugated polymers were first realized in the early 1990s,[1,2] a great number of different conjugated polymers suitable for LEDs have been investigated and developed. These conjugated polymers are especially attractive for use as the emitting layers in LEDs, because the polymers show good processability, high quantum efficiency, long lives under stress, and a wide selection of emission colors through molecular design.

Efficient organic stable blue light emitting materials are desirable both to complete the luminescence color spectrum and to serve for energy transfer when used in conjunction with small band gap fluorophores.[3–7]

The first report of blue emission from a conjugated polymer LED was for poly(*p*-phenylene) (PPP).[8] Poly(*p*-phenylene) and its derivatives[9–14] have good thermal and oxidative stability. PPP, however, exhibits low solubility and a high turn-on voltage. Low work function metals are required for efficient carrier injection into PPP derivatives. Furthermore, PPP and its derivatives are intrinsically violet-blue emitters and present some difficulties in color tunability.[15]

Poly(*p*-phenylenevinylene) (PPV) derivatives have several advantages as an emitting material such as high thermal stability, good film quality, suitable color tunability. However, the design of blue emitting electroluminescent polymers based on PPVs with interrupted conjugation suffers from the drawback that their emission is usually broadened and red-shifted because of the more conjugated segments.[16] The carbon–carbon double bond of PPV can be subject to degradation.[17,18] R. H. Friend *et al.*[19] reported that the replacement of vinylic hydrogens by phenyl groups could reduce photo-oxidative degradation by steric inhibition of the interaction between oxygen and the polymer backbone.

Poly[4,4′-biphenylylene(diphenylvinylene)] (PDPV),[20] with features of the structures of PPP and PPV, is an attractive polymer for electroluminescence (EL) because it has very high photoluminescence efficiency in the solid state along with good solubility in common organic solvents, such as chloroform or toluene, due to the phenyl substituent on the vinylene and the disorder induced by *cis–trans* isomerism. However, PDPV with symmetrical diphenyl substituents in the 1,2 positions of the C=C double bond showed yellow-green emission.[20]

Recently, we reported that a large 9,9-dihexylfluorene pendant group on the vinyl bridge of poly(biphenylylenevinylene) could lead to enhanced solubility of the resulting polymer and shorten the effective conjugation length, resulting in bright blue emission.[21]

In connection with the recent report, we designed and synthesized the new poly[4,4′-biphenylylene(α-phenylvinylene)] (PBPPV) containing an asymmetric monophenyl substituent which can enhance solubility and oxidative stability, and shorten effective conjugation length.

Experimental

Monomer synthesis

1,2-Bis(4′-bromophenyl)-1-phenylethylene (1). A mixture of 20 g (39 mmol) of 4-bromobenzylphosphonium bromide and a slight excess of sodium hydride in dry benzene (150 mL) were refluxed for 4 h. The reaction mixture was cooled to room temperature, and then 10.2 g (39 mmol) of 4-bromobenzophenone was added. The reaction mixture was refluxed for 24 h, and then the reaction mixture was cooled. After the solvent was evaporated, a viscous oil was obtained. A white product was obtained by column chromatography (silica gel, with *n*-hexane as eluent). The yield was 6.5 g (40%). Mp 72–74 °C. FT-IR (KBr pellet, cm^{-1}): 3074, 3049, 3025, 1483, 810, 571. ^{1}H-NMR($CDCl_3$, ppm): 6.9–7.5 (m, 14 H, aryl CH and vinyl CH). Anal. Calcd for $C_{22}H_{22}Br_2$: C, 59.22; H, 4.97; Br, 35.81. Found: C, 59.45; H, 4.99; Br, 35.66%.

Polymerization

Poly[4,4′-biphenylylene(α-phenylvinylene)] (PBPPV) (2). A 25 mL three-necked, round-bottomed flask was charged with anhydrous nickel(II) chloride (0.13 g, 0.001 mol), 2,2′-bipyridine (0.15 g, 0.001 mol), triphenylphosphine (1.0 g, 0.0038 mol), and zinc powder (3.0 g, 0.046 mol), and the flask was repeatedly evacuated and back-filled with nitrogen (*ca.* 20 times). Dry *N*,*N*-dimethylformamide (15 mL) was added to the flask, and the mixture was heated with stirring to 50 °C. Heating was continued until the activated catalyst was made, and then 1,2-bis(4′-bromophenyl)-1-phenylethylene (4.46 g, 0.01 mol) was added *via* a solid dropping funnel.

DOI: 10.1039/b200496h

This journal is © The Royal Society of Chemistry 2002

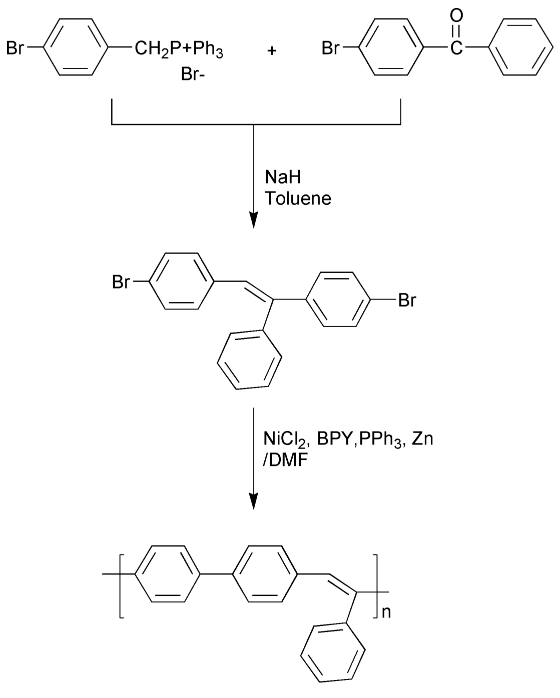
The reaction mixture was heated at 90 °C with stirring for 24 h. After stirring, excess bromobenzene was added and the reaction mixture was stirred at 90 °C for 6 h. Then, the mixture was poured into H_2O (150 mL) and the solid crude product was obtained by filtration. The crude product was extracted with $CHCl_3$, and insoluble materials were removed by filtration. The solution was poured into excess methanol and the product precipitated. The product was filtered off and the process was repeated for purification. The yield was 2.3 g (80%). FT-IR (KBr pellet, cm^{-1}): 3075, 2950, 2900, 2850, 1620, 1460, 1410, 840, 571. ^{1}H-NMR($CDCl_3$, ppm): δ 7.03–7.55 (m, 14 H, aryl CH and vinyl CH). Anal. Calcd for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.27; H, 5.43%.

Characterization

^{1}H-NMR spectra were recorded using a Bruker AM-300 spectrometer, and chemical shifts are reported in ppm units with tetramethylsilane as internal standard. FT-IR spectra were obtained with a Bomem Michelson series FT-IR spectrophotometer and UV–visible absorption spectra were obtained in chloroform on a Shimadzu UV-3100 spectrophotometer. Melting points were determined using an Electrothermal Mode 1307 digital analyzer. Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (Waters high-pressure GPC assembly Model M590 pump, μ-Styragel columns of 105, 104, 103, 500, and 100 Å, refractive index detectors, solvent THF). Thermal analysis was carried out on a Dupont TGA 2100 thermogravimetric analyzer in a nitrogen atmosphere at a rate of 10 °C min^{-1}. The photoluminescence spectra were recorded on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. For the measurement of EL, the polymer light emitting diode was constructed as follows. An ITO anode coated onto a glass substrate was patterned in strips 3 mm wide, and then cleaned with a cleaning solution, deionized water, acetone, and isopropyl alcohol in that order. The polymer film was prepared by spin casting a polymer solution containing 2.0 wt% by weight in chlorobenzene, and evaporating the solvent in a vacuum desiccator at 50 °C for 3 h. Uniform and pinhole free films with a thickness around 100 nm were easily obtained by this method. After setting a shadow mask for cathode, and an aluminium/lithium alloy (Al : Li = 99.95 : 0.05 wt%) electrode was deposited on top of the device at a high vacuum (below 4×10^{-6} Torr). The deposition rate and thickness of the layer was measured by means of a quartz resonator. The contact area of the light emitting part was 4 mm^2. The obtained sample was handled under nitrogen gas to avoid contact with air. For the measurements of device characteristics, current–voltage (*I–V*) and light intensity–voltage (*L–V*) changes were measured using a current/voltage source (Keithley 238) and an optical powermeter (Newport 835). The injected current was measured by the voltage supply while applying forward bias, and the emitted light was collected with a silicon photodetector (Newport 818SL) placed in front of the device and recorded by a computer. All processes and measurements mentioned above were carried out in air at room temperature.

Results and discussion

The synthesis of the monomer and the polymer is outlined in Scheme 1. The monomer was prepared *via* classical Wittig reaction using 4-bromobenzophenone and 4-bromobenzylphosphonium bromide. The polymerization was carried out using a nickel-catalyzed coupling reaction in good yield. After the polymerization, the end-capping reaction of the bromine end group, which hampers thermal stability and efficiency of PL, was accomplished by reaction with bromobenzene.



Scheme 1

^{1}H-NMR and FT-IR spectra, and the result of elemental analysis, agree with the proposed structure of PBPPV showing no evidence of coupling defects. The polymer obtained has good solubility in common organic solvents such as THF, toluene, chloroform, methylene dichloride, chlorobenzene, due to the phenyl substituent on the vinylene and the disorder induced by *cis–trans* isomerism. The number average molecular weight of the polymer, as determined by size-exclusion chromatography using polystyrene standards, was $M_n = 7700$ (PDI = 1.45). The thermal properties of the synthesized polymer evaluated by means of TGA show that the polymer exhibited good thermal stability. The weight loss of the polymer is less than 5% on heating to 380 °C. The DSC measurement showed a glass transition at around 130 °C.

Fig. 1 shows the optical absorption and photoluminescence spectra of a dilute solution of the polymer in chloroform. The absorption spectrum of the dilute solution has a maximum peak of 365 nm. The absorption of a thin film also shows a maximum in absorption at about 365 nm with the absorption edge at 425 nm. The maximum absorption peak of the polymer is 10–20 nm blue shifted as compared with those of PBFPPV and PDPV containing bulky a 9,9-dihexylfluorenyl group and diphenyl substituents at the vinyl bond, respectively. Usually,

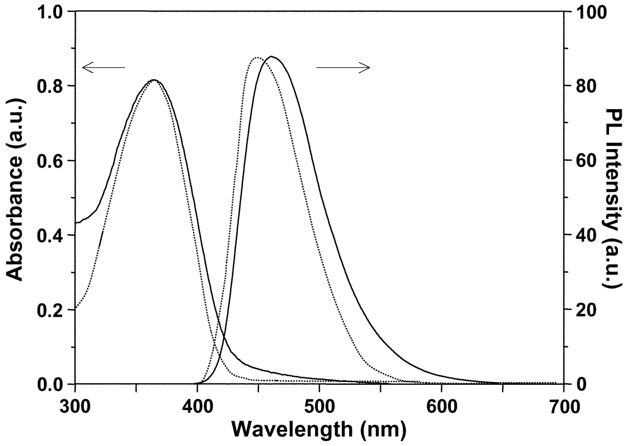


Fig. 1 The optical absorption and photoluminescence spectra of a dilute solution (···) and thin solid film (—) of polymer.

steric hindrance by bulky substituents leads to blue shifted absorption spectrum. However, the single phenyl group is a weak electron donating group and a less sterically hindered group as compared with the fluorenyl and diphenyl groups. Therefore, this shift may be explained by the electronic effect of the single phenyl group. The photoluminescence spectrum of a dilute solution of the polymer pumped by UV light (λ = 365 nm) has a maximum at 460 nm. Although the PL spectrum of a solid film of PBPPV shows a slight bathochromic shift from that of the solution, it is blue shifted by 10–20 nm from those of PBFPPV and 30–40 nm blue shifted from that of PDPV. The solid photoluminescence quantum efficiency of the PBPPV was 0. 43($\pm$10%), which is similar to the result of PDPV (0.45).

In order to study the ionization energy and the optical energy gap, the electrochemical analysis was carried out using cyclic voltammetry (CV). The CVs of polymer-coated ITO and Al plate were measured in a three-electrode compartment cell with a Pt wire counter electrode and an $Ag/AgNO_3$ (0.1 M) reference at a scan rate of 50 mV s^{-1}. The electrolyte was 0.1 M Bu_4NClO_4 solution in anhydrous acetonitrile, and the cell was purged with nitrogen. The reduction and oxidation peak potentials were then measured to be $E_{red} = -2.01$ V and $E_{ox} =$ 0.92 V, respectively. The optical energy band gap was 2.93 eV, and it was consistent with the result of the optical absorption threshold (425 nm). From the electrochemical data, the HOMO and LUMO of the polymer are at -5.72 eV and -2.79 eV, respectively.[22] PBPPV containing a single phenyl group showed much bigger HOMO and LUMO values than those of PDPV containing two phenyl groups.[23]

Fig. 2 shows electroluminescence (EL) spectra of devices using ITO as anode, PBPPV and the blend (PBPPV : PVK = 3 : 7 by weight) as emitting material, and aluminium–lithium as cathode. The electroluminescence spectra of PBPPV and the blend had maxima at about 460 nm in the blue region. The EL spectrum of the blend with PVK was slightly blue shifted and sharpened at long wavelengths compared to that of PBPPV. This result can be explained because the excimer formation of the PBPPV was decreased by the dilution effect using PVK.[24] From the above results, the introduction of a phenyl pendant group could donate electrons to the backbone, which resulted in blue emission; however, excimer formation by the intermolecular interaction was not effectively inhibited.

Fig. 3 shows the current density–voltage characteristic curves for the ITO/PBPPV/Al–Li device and the ITO/PBPPV : PVK (3 : 7)/Al–Li device. The device of structure ITO/PBPPV/Al–Li showed a turn-on voltage of 15 V (3.25 mA cm^{-2}), and the device of structure ITO/PBPPV : PVK (3 : 7)/Al–Li showed a turn-on voltage of 9 V (3.4 mA mm^{-2}). Fig. 4 shows the *L*–*I* characteristics of the ITO/PBPPV/Al–Li device and the ITO/PBPPV : PVK (3 : 7)/Al–Li device. The maximum brightness of the ITO/PBPPV/ Al–Li and the ITO/PBPPV : PVK (3 : 7)/Al–Li devices were 250 cd m^{-2} and 2700 cd m^{-2}, respectively.

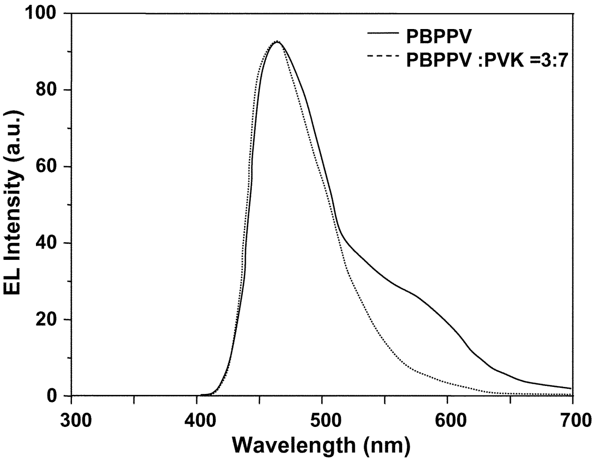


Fig. 2 The electroluminescence spectra from an ITO/PBPPV/Al–Li device and an ITO/PBPPV : PVK (3 : 7)/Al–Li device.

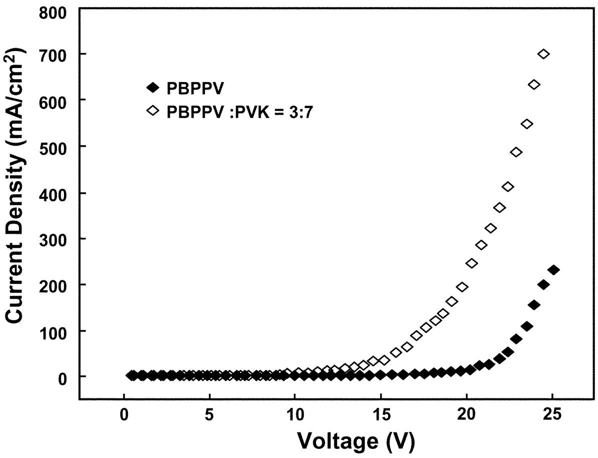


Fig. 3 Current density–voltage characteristic curves of an ITO/PBPPV/Al–Li device and an ITO/PBPPV : PVK (3 : 7)/Al–Li device.

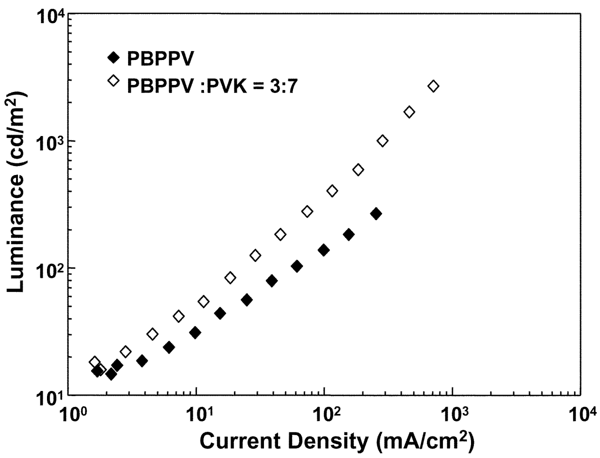


Fig. 4 *L*–*I* characteristics of an ITO/PBPPV/Al–Li device and an ITO/PBPPV : PVK (3 : 7)/Al–Li device.

In conclusion, we prepared PBPPV containing a single asymmetric phenyl substituent at the vinyl bond of a backbone composed alternating PPP and PPV. The obtained polymer had good solubility and thermal stability. The energy gap (E_g), HOMO and LUMO of the polymer are 2.93 eV, -5.72 eV and -2.79 eV, respectively. The introduction of phenyl pendant groups can lead to electron donation to backbone, which results in blue emission.

Acknowledgement

This work was supported by Korea Research Foundation Grant(KRF-2000-005-E00005) and KOSEF(R05-2000-00016).

References

1 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn and B. Holmes, *Nature*, 1990, **347**, 539.
2 D. Braun and A. Heeger, *J. Appl. Phys. Lett*, 1991, **58**(10), 1982.
3 X. C. Li, F. Cacialli, M. Giles, J. Grüner, R. H. Friend, A. B. Holmes, S. C. Moratti and T. M. Yong, *Adv. Mater.*, 1995, **7**, 898.
4 J.-K. Lee, R. R. Schrock, D. R. Baigent and R. H. Friend, *Macromolecules*, 1995, **28**, 1966.

5 M. Aguiar, F. E. Karasz and L. Akcelrud, *Macromolecules*, 1995, **28**, 4598.

6 Y. H. Kim, S. K. Kwon, D. S. You, M. F. Rubner and M. Wrighton, *Chem. Mater.*, 1997, **9**, 2699.

7 Y. H. Kim, K. M. Park and S. K. Kwon, *Bull. Korean Chem. Soc.*, 2001, **22**, 975.

8 A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402.

9 G. Grem, G. Leditzky, B. Ullrich and G. Leising, *Adv. Mater.*, 1992, **4**(1), 36.

10 G. Grem, V. Martin, F. Meghdadi, C. Paar, J. Stampfl, J. Sturm, S. Tasch and G. Leising, *Synth. Met.*, 1995, **71**, 2193.

11 Y. Yang, Q. Pei and A. J. Heeger, *Synth. Met.*, 1996, **78**, 263.

12 S. A. Chen and C. I. Chao, *Synth. Met.*, 1996, **79**, 93.

13 A. Edwards, S. Blumstengel, I. Sokolik, H. Yun, Y. Okamoto and R. Dorsinville, *Synth. Met.*, 1997, **84**, 639.

14 P. B. Balanda, M. B. Ramey and J. R. Reynolds, *Macromolecules*, 1999, **32**, 3970.

15 W. J. Feast, I. S. Millichamp, R. H. Friend, M. E. Horton, D. Phillips, S. D. D. V. Rughooputh and G. Rumbles, *Synth. Met.*, 1985, **10**, 181.

16 A. Kraft, P. L. Burn, A. B. Holmes, D. D. C. Bradley, A. R. Braun, R. H. Friend and R. W. Gymer, *Synth. Met.*, 1993, **55**, 936.

17 F. Papadimitrakopoulos, M. Yan, L. J. Rothberg, H. E. Katz, E. A. Chandross and M. E. Galvin, *Mol. Cryst. Liq. Cryst.*, 1994, **256**, 663.

18 L. J. Rothberg, M. Yan, S. Son, M. E. Galvin, E. W. Kwock, T. M. Miller, H. E. Katz, R. C. Haddon and F. Papadimitrakopoulos, *Synth. Met.*, 1996, **78**, 231.

19 A. T. H. Koch, N. T. Harrison, R. Daik, W. J. Feast and R. H. Friend, *Synth. Met.*, 1999, **100**, 113.

20 (*a*) W. J. Feast and I. S. Millichamp, *Polym. Commun.*, 1983, **24**, 102; (*b*) W. J. Feast, I. S. Millichamp, R. H. Friend, M. E. Horton, D. Phillips, S. D. D. V. Rughooputh and G. Rumbles, *Synth. Met.*, 1985, **10**, 181.

21 B. K. An, Y. H. Kim, D. C. Shin, S. Y. Park, H. S. Yu and S. K. Kwon, *Macromolecules*, 2001, **34**, 3993.

22 (*a*) Y. H. Kim, D. C. Shin, S. H. Kim, C. H. Ko, H. S. Yu, Y. S. Chae and S. K. Kwon, *Adv. Mater.*, 2001, **13**, 1690; (*b*) S. Janietz, D. D. C. Bradley, M. Grell, C. Giebeler, M. Inbasekaran and E. P. Woo, *Appl. Phys. Lett.*, 1998, **73**, 2453.

23 F. Gacialli, R. H. Friend, N. Hylett, R. Daik, W. J. Feast, D. A. Dos Santos and J. L. Bredas, *Appl. Phys. Lett.*, 1996, **69**, 3794.

24 C. Zhang, H. Von Seggern, B. Kraabel, H. W. Schmidt and A. J. Heeger, *Synth. Met.*, 1995, **72**, 185.