

# Synthesis and Characterization of Poly(9,9-dioctylfluorene-2,7-vinylene) for Light Emitting Diode Application

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## Abstract

Fluorenevinylene-based EL polymers, poly(9,9-dioctylfluorene-2,7-vinylene) (PFV) and poly[(9,9-dioctylfluorene-2,7-vinylene)-co-{2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene}] (PFV-co-MEH-PPV), have been synthesized by Gilch polymerization method. The resulting polymers were soluble in common organic solvents and easily spin cast onto the indium-tin oxide (ITO) substrate. The weight average molecular weight and polydispersity of PFV and PFV-co-MEH-PPV were in the range of  $22.2 - 43.2 \times 10^4$  and 1.9 - 3.0, respectively. Double-layer light-emitting diodes with ITO/PEDOT/Polymer/Al configuration were fabricated. PFV-co-MEH-PPV showed better EL properties than those of PFV and MEH-PPV. The turn-on voltage of poly(9,9-dialkylfluorene) derivatives were dramatically decreased to the 2.5 V compared to fluorene-based EL polymers. The maximum brightness and luminescence efficiency were up to  $1350 \text{ cd/m}^2$  and 0.51 Cd/A.

## 1. Introduction

Electroluminescence (EL) devices have been studied due to their practical application as a full-color flat panel displays. An EL phenomenon from organic molecules was first observed for anthracene in 1965.<sup>1</sup> However, the device performance such as efficiency and lifetime of resulting device was significantly lower than those obtained from inorganic molecules. In the late 1980s, a high performance device fabricated by Tang and VanSlyke using the two-layer light emitting diodes with organic fluorescent dyes was a breakthrough in the field.<sup>2</sup> Among the  $\pi$ -conjugated polymers, poly(p-phenylenevinylene) (PPV)<sup>3</sup>, poly(di-alkylfluorene) (PF)<sup>4</sup> and their derivatives are the most powerful candidate materials for application of polymer light emitting diodes (LEDs). The Gilch polymerization offers a number of important advantages for synthesizing PPV-based EL

polymers with high molecular weight, low polydispersity, reproducibility and easily designed the monomers and purification of the resulting EL polymers. Recently, poly(9,9-dialkylfluorene-2,7-vinylene) was prepared by acyclic diene metathesis (ADMET) polymerization<sup>5</sup> and Heck reaction.<sup>6</sup> We describe our recent work concerning poly(9,9-dioctylfluorene-2,7-vinylene) (PFV) synthesized by Gilch polymerization and characterization of this high molecular weight polymer and as well as its purification using membrane technology.

## 2. Experiment

### Synthesis of 2,7-bis(chloromethyl)-9,9-dioctylfluorene

To a mixture of aqueous formaldehyde (39%, 100 mL), 9,9-dioctylfluorene (33.6 g, 86 mmol) and 1,4-dioxane (80 mL) was added gaseous HCl at 80 °C until the reaction was completed. The reaction mixture was cooled to room temperature. To this solution was added 400 mL of chloroform and the organic layer was collected and washed with water. After drying over anhydrous MgSO<sub>4</sub> and removing the solvent, the crude product was subjected to purification by column chromatography on silica gel using hexane as an eluent (yield 57%, m.p. 77°C).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 7.69(d, 2H), 7.38(d, 4H), 4.7(s, 4H), 1.90(m, 4H), 1.26-1.05(m, 20H), 0.83(t, 6H), 0.58(m, 4H).

Elem. Anal: Calcd for C<sub>31</sub> H<sub>44</sub>Cl<sub>2</sub> : C 76.36, H 9.10, Cl 14.54, Found: C 74.52, H 9.02 Cl 16.46

### Synthesis of poly(9,9-dioctylfluorene-2,7-vinylene) (PFV)

A solution of 6 mL of potassium *tert*-butoxide (1.0 M THF solution, 6 mmol) was slowly added to a stirred solution of 2,7-bis(chloromethyl)-9,9-dioctylfluorene

(0.49 g, 1 mmol) in 20 mL of dry THF over 30 min using a syringe pump. The reaction mixture, which gradually increased its viscosity and its greenish blue fluorescence, was stirred for 24 hr at room temperature. A small amount of 4-*tert*-butylbenzyl bromide was added to the mixture in order to end-cap the polymer chain and further stirred for 1 hr. The polymerization solution was poured into 600 mL of methanol and the crude polymer was Soxhlet extracted with methanol to remove the catalyst impurities and oligomers. The resulting EL polymers, PFV and PFV-co-MEH-PPV, were further purified using a polyvinylidene fluoride dialysis membrane in order to improve the color purity and device performance. After the normal procedures of polymer purification, as mentioned above, were followed the polymer solution in chloroform was dialysed against chloroform solvent for a week while stirring to remove the low and medium molecular weight polymer portions. After dialysis, the purified fibrous polymers were obtained by pouring them into 500 mL of methanol, filtered and vacuum dried to give a bright green polymer fiber, PFV (82 %).

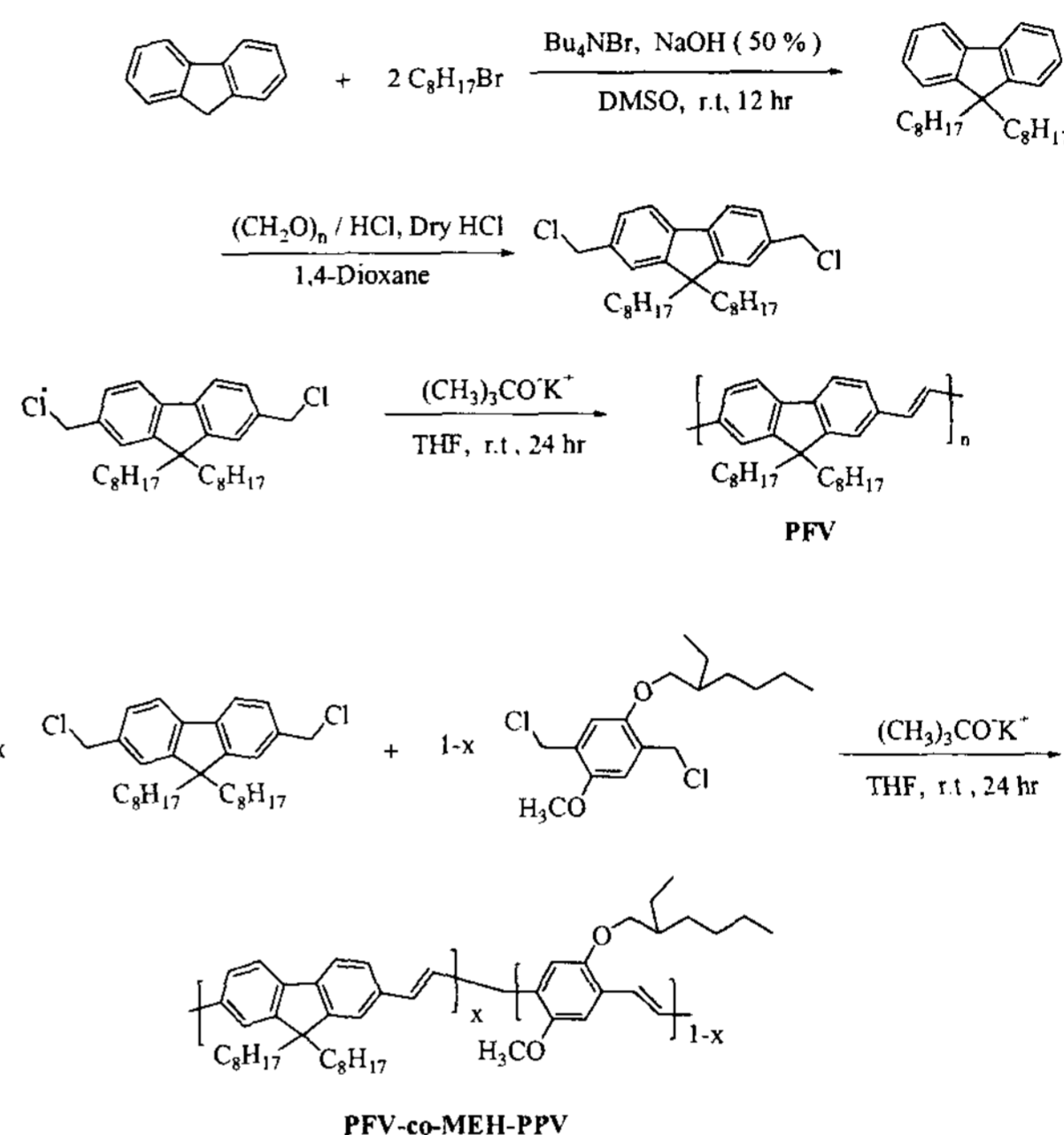
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.6-7.3 (br, 6H, aromatic protons), 7.18-7.0 (br, 2H, vinylic protons), 2-1.80 (br, 2H), 1.2-0.6 (br, 30H)

Poly[(9,9-dioctylfluorene-2,7-vinylene)-co-{2-ethoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene}] (PFV-co-MEH-PPV) with various feed ratios of 1,4-bis(chloromethyl)-2-(2-ethylhexyloxy)-5-methoxy benzene was synthesized using a similar method for PFV.

### 3. Results and Discussion

Scheme 1 outlines the synthetic route for the monomer and corresponding polymer. Fluorene-based EL polymers have many advantages such as easily introducing the substituents at C-9 position, high PL and EL efficiencies, thermal and chemical stabilities and tuning the emission colors by controlling the coplanarity or copolymer system. The electronic and optical properties of conjugated polymers are governed by the modification of chemical structure of the backbone itself. In order to adjust the emission colors and electro-optical properties of the fluorene-based EL polymers, we firstly synthesized fluorenevinylene-based EL polymers via Gilch polymerization. The structure and purity of intermediate and monomer were confirmed by  $^1\text{H}$ -,  $^{13}\text{C}$ -NMR and elemental analyses. The polymerization

of the monomer was performed with an excess of potassium *tert*-butoxide in THF at room temperature for 24 hr under  $\text{N}_2$  atmosphere. The key factor for obtaining the high molecular weight polymer by Gilch polymerization is the introduction of chloromethyl group. However, the polymerization of fluorene-based monomer with bromomethyl group gave a relatively low polymerization yield and molecular weight of the resulting polymer due to the synthesis of 2,7-bis(*tert*-butoxymethyl)-9,9-di-*n*-octyl-9H-fluorene byproduct.



Scheme 1

The resulting EL polymers, PFV and PFV-co-MEH-PPV were completely soluble in various organic solvents. In order to improve the device performance, the PFV and PFV-co-MEH-PPV were further purified by multiple precipitations into the different solvents such as methanol, isopropyl alcohol, hexane and finally dialyzed against chloroform solvent with dialysis membrane by SPECTRUM Co., for 3 days to remove the medium molecular weight polymer (weight average molecular weight cut off, 80,000). The remaining solution in dialysis membrane was poured into methanol, filtered and dried under vacuum. From these processes, the highly purified PFV and PFV-co-MEH-PPV were obtained. The molecular weights of the PFV were determined by size exclusion chromatography (SEC) using polystyrene standards in THF. The weight average molecular weight (Mw) and polydispersity of the

PFV, before the molecular fractionation experiment, were  $13.9 \times 10^4$  and  $18.4$ , respectively. However, after removing the medium molecular weight portion in bimodal GPC curve, PFV exhibits the narrow polydispersity and unimodal GPC curve. The value of Mw and polydispersity of the PFV were  $22.2 \times 10^4$  and  $2.1$ , respectively. In a previous work, the molecular weight of a poly(9,9-di-n-octylfluorene-2,7-vinylene) was  $6.9 \times 10^4$  by ADMET polymerization.<sup>5</sup> Most of polyfluorene-based polymers do not show very distinct glass transition temperature. However, PFV has a glass transition temperature at  $173^\circ\text{C}$  as determined by DSC. This value is higher than those of poly(9,9-dialkylfluorene)s ( $75 \sim 113^\circ\text{C}$ ). PFV exhibit a higher thermal stability than that of poly(9,9-dialkylfluorene) derivatives, showing 5% weight loss at  $415^\circ\text{C}$ . The high thermal stability of the PFV prevents the deformation and degradation of the emitting layer from current-induced heat during the operation of the EL devices.

The PEDOT:PSS (20 nm) was spin-coated from aqueous solution with isopropyl alcohol (10 wt%) on the surface treated ITO substrate and cured for 30 min. The emissive layer (80 nm) was deposited on the top of the PEDOT film. After that, aluminum cathode (100 nm) was thermally evaporated at  $\sim 10^{-6}$  mbar. Figure 1 shows the optical absorption (Abs), photoluminescence (PL) spectra in the thin film and EL spectrum of ITO/PEDOT/PFV/Al device.

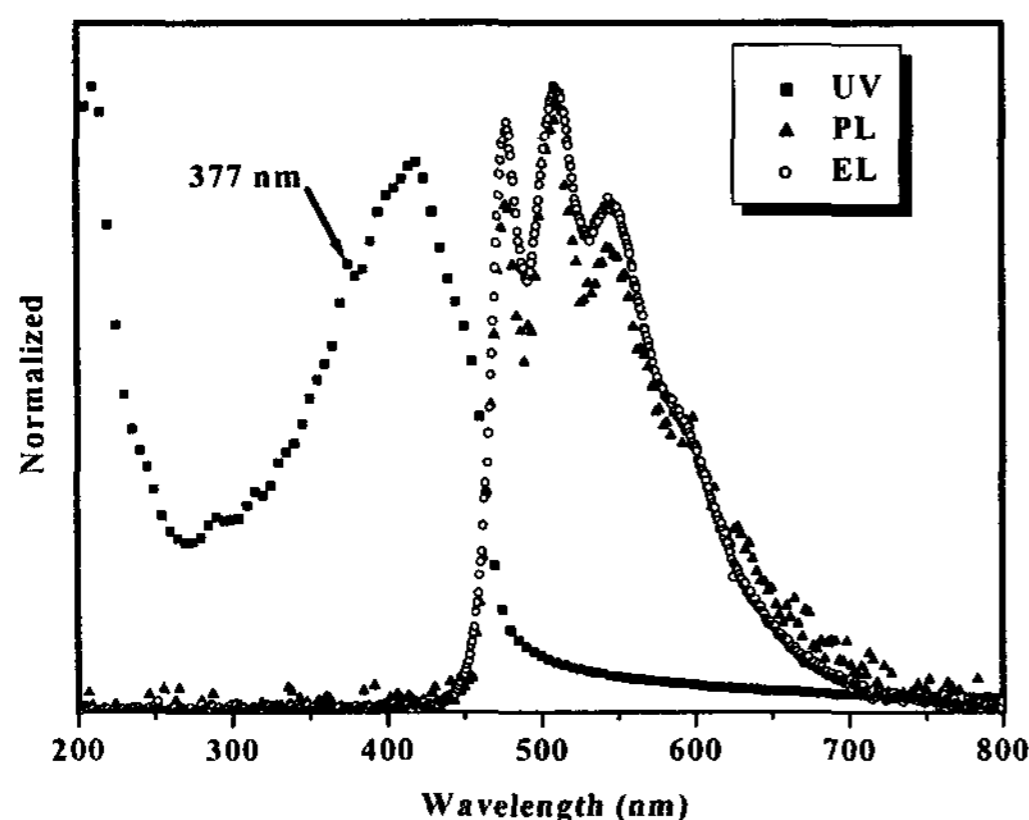
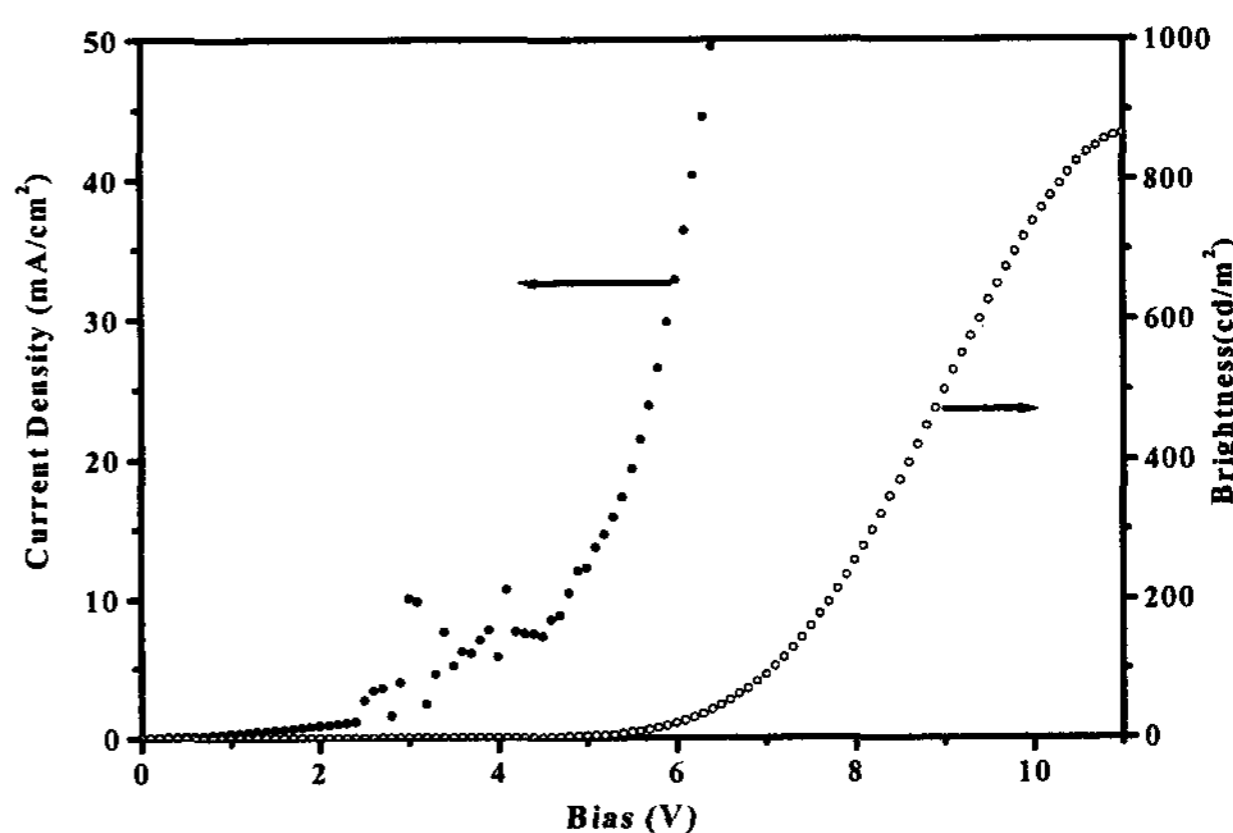


Figure 1. UV-vis absorption (a), PL spectra (b) in the solid state and EL spectrum of the ITO/PEDOT/PFV/Al device.

The absorption wavelength is located around 420 nm due to the  $\pi-\pi^*$  transition of the conjugated polymer backbone with shoulder at 377 nm which is characteristic peak of the fluorene unit. The absorption of PFV is approximately 40 nm red-shifted relative to that of poly(9,9-di-alkylfluorene) derivatives. The maximum emission peak is at 507 nm, which corresponds to greenish-blue light. The EL spectrum was almost identical to the PL spectrum. An energy band diagrams of the PFV and poly(9,9-di-hexylfluorene) were determined from optical absorption spectrum for band gap and cyclic voltammogram for HOMO energy level. The band gap and HOMO for PFV and poly(9,9-di-n-hexylfluorene) are 2.6 eV, 5.3 eV and 2.9 eV and 5.7 eV, respectively. The barrier heights were found to be 0.35 and 0.7 eV at the interface of ITO (4.3 eV)/HOMO state for hole injection and 1.55 and 1.40 eV at the interface of Al (4.3 eV)/LUMO state for electron injection of the PFV and poly(9,9-di-n-hexylfluorene), respectively. Both polymers show that the major carrier is the holes rather than electrons, due to the lower band offset between the anode and HOMO energy level. Figure 2 shows the current-voltage-luminescence (I-V-L) characteristics of



ITO/PEDOT/PFV/Al device.

Figure 2. Current-voltage-luminescence (I-V-L) characteristics of the ITO/PEDOT/PFV/Al device.

The turn-on voltage is approximately 2.5 V and current density increase as exponential manner with increasing forward bias, which is a typical diode characteristic. However, the turn-on voltage of the

poly(9,9-di-n-octylfluorene) is about 4 V with ITO/PEDOT(50nm)/poly(9,9-di-n-octylfluorene) (100nm)/Ca(80nm)/Al(370nm) device. The relatively lower turn-on voltage of the PFV than that of poly(9,9-di-octylfluorene) even though Al electrode may be due to the introduction of vinylene unit into the fluorene backbone which is lower the HOMO binding energy. The polymer LED emits bright greenish-blue light at room temperature. The maximum luminescence and luminescence efficiency were about 1350 cd/m<sup>2</sup> at 10 V and 0.51 Cd/A, respectively. In conclusion, we have synthesized a new class of high molecular weight fluorenevinylene-based EL polymer by Gilch polymerization and compared with the ADMET polymerization. The resulting EL polymer, PFV had high thermal stability up to 415°C. The resulting polymer exhibits low turn-on voltage (2.5 V) and bright greenish-blue emission under 10 V with single layer device.

#### 4. Acknowledgements

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#### 5. References

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