Syntheses and light-emitting properties of poly(9,9-di-n-octylfluorenyl-2,7-vinylene) and PPV copolymers

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A new class of light-emitting poly(*p*-phenylenevinylene) (PPV) derivative, poly(9,9-di-n-octylfluorenyl-2,7-vinylene) (PFV), and its PPV copolymers, poly[(9,9-di-n-octylfluorenyl-2,7-vinylene)-*co*-(1,4-phenylenevinylene)]s [poly(FV-*co*-PV)s] were synthesized through Gilch polymerization, and their light-emitting properties were investigated. The copolymers showed almost the same optical properties as the PFV homopolymer, regardless of copolymer composition. The PFV and copolymers all showed their peak absorption and band edge at around 419 and 490 nm, respectively. The PFV and poly(FV-*co*-PV)s all showed PL emission maxima at approximately 465 nm. Light-emitting devices were fabricated with the configuration ITO (indium–tin oxide)/PEDOT/polymer/Al. Interestingly, the EL spectra of these devices were similar to the PL spectra of the corresponding polymer film. However, the EL devices constructed from the poly(FV-*co*-PV)s showed 10 times higher efficiency than the devices constructed from the PFV homopolymer. This higher efficiency is possibly a result of better charge carrier balance in the copolymer systems due to the lower HOMO level (~ 5.5 eV) of the poly(FV-*co*-PV)s in comparison to that of PFV (~ 5.7 eV).

Introduction

Over the past few decades, semiconductors and electro-active materials prepared from conjugated polymers have attracted much interest due to their diverse applications,[1–5] for example in transistors,[1] photovoltaic devices,[2] nonlinear optical devices,[3] and light-emitting diodes (LEDs).[4,5] In particular, interest in LEDs fabricated from conjugated polymers[6,7] has increased since poly(*p*-phenylenevinylene) (PPV) was first employed in a polymer electroluminescent (EL) device in 1990,[4] because polymer LEDs have properties well-suited to flat panel displays—good processibility, low operating voltages, fast response times and facile color tunability over the full visible range.

Of the conjugated polymers studied to date, PPV and its derivatives have attracted particular attention as candidate EL materials on account of their good mechanical strength and thermal stability, as well as their tendency to change color with changes in the substituents on the aromatic ring. PPV derivatives have been synthesized with a variety of substituents, including alkoxy,[8,9] phenyl,[10–13] cyano,[14,15] halogen,[16,17] and silyl[18,19] groups. However, the utility of the PPV derivatives synthesized to date as light-emitting materials for full color displays has been limited by inadequate emission in the pure green or blue region. Although PPV derivatives have been prepared that emit in most regions of the color spectrum, only dialkoxy- or alkoxyphenyl-substituted PPV derivatives, which emit in the orange-red color region, have shown sufficient device performances for practical applications. Therefore the design and synthesis of new green or blue light-emitting PPV derivatives are of primary importance for the realization of full-color polymer LEDs.

PPV can be prepared *via* various routes, including the conventional water-soluble precursor route, dehydrohalogenation polymerization known as Gilch polymerization, or other synthetic methods such as the Wittig and Heck coupling reactions. Gilch polymerization is regarded as a good synthesis method to obtain high molecular weight PPV derivatives suitable for practical applications. The water-soluble precursor and Gilch route syntheses of PPV are shown in Scheme 1. However, it is known that poly(4,4′-biphenylenevinylene) (PBPV) cannot be obtained through the water-soluble precursor or Gilch polymerization route because, due to the single rotation between two benzene rings, the biphenyl cannot form the coplanar structure required for the first stage of these polymerization reactions (which involves 1,6-elimination) to proceed.[10,11,20,21] However, this problem was not expected to complicate the synthesis of poly(fluorenyl-2,7-vinylene) (PFV) in the present work because the two phenyl groups in fluorene have a perfect coplanar structure. In fact, Jin *et al.* recently synthesized a new class of PPV derivative, poly(9,9-di-n-octylfluorenyl-2,7-vinylene) (PFV), using Gilch polymerization.[22] In the present study, high molecular weight and completely soluble PFV was prepared and was shown to give efficient blue-green light emission.

The high barrier to hole injection between ITO and light emitting polymer resulted in poor light emitting efficiency for polymers with high work functions such as polyfluorenes (~ 5.8 eV) and PFV (~ 5.7 eV). The poor efficiency of polyfluorene has been improved by blending, copolymerization, or end-capping with hole transporting materials due to improved hole injection. A similar approach can be taken to improve the device efficiency of PFV by introducing phenylenevinylene units as the hole transporting moiety.

In the present study we characterized the properties of PFV in detail, and synthesized a series of random copolymers of PFV and PPV to improve EL device performance. PFV and the poly[(9,9-di-n-octylfluorenyl-2,7-vinylene)-*co*-(1,4-phenylenevinylene)]s [poly(FV-*co*-PV)s] were synthesized through Gilch polymerization and their light-emitting properties were
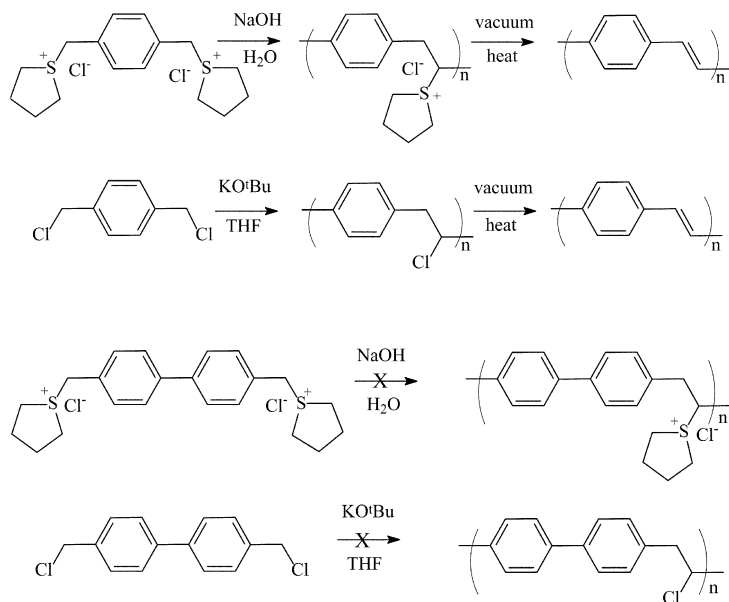
Scheme 1
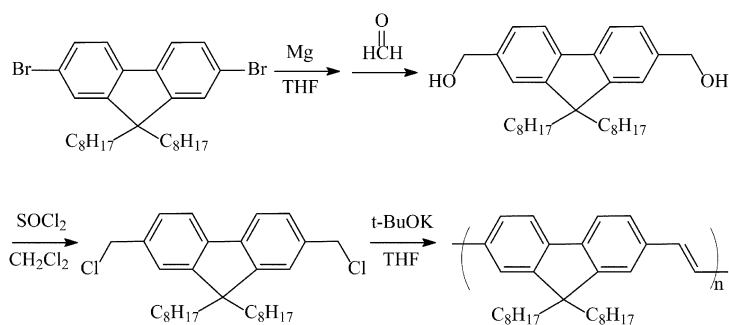
Scheme 2
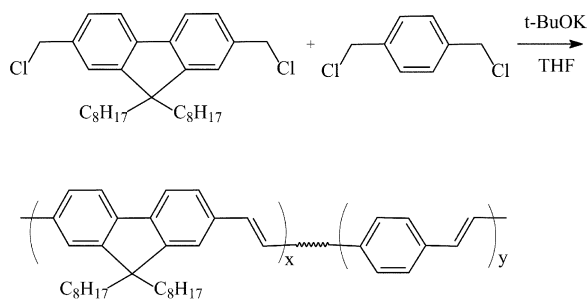
Scheme 3

characterized. The synthetic scheme and polymer structures are shown in Schemes 2 and 3.

Experimental

Measurements and LED fabrication

^{1}H and ^{13}C NMR spectra were recorded using a Bruker AM-300 spectrometer. UV-visible spectra were recorded on a Shimadzu UV-3100 spectrophotometer with baseline corrections and normalizations carried out using Microsoft Excel software. The molecular weights and polydispersity indices of the polymers were determined by gel permeation chromatography (GPC) analysis relative to a polystyrene standard using a Waters high-pressure GPC assembly Model M590. Thermal analyses were carried out on a Dupont TGA 9900 thermogravimetric analyzer under a nitrogen atmosphere at a heating

rate of 10 °C min^{-1}. The ionization potentials of the polymer films were measured with a low-energy photo-electron spectroscope (Riken-Keiki AC-2).[23] Emission spectra were recorded using dilute ($\sim 10^{-6}$ M) solutions; the spectra were collected on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. EL devices were fabricated as follows. First, a glass substrate was coated with a transparent layer of ITO and then thoroughly cleaned by successive sonication treatments in acetone, isopropyl alcohol and distilled water. The resulting glass/ITO system was dried with nitrogen gas and then dried by heating at 100 °C. The polymer film was prepared by spin casting a polymer solution containing 0.5% by weight of chloroform. Uniform and pinhole-free films with thicknesses of around 100 nm were easily obtained. Aluminium metal was then deposited on top of the polymer film through a shadow mask by vacuum evaporation at a pressure of less than 4×10^{-6} Torr, yielding active areas of 4 mm^2. For the measurement of the device characteristics, current–voltage–luminance (I–V–L) changes were measured using a current/voltage source (Keithley 238), an optical power meter (Newport 818-SL) and a luminance meter (Topcon BM-7). All processes and measurements mentioned above were carried out in the open air at room temperature.

Materials

Fluorene, paraformaldehyde, tetrabutylammonium bromide, 1-bromooctane, thionyl chloride, and potassium *tert*-butoxide were purchased from Aldrich and used without further purification. Poly(ethylenedioxythiophene)–poly(styrenesulfonate)

(PEDOT/PSS) (Bayer), used in LED fabrication, was filtered through a 0.45 µm nylon filter prior to spin coating. The solvents [tetrahydrofuran (THF), dichloromethane and toluene] were freshly distilled and dried following literature methods. 2,7-Dibromo-9,9-dioctylfluorene was prepared according to the reported method.[24]

Syntheses of monomers and polymers

2,7-Bis(hydroxymethyl)-9,9-di-n-octylfluorene. Clean magnesium turnings (6.1 g, 0.25 mol) and anhydrous THF (1 L) were used to charge a 2 L round bottomed flask connected to a reflux condenser and thermometer under nitrogen atmosphere. 2,7-Dibromo-9,9-dioctylfluorene (54.8 g, 0.1 mol) dissolved in 300 mL anhydrous THF was then slowly added to this reaction flask. The resulting reaction was highly exothermic and the magnesium was readily consumed. The reaction mixture was refluxed for 4 hours and then cooled to 0 °C. An excess amount of formaldehyde gas, which had been prepared in a separate flask by heating an excess of paraformaldehyde, was supplied to the reaction mixture through a glass tube for 1 hour. The reaction mixture was then stirred for an additional period of 1 hour at room temperature. The reaction was then quenched by addition of a dilute aqueous HCl solution, after which the reaction mixture was extracted three times with 500 mL of diethyl ether. Then, the organic layer was separated and dried with magnesium sulfate. A viscous liquid was obtained after removing the solvent. A white crystalline solid was obtained in a yield of 70% (31.5 g) by silica gel column chromatography (eluent: ethyl acetate/hexane = 1/4). Mp. 127.2–128.1 °C. ^{1}H-NMR (CDCl$_3$, ppm) 0.50–0.64 (m, 4H, 2CH$_2$), 0.80 (t, J = 6.9, 6H, 2CH$_3$), 0.96–1.26 (m, 2OH, 10CH$_2$), 1.88–2.00 (m, 4H, 2CH$_2$), 4.76 (s, 4H, CH$_2$O), 7.31 (d, J = 7.2, 2H, aromatic), 7.32 (s, 2H, aromatic), 7.66 (d, J = 7.2, 2H, aromatic). Elemental analysis for C$_{31}$H$_{46}$O$_2$: calculated C 82.67; H 10.22; found C 81.54; H 10.03%.

2,7-Bis(chloromethyl)-9,9-dioctylfluorene. 2,7-Bis(hydroxymethyl)-9,9-dioctylfluorene (31.5 g, 0.07 mol) was dissolved in 300 mL of dichloromethane, and then 13 mL (0.175 mol) of thionyl chloride was added to this solution in a drop-wise manner at room temperature. After the thionyl chloride addition was complete, the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was then extracted three times with 300 mL of distilled water and 200 mL of dichloromethane, and finally the organic layer was extracted with a dilute aqueous NaHCO$_3$ solution. A viscous liquid was obtained after the organic layer was dried with magnesium sulfate and concentrated. The crude product was purified using silica gel column chromatography (eluent: hexane/hexane = 1/40). A white crystalline solid was obtained in a yield of 93% (31.5 g). Mp. 42.1–43.8 °C. ^{1}H-NMR (CDCl$_3$, ppm) 0.52–0.66 (m, 4H, 2CH$_2$), 0.81 (t, J = 7, 2H, 2CH$_3$), 0.96–1.26 (m, 2OH, 10CH$_2$), 1.88–2.00 (m, 4H, 2CH$_2$), 4.67 (s, 4H, CH$_2$Cl), 7.33 (s, 2H, aromatic), 7.35 (d, J = 7.8, 2H, aromatic), 7.66 (d, J = 7.8, 2H, aromatic) ^{13}C-NMR (CDCl$_3$, ppm): 151.6, 140.7, 136.5, 127.5, 123.2, 119.9, 55.1, 46.8, 40.1, 31.7, 29.8, 29.13, 29.1, 23.6, 22.5, 14.0. Elemental analysis for C$_{31}$H$_{44}$Cl$_2$: calculated C 76.36; H 9.10; Cl 14.54; found C 74.52; H 9.02; Cl 16.46%.

Poly(9,9-di-n-octylfluorenyl-2,7-vinylene). A solution of 6 mL of potassium *tert*-butoxide (1.0 M THF solution, 6.0 mmol) was added to a stirred solution of 2,7-bis(chloromethyl)-9,9-di-n-octylfluorene (1.0 g, 2.1 mmol) in 100 mL of dry THF over 30 min using a syringe pump. The reaction mixture, which exhibited gradually increasing viscosity and green fluorescence, was stirred for 24 h at room temperature. The resulting polymer was sequentially end-capped with a small amount of 4-*tert*-butylbenzyl bromide and then stirred for a further 1 h.

The polymerization solution was poured into 600 mL of methanol and the crude polymer was successively Soxhlet extracted with methanol, isopropyl alcohol and hexane to remove the unreacted monomers, impurities and oligomers.

[Poly(FV-*co*-PV)]s. Random copolymers of PFV and PPV were prepared according to the above procedures using different monomer feed ratios of 2,7-bis(chloromethyl)-9,9-di-n-octylfluorene and α,α'-bis(chloromethyl)-p-xylene.

Results and discussion

Characterization

2,7-Bis(chloromethyl)-9,9-dioctylfluorene was prepared *via* 2,7-bis(hydroxymethyl)-9,9-di-n-octylfluorene as shown in Scheme 2. This route was chosen instead of the previously reported method[22] because it was more convenient and gave a higher product yield. The synthesized PFV and poly(FV-*co*-PV)s dissolved in common organic solvents such as THF, chloroform, and toluene without evidence of gel formation. The formation of PFV and poly(FV-*co*-PV)s was confirmed by ^{1}H NMR spectroscopy: the spectra of the PFV and poly(FV-*co*-PV) solutions showed no chloromethyl proton peaks at around 4.6 ppm characteristic of the monomers but did show vinylic proton peaks at 7.1 ppm with aromatic proton peaks that are not observed in the monomer spectra. ^{1}H NMR spectroscopy was also used to determine the copolymer compositions. The feed ratios of α,α'-bis(chloromethyl)-p-xylene used in the present work were 5 mol% and 50 mol% of the total amount of monomer and the resulting ratios of PV units in poly(FV-*co*-PV) were 9.4 and 40.8 mol%, respectively. The relative reactivities of 2,7-bis(chloromethyl)-9,9-di-n-octylfluorene and α,α'-bis(chloromethyl)-p-xylene monomers in the polymerization reaction was difficult to assess because the dehydro-halogenation reaction was highly sensitive to factors such as the monomer and base concentrations, the rate of base addition, the stirring rate, and the temperature. The number average molecular weight (M_n) of the PFV and poly(FV-*co*-PV)s, as determined by gel permeation chromatography using a polystyrene standard, ranged from 57000 to 100000 with a polydispersity index ranging from 1.3 to 2.1 after purification (Table 1).

Optical and thermal properties

Fig. 1 shows TGA thermograms of the synthesized polymers obtained under a nitrogen atmosphere. All of the polymers exhibit good thermal stabilities, losing less than 5% of their weight on heating to approximately 400 °C. Some poly(alkylfluorene)s have been reported to form stable liquid crystals. For example Grell *et al.* found that poly(di-n-octyl)fluorenes have very stable liquid crystalline states and Bernius *et al.* observed polarized light emission from poly(alkylfluorene)s characteristic of a liquid crystalline structure.[25,26] In addition, we previously found that poly[bis(dimethyloctylsilyl)-1,4-phenylenevinylene] (BDMOS-PPV) has liquid crystalline properties

Table 1 Molecular weights, polydispersity indices, UV and PL results of the polymers

Polymer[a]	M_n	PDI	UV$_{max}$/ nm	PL$_{max}$/ nm	PL Efficiency (%)
PFV	100000	1.3	418	506	34
Poly(91FV-*co*-9PV)	87000	1.4	418	506	36
Poly(59FV-*co*-41PV)	57000	2.1	419	506	36

[a]The numerical values represent the mole percentage of each monomer unit in the final copolymer. FV: fluorenyl-2,7-vinylene unit. PV: 1,4-phenylenevinylene unit.
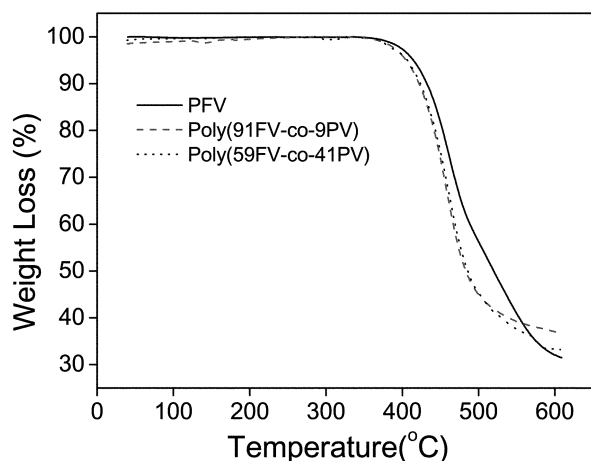
Fig. 1 TGA thermograms of the synthesized polymers.

Fig. 3 PL emission spectra of the polymer films.

and emits polarized light.[27] On the basis of these previous results, it might be expected that the PFV synthesized in the present work, which has a highly rigid backbone and long flexible alkyl groups on the side chain, would form a liquid crystalline structure. However, no evidence of a significant mesophase or liquid crystalline texture was found in DSC measurements and polarized microscopy examinations.

Fig. 2 shows UV-Vis absorption spectra of thin films of PFV and the copolymers coated onto fused quartz plates. The PFV thin film shows the peak UV-visible absorption and absorption onset at 418 nm and 485 nm, respectively. Interestingly, the absorption spectra of the copolymers are almost the same as that of PFV, indicating that the introduction of phenylene-vinylene units does not change the optical properties of PFV. This result agrees well with the finding of Cho *et al.*[28,29] that the optical properties of an alternating copolymer of PFV and PPV synthesized by Heck coupling reaction, poly(FV-*alt*-PV), shows absorption and PL emission spectra that are almost the same as those of PFV. To account for this observation, Cho *et al.* conjectured that the *p*-phenylenevinylene unit does not disturb the coplanarity between the fluorene and vinylene units, and thus PFV and poly(FV-*alt*-PV)s have almost the same π–π^* band gap.

Fig. 3 shows PL emission spectra of thin films of PFV and the copolymers coated onto fused quartz plates. The maximum photoluminescence of the PFV film appeared at 465 nm when it was excited at 350 nm with a xenon lamp. The PL spectra of the copolymers were similar to that of PFV, as was the case in the UV-visible spectra. The PL spectra of the PFV and copolymer films each showed a relatively broad emission band compared
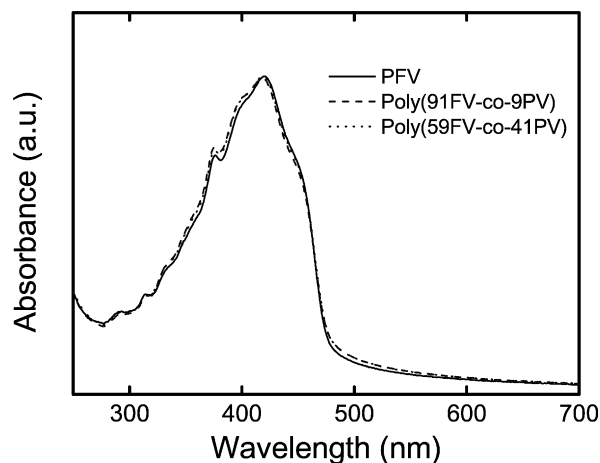
with the poly(alkylfluorene) or PPV spectra, and showed four well-defined equally spaced phonon side bands at 470, 500, 530 and 560 nm.

The absolute PL quantum efficiencies of the PFV and copolymer films were measured to be 34–36% by using an integrating sphere. In comparison, the reported PL quantum efficiencies of PPV and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV)[30] were 27% and 15%, respectively.

Electroluminescent devices

Double-layered EL devices of configuration ITO/PEDOT/polymer/Al were fabricated and characterized as a function of applied voltage. The EL spectra of the devices are shown in Fig. 4. These spectra are similar to the PL spectra of the corresponding polymer films (Fig. 3). The CIE coordinates of all three devices are $x = 0.23$, $y = 0.38$ at a brightness of 100 cd m^{-2}.

Fig. 5 and 6 shows the current–voltage and the luminance–voltage characteristics, respectively, of the EL devices. In the EL device constructed from the PFV homopolymer, the forward current increases with increasing forward bias voltage and the curve shows a shape typical of a diode. Light emission from this device was observable at voltages greater than 4.6 V. The maximum brightness of the device was 600 cd m^{-2} with an efficiency of 0.13 cd A^{-1}. Interestingly, the EL devices constructed from the copolymers show significantly better device performance in comparison to the device constructed from the PFV homopolymer. The EL device constructed
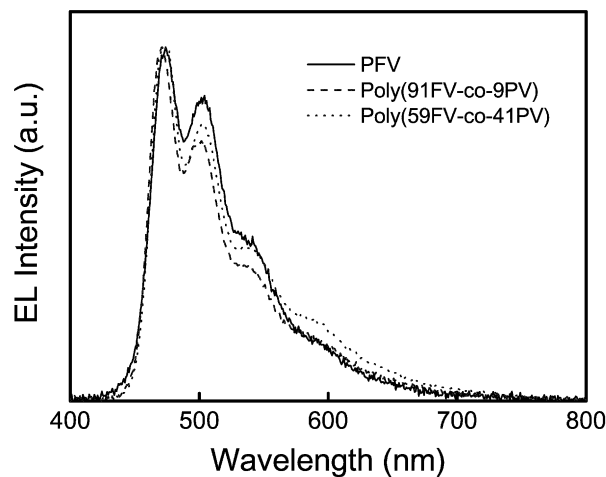

Fig. 2 UV-visible absorption spectra of the polymer films.

Fig. 4 EL spectra of the devices with an ITO/PEDOT/polymer/Al configuration.
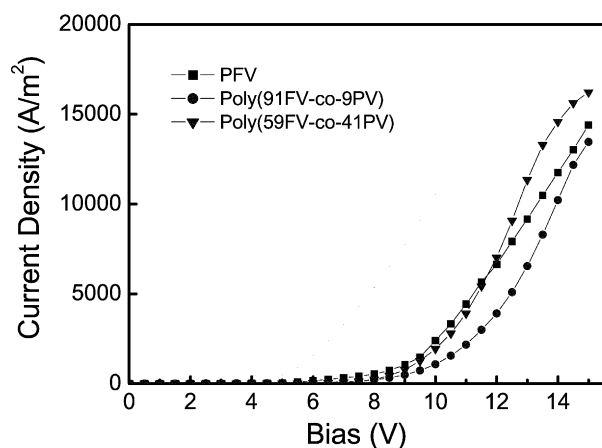
Fig. 5 Current–voltage curves of the EL devices.

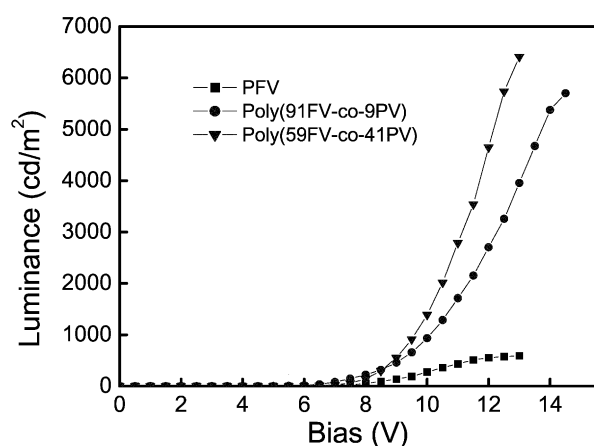Fig. 7 Efficiency–current curves of the EL devices.

Fig. 6 Luminance–voltage curves of the EL devices.

Fig. 8 Band diagram of the ITO, poly(FV-*co*-PV), PEDOT and Al electrode.

from poly(91FV-*co*-9PV) shows a maximum brightness of 5700 cd m^{-2} and an efficiency of 1.05 cd A^{-1}, while the device constructed from poly(59FV-*co*-41PV) shows a maximum brightness of 6400 cd m^{-2} and an efficiency of 0.71 cd A^{-1}. The luminance–voltage and efficiency–current curves of the EL devices are shown in Fig. 6 and 7.

One explanation for the dramatic improvement in EL device efficiency achieved by using the copolymers instead of the homopolymer is that the introduction of PV units facilitates hole injection and transportation. To test this hypothesis, we measured the ionization potentials of the polymer films to determine the HOMO levels. The measured ionization potential of the PFV thin film was 5.73 eV. Given that the optical band gaps of PFV and the copolymers were measured to be 2.60 eV from the absorption onset, we conclude that the LUMO level of the PFV thin film is 3.13 eV. The measured ionization potentials of the poly(91FV-*co*-9PV) and poly(59FV-*co*-41PV) thin films were 5.53 and 5.55 eV, respectively. The HOMO level of the PEDOT layer is known to be ~5.2 eV. Thus, hole injection and transportation from PEDOT to the copolymers is easier than to the PFV

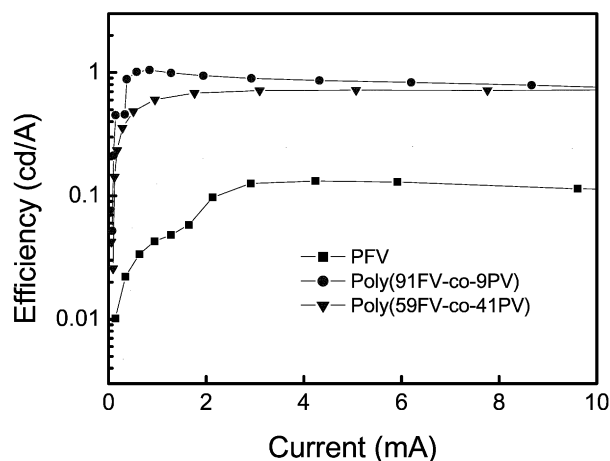homopolymer (5.73 eV), and as a consequence, the charge carrier balance is better in the devices constructed from the copolymers. The relative band diagram of ITO, PEDOT, the polymers, and the Al electrode is shown in Fig. 8, and the characteristics of the EL devices are summarized in Table 2.

Further optimization of the EL device by introduction of an electron-transport layer (ETL) or lower work function metal as a cathode is under investigation.

Conclusion

High molecular weight and soluble PFV and poly(FV-*co*-PV)s were synthesized through Gilch polymerization and their

Table 2 Summary of the characteristics of the EL devices

Polymer	Turn-on voltage/V	Efficiency/ cd A^{-1}	Maxmimum brightness/cd m^{-2}	EL$_{max}$/ nm	CIE coordinates[a] (x,y)
PFV	4.6	0.13	600	472	(0.23,0.38)
Poly(91FV-*co*-9PV)	4.8	1.05	5700	472	(0.23,0.38)
Poly(59FV-*co*-41PV)	4.8	0.71	6400	475	(0.23,0.38)

[a]The CIE coordinates were measured at 100 cd m^{-2} brightness.

light-emitting properties were investigated. A thin film of PFV showed blue-green emission with maximum PL emission at 465 nm. Poly(FV-*co*-PV) thin films showed almost the same UV absorption, PL, and EL spectra as the PFV homopolymer. Although PV units do not change the optical properties of PFV, they do improve the charge injection and transporting ability of PFV. The EL devices constructed from the copolymers showed significantly better performance in terms of efficiency and brightness in comparison to the device constructed from the PFV homopolymer.

Acknowledgements

References

1 H. Shirringhaus, N. Tessler and R. H. Friend, *Science*, 1998, **280**, 1741.
2 J. J. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti and A. B. Holmes, *Nature*, 1995, **376**, 498.
3 P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Effects in Monomers and Polymers*, John Wiley & Sons, New York, 1991.
4 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn and A. B. Holmes, *Nature*, 1990, **347**, 539.
5 G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri and A. J. Heeger, *Nature*, 1992, **357**, 477.
6 P. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend and R. W. Gymer, *Nature*, 1992, **356**, 47.
7 A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402.
8 J. I. Jin, C. K. Park, H. K. Shim and Y. W. Park, *J. Chem. Soc., Chem. Commun.*, 1989, 1206.
9 H. K. Shim, D. H. Hwang and K. S. Lee, *Makromol. Chem. Phys.*, 1993, **194**, 1115.
10 H. Becker, H. Spreitzer, K Ibrom and W. Kreuder, *Macromolecules*, 1999, **32**, 4925.
11 H. Becker, H. Spreitzer, W. Kreuder, E. Kluge, H. Schenk, I. Parker and Y. Cao, *Adv. Mater.*, 2000, **12**, 43.
12 S. W. Ko, B. J. Jung, T. Ahn and H. K. Shim, *Macromolecules*, 2002, **35**, 6217.
13 S. H. Jin, M. S. Jang, H. S. Suh, H. N. Cho, J. H. Lee and Y. S. Gal, *Chem. Mater.*, 2002, **14**, 643.
14 H. K. Shim, S. W. Kang and D. H. Hwang, *Bull. Korean Chem. Soc.*, 1993, **14**, 43.
15 D. H. Hwamg, J. I. Lee, H. K. Shim, W. Y. Hwang, J. J. Kim and J. I. Jin, *Macromolecules*, 1994, **27**, 6000.
16 I. N. Kang, D. H. Hwang and H. K. Shim, *Synth. Met.*, 1995, **69**, 547.
17 I. N. Kang, H. K. Shim and T. Zyung, *Chem. Mater.*, 1997, **9**, 746.
18 D. H. Hwang, S. T. Kim, H. K. Shim, A. B. Holmes, S. C. Moratti and R. H. Friend, *Chem. Commun.*, 1996, 2241.
19 D. H. Hwang, K. H. Choi, H. M. Lee, L. M. Do, S. D. Jung, A. B. Holmes, H. K. Shim and T. Zyung, *Mol. Cryst. Liq. Cryst.*, 1998, **316**, 281.
20 P. M. Lahti, D. A. Modarelli, F. R. Denton, R. W. Lenz and F. E. Karasz, *J. Am. Chem. Soc.*, 1988, **110**, 7258.
21 A. Issaris, D. Vanderzande and J. Gelan, *Polymer*, 1997, **38**, 2572.
22 S. H. Jin, H. J. Park, J. Y. Kim, K. Lee, S. Lee, S. D. K. Moon, H. J. Lee and Y. S. Gal, *Macromolecules*, 2002, **35**, 7532.
23 T. Sano, Y. Hamada and K. Shibata, *IEEE J. Sel. Top. Quantum Electron.*, 1998, **4**, 34.
24 N. S. Cho, D. H. Hwang, J. I. Lee, B. J. Jung and H. K. Shim, *Macromolecules*, 2002, **35**, 1224.
25 M. Grell, D. Bradley, M. Inbasekaran and E. Woo, *Adv. Mater.*, 1997, **9**, 798.
26 M. T. Bernius, M. Inbasekaran, J. O'Brien and W. Wu, *Adv. Mater.*, 2000, **12**, 1737.
27 D. H. Hwang and H. K. Shim, *Thin Solid Films*, 2002, **417**, 166.
28 H. N. Cho, D. Y. Kim, Y. C. Kim, J. Y. Lee and C. Y. Kim, *Adv. Mater.*, 1997, **9**, 326.
29 D. Y. Kim, H. N. Cho and C. Y. Kim, *Prog. Polym. Sci.*, 2000, **25**, 1089.
30 N. C. Greenham, I. D. W. Samuel, G. R. Heys, R. T. Philips, Y. A. R. R. Kessener, S. C. Moratti, A. B. Holmes and R. H. Friend, *Chem. Phys. Lett.*, 1995, **241**, 89.