EL Properties of PFV and PPV Copolymers

Do-Hoon Hwang[1], Jong-Don Lee[1], Jong-Min Kang[1], Chang-Hee Lee[2] and Sung-Ho Jin[3]
[1]Dept. of Applied Chemistry, Kumoh National Institute of Technology, Kumi 730-701, Korea
[2]Dept. of Physics, Inha University, Incheon 402-751, Korea
[3]Dept. of Chemistry Education, Pusan National University, Pusan 609-735, Korea
Phone : +82-54-467-4369 , E-mail : dhhwang@kumoh.ac.kr

Abstract

A new class of light-emitting poly(p-phenylenevinylene) (PPV) derivatives, 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] was synthesized through Gilch polymerization, and their light-emitting properties were investigated. The copolymers showed almost the same UV absorption and PL emission as the PFV homopolymer, regardless of copolymer composition. 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 the PFV (~5.7 eV).

1. Introduction

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 [1-5].

PPV can be prepared via various routes, including the conventional water-soluble precursor route, dehydrohalogenation polymerization known as the Gilch polymerization, or other synthetic methods such as the Wittig and Heck coupling reactions. Gilch polymerization is regarded as a good synthetic method to obtain high molecular weight PPV derivatives suitable for practical applications. 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. 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 [7]. In the present study, high molecular weight and completely soluble PFV was prepared and was shown to give efficient blue-green light emission.

In the present study we characterized the properties of PFV in detail, and synthesized of 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 characterized. The polymer structures are shown in Figure 1.
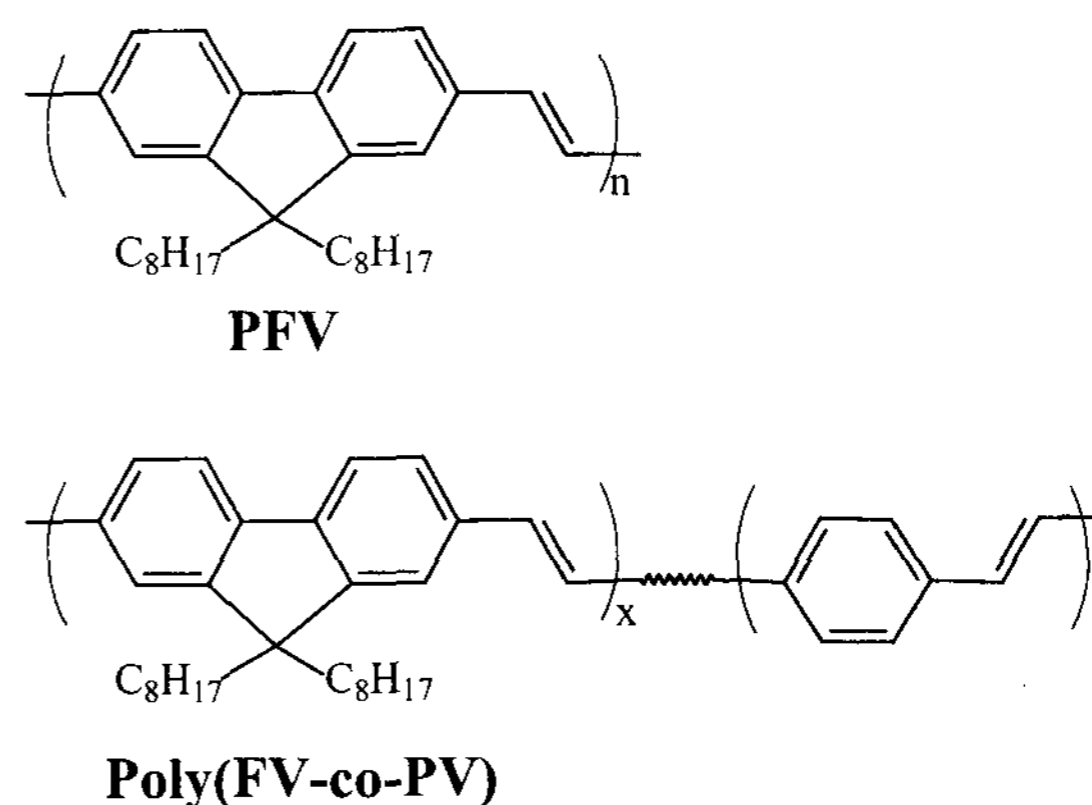

PFV

Poly(FV-co-PV)

Figure 1. Polymer structures of PFV and copolymers.

2. Experimental

UV-visible spectra were recorded on a Shimadzu UV-3100 spectrophotometer with baseline corrections and normalizations carried out using Microsoft Excel software. The ionization potentials of the polymer films were measured with a low-energy photo-electron spectroscope (Riken-Keiki AC-2) [8]. Emission spectra were recorded using dilute (~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. The EL devices were fabricated as follows. The polymer film was prepared by spin casting a polymer solution containing 0.5% by weight of chloroform onto ITO glass. Uniform and pinhole-free films with thicknesses of around 100 nm were easily obtained. Aluminum metal was then deposited on top of the polymer film through a shadow mask by vacuum evaporation at a pressure of less than 4 x 10^{-6} Torr, yielding active areas of 4 mm^2. For the measurements of 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.

3. Results and discussion

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 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 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 57,000 to 100,000 with a polydispersity index ranging from 1.3 to 2.1 after purification.
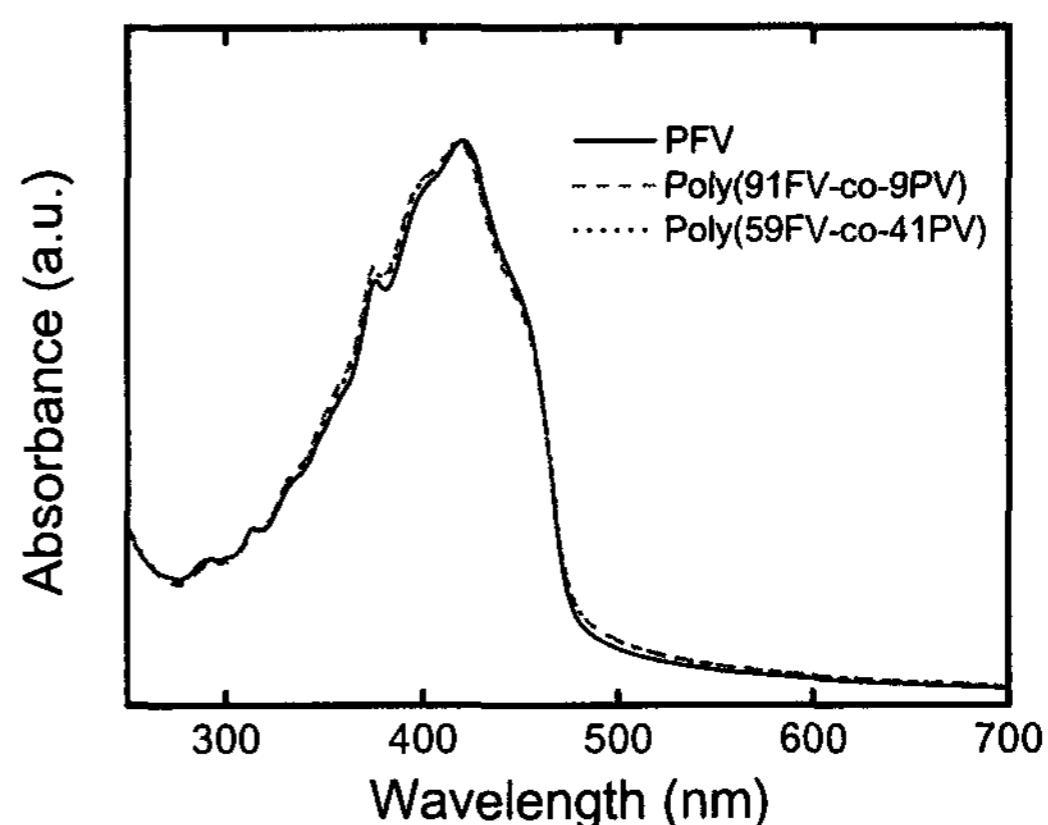

Figure 2. UV-visible absorption spectra of the polymers

Figure 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 phenylenevinylene units does not change the optical properties of PFV.

Figure 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.
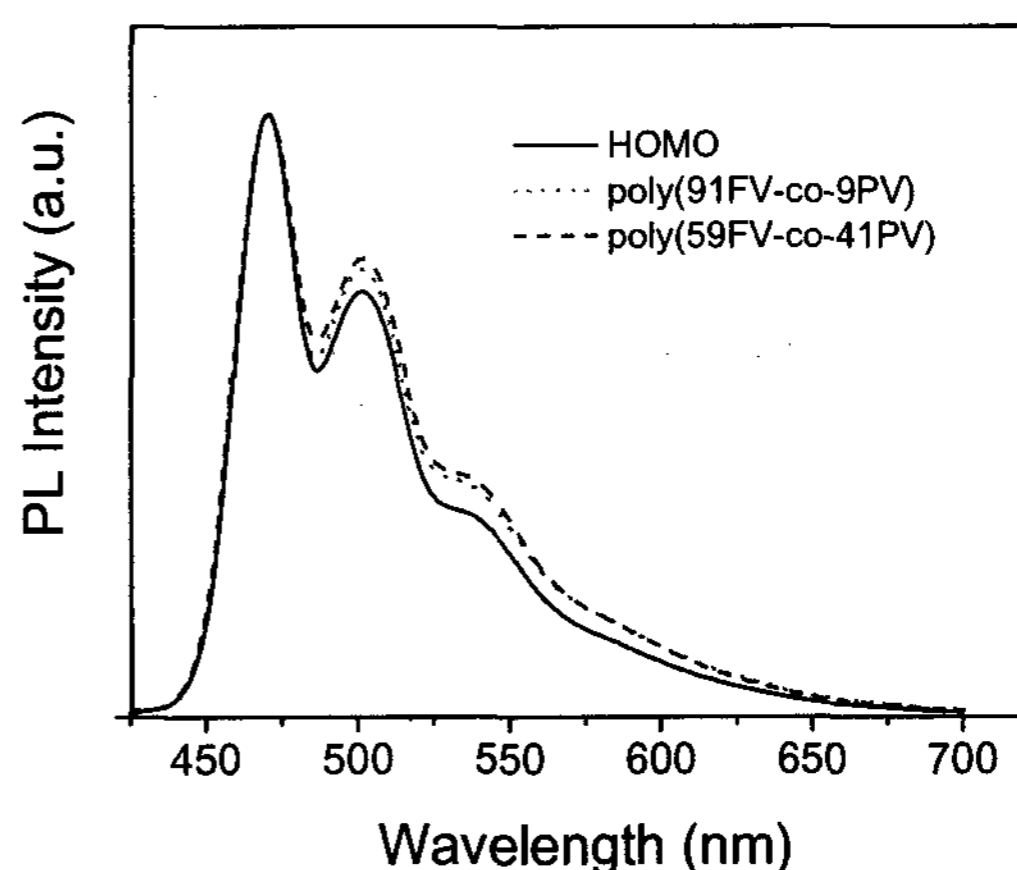

Figure 3. PL emission spectra of the polymers

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. 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) were 27% and 15%, respectively.

Double-layered EL devices of configuration ITO/PEDOT/polymer/Al were fabricated and characterized as a function of applied voltage.

Figure 4 shows the current-voltage and luminance-voltage characteristics 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. Maximum brightness of the device was 600 cd/m^2 with an efficiency of 0.13 cd/A. 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 from poly(91FV-co-9PV) shows a maximum brightness of 5,700 cd/m^2 and an efficiency of 1.05 cd/A, while the device constructed from poly(59FV-co-41PV) shows a maximum brightness of 6,400 cd/m^2 and an efficiency of 0.71 cd/A. The luminance-voltage curves are shown in Figures 5.
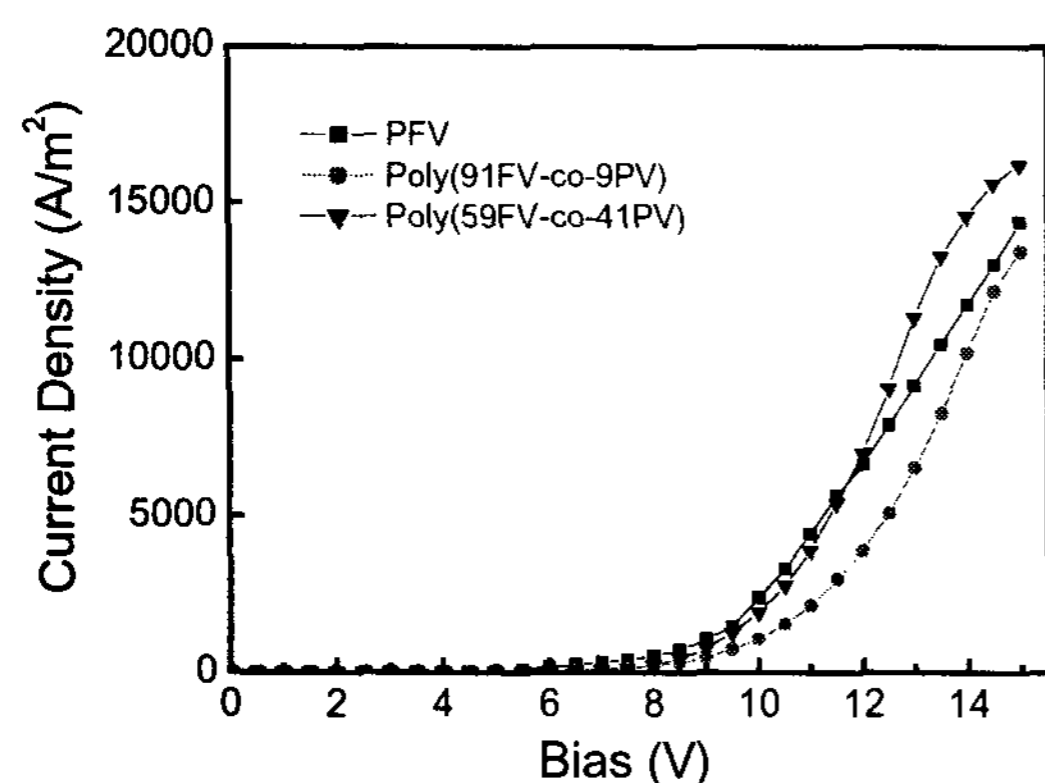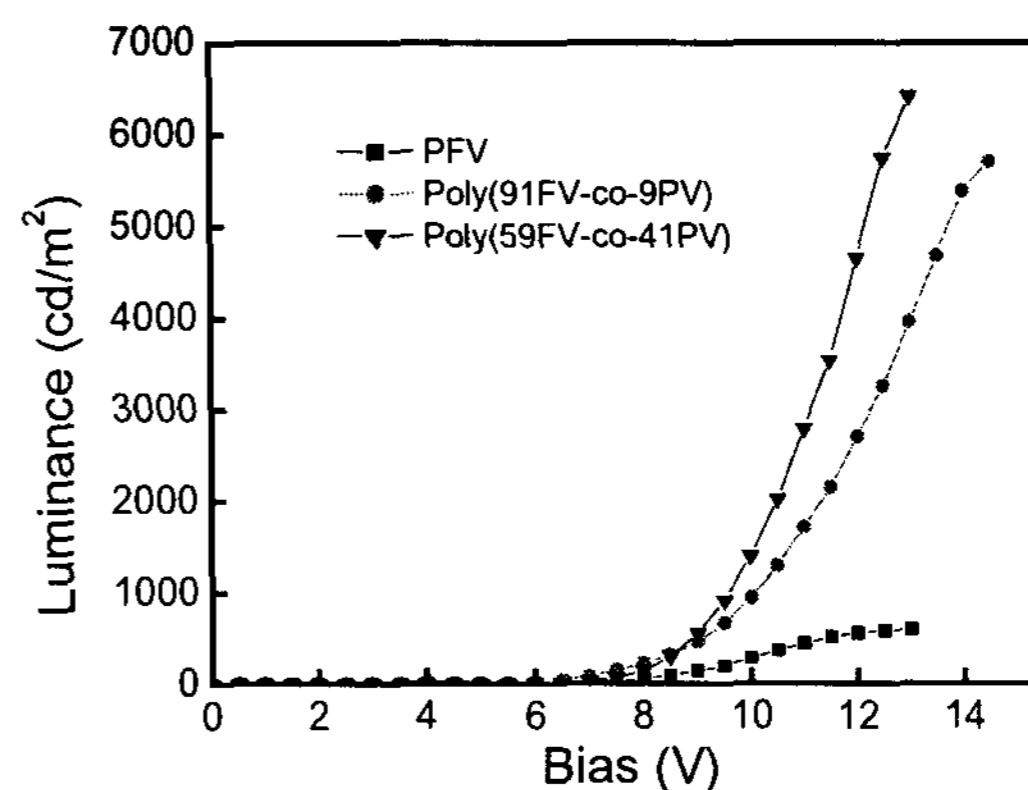

Figure 5. The L-I curves of the EL devices.

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.

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

4. Conclusion

High molecular weight and soluble PFV and poly(FV-co-PV)s were synthesized through Gilch polymerization and their light-emitting properties were investigated. A thin film of PFV showed blue-green emission with maximum PL emission at 465

Figure 4. The I-V curves of the EL devices.

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.

5. Acknowledgements

6. References

[1] J.I. Jin, C.K. Park, H.K. Shim and Y.W. Park. *J. Chem. Soc. Chem. Commun.* 1989, 1206.

[2] H.K. Shim, D.H. Hwang and K.S. Lee, *Makromol. Chem. Phys.* 1993, **194**, 1115.

[3] H. Becker, H. Spreitzer, K, Ibrom and W. Kreuder, *Macromolucules* 1999, **32**, 4925.

[4] S.W. Ko, B.J. Jung, T. Ahn and H.K. Shim, *Macromolecules* 2002, **35**, 6217.

[5] D.H. Hwang, S.T. Kim, H.K. Shim, A.B. Holmes, S.C. Moratti and R.H. Friend, *J. Chem. Soc. Chem. Commun.* 1996, 2241.

[7] S.H. Jin, H.J. Park, J.Y. Kim, K. Lee, S. Lee, S. D.K. Moon, H.J. Lee, Y.S. Gal, *Macromolecules* 2002, **35**, 7532.

[8] T. Sano, Y. Hamada, K Shibata, *IEEE J. Sel. Top. Quant.* 1998, **4**, 34.