Synthesis and Electroluminescence Properties of Poly(9,9-di-*n*-octylfluorenyl-2,7-vinylene) Derivatives for Light-Emitting Display[†]

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ABSTRACT: 9,9-Dialkylfluorenevinylene-based electroluminescence (EL) polymers, poly(9,9-di-*n*-octylfluorenyl-2,7-vinylene) poly(FV) and poly[(9,9-di-*n*-octylfluorenyl-2,7-vinylene)-*co*-{2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene}] poly(FV-*co*-MEHPV), have been synthesized by the Gilch polymerization method. The structure and properties of those polymers were characterized using ^{1}H, ^{13}C NMR, UV−vis spectroscopy, elemental analysis, GPC, DSC, TGA, photoluminescence (PL), and EL spectroscopy. The 9,9-dialkylfluorenevinylene-based EL polymers were soluble in common organic solvents and easily spin-coated onto the indium−tin oxide (ITO)-coated glass substrates. The weight-average molecular weight (M_w) and polydispersity of poly(FV) and poly(FV-*co*-MEHPV) were in the range (22.2−43.2) × 10^4 and 1.9−3.0, respectively. Double-layer light-emitting displays (LEDs) with an ITO/PEDOT/polymer/Al configuration were fabricated, and the devices using poly(FV-*co*-MEHPV) showed better EL properties than those using pure poly(FV) or MEH−PPV. The emission maxima of poly(FV) and poly(FV-*co*-MEHPV), with various feed ratios of MEH−PPV contents, were observed at 507 and 585 nm, respectively, regardless of copolymer compositions. This phenomenon can be explained by energy transfer from poly(FV) segments with wide band gap to MEH−PPV blocks with smaller band gap in these copolymer systems. The turn-on voltages of poly(FV) and its copolymers dramatically decreased to 2.5 V as compared with those for poly(9,9-dialkylfluorene)s (PF)s. Maximum brightness and luminescence efficiencies were increased up to 1350 cd/m^2 and 0.51 cd/A, respectively.

Introduction

Electroluminescence (EL) devices have been studied due to their practical application as full-color flat panel displays. The EL phenomenon from organic molecules was first observed for anthracene in 1965.[1] However, the qualities of the devices such as efficiency and lifetime were significantly lower than those obtained from inorganic molecules. Ever since the first report was published on a high-performance bilayer light-emitting display (LED) by Tang and Vanslyke, significant effort has been put forth in realizing the potential of commercial available polymer LEDs.[2,3] Advantages of conjugated-polymer-based LED over small-molecule-based LED are low cost, large area, flexibility, and easy design of the molecular structure for EL polymers.[4]

Among the π-conjugated polymers, it was reported that poly(*p*-phenylenevinylene) (PPV),[5−7] polythiophene (PTh),[8] poly(9,9-dialkylfluorene) (PF),[9−12] and their derivatives have been widely used as the most powerful candidate materials for the application of polymer LEDs. Various polymerization methods for the synthesis of emitting polymers have been developed such as the Wittig reaction,[13] Heck reaction,[14] Suzuki reaction,[15] Ni(0)-mediated Yamamoto coupling reaction,[16] and Gilch polymerization.[17] Among them, Gilch polymerization offers a number of important advantages for the introduction of vinylene units along the polymer backbone with high molecular weight and low polydispersity and allows for easy purification.

It has been reported that organic and polymeric LED efficiency strongly depends on the balance between holes and electrons. However, most of the conjugated polymers are less efficient when injecting and transporting of the electrons as compared to injecting and transporting of the holes. Many approaches have been proposed to improve device performance such as using a triplet emitter,[18,19] modification of the device structure by introducing an electron-transport layer[20,21] or a multiple quantum-well,[22,23] and blending[24−26] or copolymer systems.[27,28] Copolymer systems have many benefits such as having the nature of two monomers, tuning the optical properties and improving device fabrication, and performance by energy transfer between different band gaps of two components.

In our previous work, we synthesized various types of novel PPV derivatives, which showed high-performance polymer LED as well as controlling emission color of the polymers.[29−35] In the present article, we report the synthesis and characterization of a new poly(9,9-di-*n*-octylfluorenyl-2,7-vinylene) poly(FV) and its copolymers with various feed ratios of MEH−PPV units synthesized by the Gilch polymerization method. This new poly(FV) and its copolymers have a high molecular

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[†] This paper is dedicated to Prof. Won-Jei Cho on the occasion of his retirement.

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weight, high thermal stability, and applicability for LEDs.

Ever since the first report was published about blue emission color being emitted by a PF by Ohmori et al.,[38] the light-emitting properties of PF-based homopolymers and copolymers have been demonstrated by several research groups[36,37] However, to our knowledge, this is the first paper reporting synthesis of poly(FV) and poly[(9,9-di-*n*-octylfluorenyl-2,7-vinylene)-*co*-{2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene}] poly(FV-*co*-MEHPV) derivatives via Gilch polymerization and characterization of their EL properties.

Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AM-300 spectrometer, and chemical shifts were recorded in ppm. The UV−vis spectrum was recorded on a Shimadzu UV-3100 spectrophotometer with baseline corrections and normalizations carried out using Microsoft Excel software. Molecular weights and polydispersities of polymers were determined by gel permeation chromatography (GPC) analysis relative to polystyrene calibration (Waters high-pressure GPC assembly model M590 pump, μ-Styragel columns of 10^5, 10^4, 10^3, 500, and 100 Å, refractive index detectors) in THF solution. Thermal analyses were carried out on a Dupont TGA 9900 thermogravimetric analyzer under a nitrogen atmosphere at a heating rate of 10 °C/min. Emission spectra were made on a dilute ($\sim 10^{-6}$ M) solution collected on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. Solid-state emission measurements were achieved using film supported on a glass substrate and mounted with front-face excitation at an angle of <45°. The polymer film was excited with several portions of visible light from a xenon lamp. To measure EL, a polymer LED was constructed as follows: The glass substrate, coated with a transparent ITO electrode, was thoroughly cleansed by successive ultrasonic treatments in acetone, isopropyl alcohol, and distilled water, dried with nitrogen gas, and heated for drying. The polymer film was prepared by spin-casting a polymer chloroform solution (0.5 wt %). Uniform and pinhole-free films with a thickness around 100 nm were easily obtained from the resulting polymer solution. Aluminum metal was deposited on the top of the polymer film through a mask by vacuum evaporation at pressure below 4×10^{-6} Torr, yielding active areas of 4 mm^2. For the measurements of device characteristics, current−voltage−luminescence ($I-V-L$) changes were measured using a current/voltage source (Keithley 238), an optical power meter (Newport 818-SL), and Topcon BM-7. All processes and measurements mentioned above were carried out in the open air at room temperature.

Materials. Fluorene, 1-bromooctane, 4-methoxyphenol, 2-ethylhexyl bromide, potassium *tert*-butoxide (1 M solution in THF), tetrabutylammonium bromide, and paraformaldehyde were purchased from Aldrich Chemical Co. and used without further purification unless otherwise noted. Solvents were dried and purified by fractional distillation over sodium/benzophenone and handled in a moisture-free atmosphere. Column chromatography was performed using silica gel (Merck, 250−430 mesh). The poly(vinylidene fluoride) dialysis membrane was purchased from Spectrum Co. 1,4-Bis(chloromethyl)-2-(2-ethylhexyloxy)-5-methoxybenzene and 9,9-di-*n*-octylfluorene were prepared by following already reported procedures.[39,40]

Synthesis of 2,7-Bis(chloromethyl)-9,9-di-*n*-octylfluorene. To mixture of aqueous formaldehyde (39%, 100 mL), 9,9-di-*n*-octylfluorene (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 $MgSO_4$ and removing the solvent, the crude product was subjected to purification by column chromatography on silica gel using hexane as an eluent (yield 57%, mp 77 °C). ^{1}H NMR ($CDCl_3$): δ (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). ^{13}C NMR ($CDCl_3$): δ (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. Anal. Calcd for $C_{31}H_{44}Cl_2$: C, 76.36; H, 9.10; Cl, 14.54. Found: C, 74.52; H, 9.02; Cl, 16.46.

Synthesis of Poly[(9,9-di-*n*-octylfluorenyl-2,7-vinylene)-*co*-{2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene}], Poly(FV-*co*-MEHPV) (50:50 mol %). A solution of 6 mL of potassium *tert*-butoxide (1.0 M THF solution, 6 mmol) was added to a stirred solution of 2,7-bis(chloromethyl)-9,9-di-*n*-octylfluorene (0.2 g, 0.41 mmol) and 1,4-bis(chloromethyl)-2-(2-ethylhexyloxy)-5-methoxybenzene (0.14 g, 0.41 mmol) in 20 mL of dry THF over 30 min using a syringe pump. The reaction mixture, with gradually increased viscosity and orange fluorescence, was stirred for 24 h at room temperature. The polymer was sequentially end-capped with a small amount of 4-*tert*-butylbenzyl bromide after 24 h of polymerization and further stirred for 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. After the normal procedures of polymer purification, as mentioned above, the polymer solution in chloroform was dialyzed against chloroform solvent for 7 days while stirring to remove the medium molecular weight polymer portions. After dialysis, the purified fibrous EL polymer was obtained by pouring them into 500 mL of methanol, filtered, and vacuum-dried to give a bright green polymer fiber, poly(FV-*co*-MEHPV) (50:50) (0.16 g, 49%). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.8−6.8 (br 15H, aromatic and vinylic protons), 4.1−3.9 (br, 5H), 2.2−1.8 (br, 6H), 1.6−0.8 (br, 70H). Anal. Calcd for $(C_{48}H_{66}O_2)_n$: C, 85.40; H, 9.85; O, 4.74. Found: C, 86.13; H, 9.57; O, 4.29.

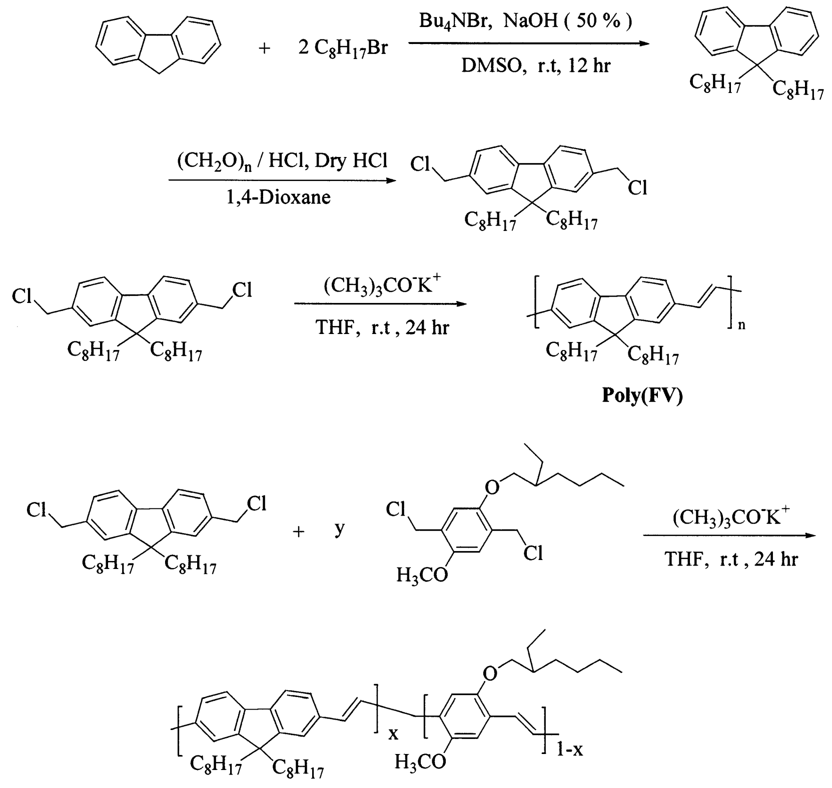
The copolymers poly[(9,9-di-*n*-octylfluorenyl-2,7-vinylene)-*co*-{2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene}], poly(FV-*co*-MEHPV), with various feed ratios of 1,4-bis(chloromethyl)-2-(2-ethylhexyloxy)-5-methoxybenzene and poly(FV) were synthesized using a similar method for poly(FV-*co*-MEHPV) (50:50). The composition ratio of the polymers cited are initial monomer mole ratios used during the polymerization processes.

Results and Discussion

Synthesis and Characterization of Monomer and Polymers. Fluorene-based EL polymers have many advantages such as easily introducing substitutents at the 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 modifying the backbone's chemical structure. To adjust the HOMO and LUMO energy level and the formation of amorphous morphology of the fluorene-based EL polymers, we first synthesized 9,9-dialkylfluorenevinylene-based homopolymer and copolymers via Gilch polymerization.

Scheme 1 shows the synthetic route for the monomer and the corresponding polymers. 2,7-Bis(chloromethyl)-9,9-di-*n*-octylfluorene[35] and 1,4-bis(chloromethyl)-2-(2-ethylhexyloxy)-5-methoxybenzene[39] were synthesized according to the procedures from the literature. The homopolymerization of 2,7-bis(chloromethyl)-9,9-di-*n*-octylfluorene and copolymerization with 1,4-bis(chloromethyl)-2-(2-ethylhexyloxy)-5-methoxybenzene were performed with an excess of potassium *tert*-butoxide in THF at room temperature for 24 h under a nitrogen atmosphere. The polymerization of 2,7-bis(bromomethyl)-9,9-di-*n*-octylfluorene gave a polymer of low molecular weight with a relatively low polymerization yield because of potassium *tert*-butoxide acting as a nucleophile

Scheme 1. Synthesis of the Monomer and the Polymers



x = 0.95, y = 0.05 Poly(FV-co-MEHPV) (95:5)
x = 0.90, y = 0.10 Poly(FV-co-MEHPV) (90:10)
x = 0.80, y = 0.20 Poly(FV-co-MEHPV) (80:20)
x = 0.50, y = 0.50 Poly(FV-co-MEHPV) (50:50)

and easily substituted at the bromomethyl carbon in the 2- and 7-position of the fluorene unit. The polymerization and the reaction mixture of poly(FV) and poly(FV-*co*-MEHPV) became progressively viscous and remained homogeneous without any formation of a gel portion. The resulting EL polymers, poly(FV) and poly(FV-*co*-MEHPV), were completely soluble in various organic solvents such as chloroform, chlorobenzene, toluene, xylene, etc.

Molecular structures of the monomer and the corresponding EL polymers were identified by ^{1}H NMR and UV−vis spectroscopies. The disappearance of the characteristic chloromethyl proton peaks at around 4.6 ppm for monomers and the appearance of new vinylic proton peaks at 7.1 ppm with aromatic proton peaks in poly(FV) and poly(FV-*co*-MEHPV) confirmed the polymerization reaction. The copolymer compositions were calculated by comparing the peak area at 2.0 ppm of the methylene proton peak in an octyl group and 3.8−4.0 ppm of a methylene proton next to oxygen and a methoxy group as side chains. To improve color purity and device performance, the resulting EL polymers were further purified by multiple Soxhlet extraction with different solvents including methanol, isopropyl alcohol, and hexane and finally dialyzed against chloroform solvent with a dialysis membrane for a week to remove polymers of medium molecular weight (MWCO of 80 000). The remaining solution in the dialysis membrane was poured into methanol, filtered, and dried under vacuum. From these processes, highly purified and narrow polydispersity of EL polymers were obtained.

Table 1. Polymerization Results, Molecular Weights, and Thermal Data of Poly(FV) and Poly(FV-*co*-MEHPV)

polymer	yield (%)	M_w ($\times 10^{-4}$)[a]	PDI	TGA (5%)[b]	T_g[c]
poly(FV)	82	22.2	2.1	415	173
poly(FV-*co*-MEHPV) (95:5)[d]	60	30.9	2.6	410	176
poly(FV-*co*-MEHPV) (90:10)	59	26.7	1.9	390	170
poly(FV-*co*-MEHPV) (80:20)	69	29.7	2.6	385	172
poly(FV-*co*-MEHPV) (50:50)	49	43.2	3.0	355	169

[a] Determined by GPC in THF based on polystyrene standards. [b] Temperature at 5% weight loss under nitrogen. [c] Determined by DSC at a heating rate of 10 °C/min under nitrogen. [d] Composition determined from initial monomer mole ratio.

Table 1 summarizes the polymerization results, molecular weights, and thermal characteristics of poly(FV) and poly(FV-*co*-MEHPV). The weight-average molecular weight (M_w) and polydispersity of poly(FV) and poly(FV-*co*-MEHPV) after the molecular fractionation experiment were found to be (22.2−43.2) × 10^4 and 1.9−3.0, respectively. In previous work, the molecular weight of a poly(9,9-di-*n*-octylfluorenyl-2,7-vinylene) was recorded as 6.9 × 10^4 by acyclic diene metathesis (ADMET) polymerization.[41] Thermal behavior of the resulting EL polymers was investigated by DSC and TGA. Most fluorene-based EL polymers do not show a very distinct glass transition temperature. However, the glass transition temperatures of poly(FV) and poly(FV-*co*-MEHPV) were found in the range 176−169 °C as determined by DSC. This value is higher than those of PFs (75−113 °C).[42,43] Thermotropic liquid crystallinity of polyfluorene homopolymers was first reported by Grell et al.[44,45] We measured the DSC thermogram up to 300 °C at a heating rate of 5 °C/min to investigate the liquid crystallinity of the resulting polymers. However, we did not observe any significant liquid crystal-

Table 2. Optical Data and Device Performance of ITO/PEDOT/Polymer/Al Devices

polymer	solution $\lambda_{\max}$ (nm)[a] Abs	solution $\lambda_{\max}$ (nm)[a] PL	film $\lambda_{\max}$ (nm)[b] Abs	film $\lambda_{\max}$ (nm)[b] PL	EL $\lambda_{\max}$ (nm)	E_g (eV)[c]	luminescence (cd/m^2)	luminescence efficiency (cd/A)
poly(FV)	417	463	419	507	508	2.6	760	0.16
poly(FV-*co*-MEHPV) (95:5)	415	463	418	576	574	2.57	762	0.31
poly(FV-*co*-MEHPV) (90:10)	418	464	421	580	576	2.54	1352	0.51
poly(FV-*co*-MEHPV) (80:20)	418	463	420	589	589	2.54	595	0.12
poly(FV-*co*-MEHPV) (50:50)	417	463	422	593	592	2.1	127	0.026
MEH−PPV	504	592	502	582	586	2.1	87	0.0023

[a] Measured in chloroform solution. [b] Polymer cast from chloroform solution. [c] Band gap estimated from the onset wavelength of the optical absorption.

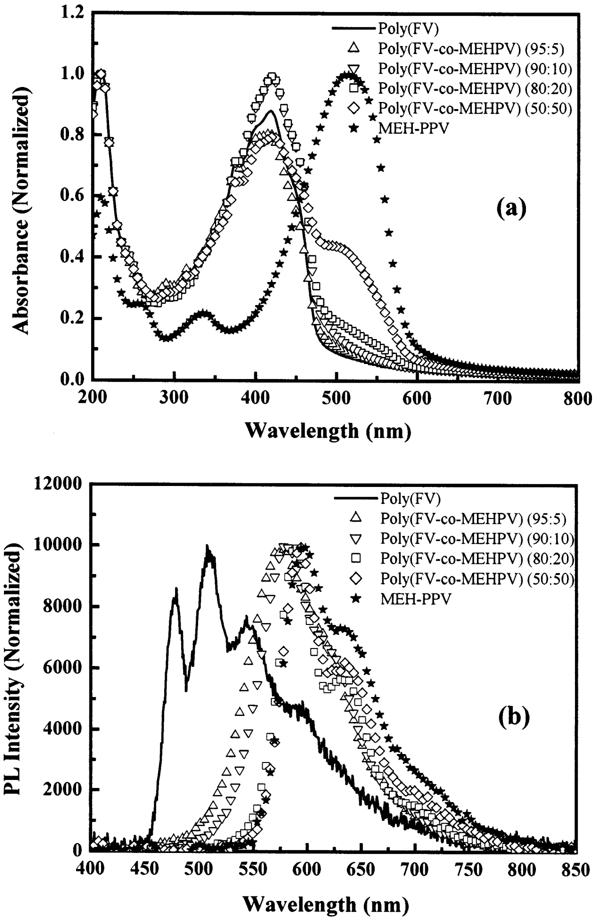


Figure 1. UV−vis absorption (a) and PL spectra (b) of poly(FV), poly(FV-*co*-MEH PV), and MEH−PPV in the solid state.

line texture by DSC measurement and also by polarized optical microscopy. Comparison of TGA thermogarams of poly(FV), poly(FV-*co*-MEHPV), MEH−PPV, and poly(9,9-diethylhexylfluorene) revealed that poly(FV) has higher thermal stability than those of poly(FV-*co*-MEHPV) and MEH−PPV and similar thermal stability to that of poly(9,9-diethylhexylfluorene), showing a 5% weight loss at 415 °C under a nitrogen atmosphere. High thermal stability of the present EL polymers prevents deformation and degradation of the emitting layer by current-induced heat during the operation of EL devices.

Optical and Electroluminescent Properties. Figure 1 shows the optical absorption (Abs) and PL spectra of poly(FV), poly(FV-*co*-MEHPV), and MEH−PPV thin films coated on a carboglass. Regardless of copolymer compositions, poly(FV) and poly(FV-*co*-MEHPV) exhibited absorption maxima around 420 nm due to the $\pi-\pi^*$ transition of the conjugated polymer backbone with a shoulder at 377 nm, which is a characteristic peak of a fluorene unit. However, as the MEH−PPV content in poly(FV-*co*-MEHPV) is increased, the absorption maximum at 511 nm is consistently increased. The absorption of all polymers is approximately 40 nm red-shifted relative to that of PF derivatives.[44] This is probably due to the introduction of vinylene units and the extension of effective conjugation length along the polymer backbone. The absorption and emission maxima of poly(FV), poly(FV-*co*-MEHPV), and MEH−PPV are summarized in Table 2. The emission spectrum of poly(FV) shows the three characteristic peaks at 478, 507, and 543 nm. However, no emission peak from poly(FV) units can be observed, even though there is a 5 mol % amount of MEH−PPV in poly(FV-*co*-MEHPV), indicating that efficient energy transfer occurs from wide band gap of poly(FV) to the small band gap of MEH−PPV components. PL maximum peaks of poly(FV-*co*-MEHPV) look to be almost similar to and gradually become identical to those of PL peaks with MEH−PPV as the portion of MEH−PPV increases.

Figure 2a shows the absorption spectrum of MEH−PPV and the PL spectra of poly(FV) and poly(FV-*co*-MEHPV) in the thin film state. To facilitate Förster type energy transfer in blending or copolymer systems, the emission peak of the donor component with wide band gap must overlap with the absorption peak of acceptor segments of small band gap. It can be seen from Figure 2a that the PL spectrum of poly(FV) overlaps with a major portion of the absorption spectrum of MEH−PPV. Thus, Förster type intramolecular and intermolecular energy transfer from poly(FV) to MEH−PPV is expected to be efficient if the copolymers are composed with poly(FV) and MEH−PPV segments. From these results, efficient Förster type energy transfer is observed even in the case of 5 mol % of MEH−PPV in copolymer compositions.

From Figure 2b, intramolecular transfers of holes and electrons are expected to be energetically feasible and occur from poly(FV) to MEH−PPV segments. The HOMO energy level of MEH−PPV is about 0.44 eV lower in energy than that of poly(FV) and the LUMO about 0.05 eV higher in energy. This means that both holes and electrons will be trapped on the MEH−PPV segment in the poly(FV-*co*-MEHPV) systems, and thus intramolecular exciton transfers take place from a poly(FV) segment to a MEH−PPV segment.

The double-layer PLEDs with the configuration of ITO/PEDOT/polymer/Al devices were fabricated to investigate the EL properties of novel poly(FV) and poly(FV-*co*-MEHPV). To improve device performance, the hole-injection-transport layer, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), was spin-coated onto the surface-treated ITO substrate, and the resulting EL polymer layers were fabricated on top of PEDOT film. After that, the Al cathode was thermally evaporated at 4×10^{-6} mbar.

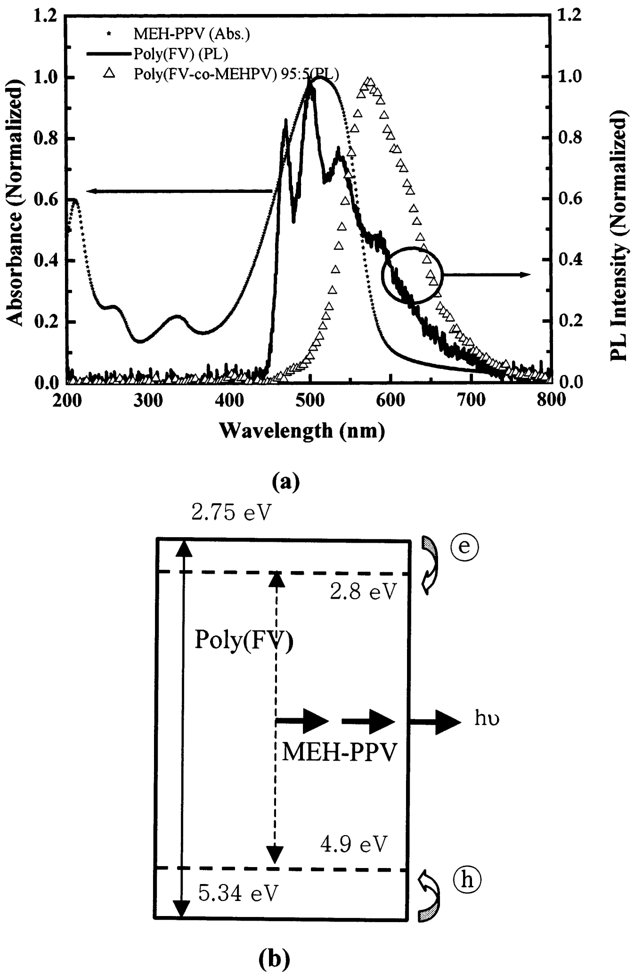


Figure 2. UV–vis absorption spectrum of the MEH–PPV and PL spectra of the poly(FV) and poly(FV-*co*-MEHPV) (a) and intramolecular holes and electrons transfer process (b).

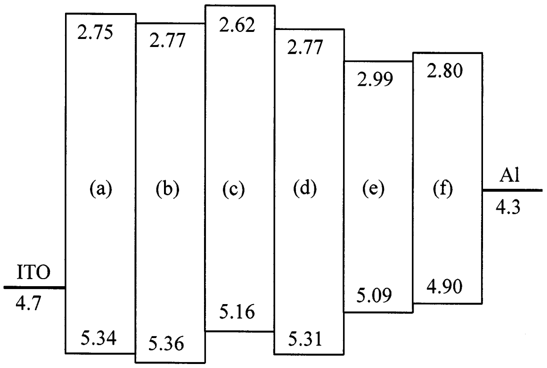


Figure 3. Hypothesized energy band diagram of the ITO/PEDOT/polymer/Al devices, poly(FV) (a), poly(FV-*co*-MEHPV) (95:5) (b), poly(FV-*co*-MEHPV) (90:10) (c), poly(FV-*co*-MEHPV) (80:20) (d), poly(FV-*co*-MEHPV) (50:50) (e), and MEH–PPV (f).

The band gap of poly(FV), poly(FV-*co*-MEHPV), and MEH–PPV, taken from the onset of the absorption spectrum, were in the range 2.1–2.6 eV. Energy band diagrams of poly(FV), poly(FV-*co*-MEHPV), and MEH–PPV for comparison were determined from an optical absorption spectrum for band gap and cyclic voltammogram for an HOMO energy level, which are depicted in Figure 3. The LUMO level was approximated by subtracting the optical band gap from the HOMO binding energy. All of poly(FV), poly(FV-*co*-MEHPV), and MEH–PPV show that the major carriers are the holes rather than electrons, due to the lower band offset between the ITO and HOMO energy levels. As the MEH–PPV contents increased, the HOMO energy levels of poly(FV-*co*-MEHPV) decreased in comparison to poly(FV), and the band offsets were in the range 0.2–0.66 eV for hole injections at the interface of the ITO/HOMO state. However, the LUMO energy levels of poly(FV-*co*-MEHPV) slightly increased in comparison to poly(FV), which the electrons are move easily injected from the Al electrode.

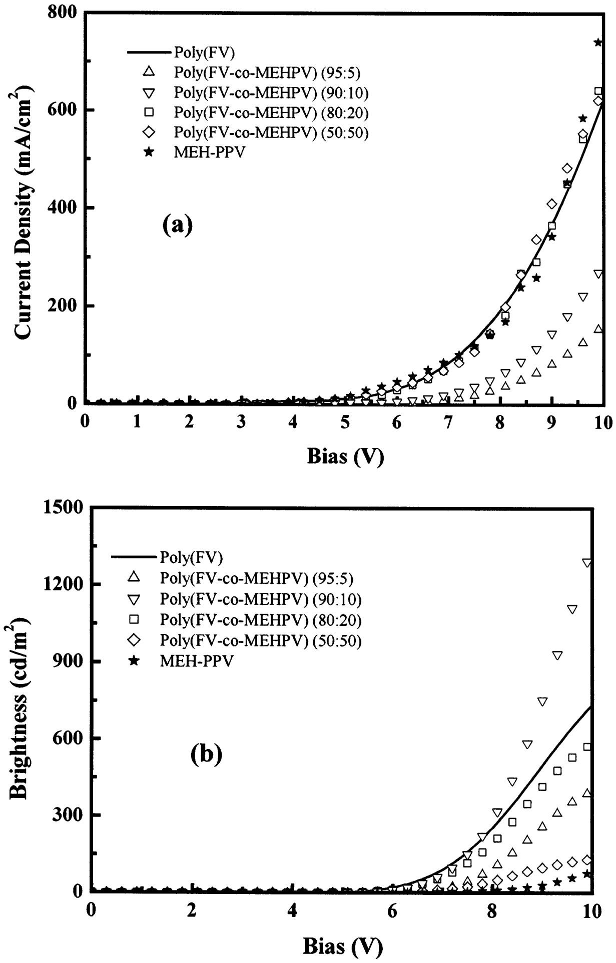


Figure 4. Current–voltage (*I*–*V*) (a) and luminescence–voltage (*L*–*V*) (b) characteristics of the ITO/PEDOT/polymer/Al devices.

Figure 4 shows the current–voltage (*I*–*V*) and luminescence–voltage (*L*–*V*) characteristics of ITO/PEDOT/polymer/Al devices. The turn-on voltages of poly(FV), poly(FV-*co*-MEHPV), and MEH–PPV are approximately 2.5 V, and the current density increases in an exponential manner with an increasing forward bias, which is a typical diode characteristic. Most of the PF-based LEDs exhibited turn-on voltages at about 8 V with a stable and efficient blue emission with an Al electrode.[11] The relatively lower turn-on voltages and excellent device performance of poly(FV) and poly(FV-*co*-MEHPV), with an Al cathode possibly attributing a synergistic effect, compared to that of crystalline poly(9,9-dihexylfluorene), were due to the fact that the fluorene and vinylene repeating units can tune HOMO and LUMO binding energy levels. These energy levels realize efficient hole and electron injection from both electrodes. Poly(FV) and poly(FV-*co*-MEHPV) with a

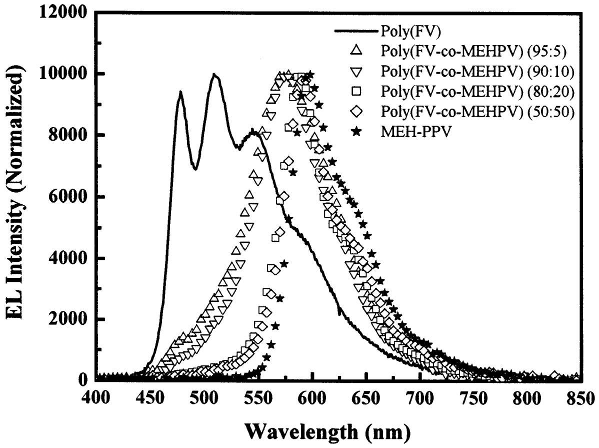


Figure 5. EL spectra of the ITO/PEDOT/polymer/Al devices.

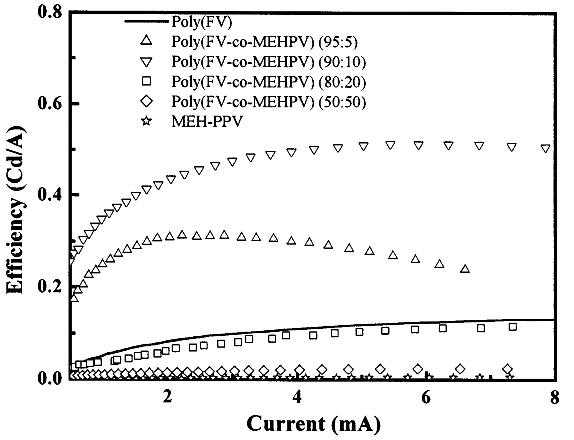


Figure 6. Current−luminescence efficiency curves of the ITO/PEDOT/polymer/Al devices.

vinylene unit exhibited amorphous morphology from DSC thermograms without phase transition at higher temperature, which improved the cohesion between PEDOT/polymer and polymer/Al interface. The maximum brightness of poly(FV) and poly(FV-*co*-MEHPV) was about 760 and 1350 cd/m^2 at 10 V with a greenish-blue and an orange-red color.

Figure 5 shows the EL spectra of ITO/PEDOT/polymer/Al devices. The EL spectrum peaks of poly(FV), poly(FV-*co*-MEHPV), and MEH−PPV are almost identical to those of a PL spectra as shown in Figure 1b. These results suggest that the mechanism of PL and EL emission is due to the same excited singlet exciton state. The EL peaks of poly(FV-*co*-MEHPV) were about 83 nm red-shifted relative to that of poly(FV).

The current−luminescence efficiency curves of ITO/PEDOT/polymer/Al devices are shown in Figure 6. The device characteristics of poly(FV-*co*-MEHPV) were greatly improved as compared to those of poly(FV) and MEH−PPV, and the results are summarized in Table 2. The maximum luminescence efficiency of poly(FV-*co*-MEHPV) (90:10 mol %) was about 0.51 cd/A with 5.8 mA at 5.9 V. According to Figures 2 and 6, the luminescence efficiency of poly(FV-*co*-MEHPV) (90:10) was exhibited to be about 220 times higher than that of MEH−PPV. The resulting EL polymers having 9,9-dialkylfluorenyl-2,7-vinylene units may have useful applications for electrooptic devices.

Conclusions

We were first to synthesize a new class of high-molecular-weight poly(9,9-di-*n*-octylfluorenyl-2,7-vinylene) poly(FV) and its copolymers with an MEH−PPV segment by the Gilch polymerization. The resulting EL polymers showed high thermal stability up to 415 °C. Poly(FV) and poly(FV-*co*-MEHPV) exhibited a high glass transition temperature and can be easily spin-casted onto the ITO substrates. The emission color of poly(FV-*co*-MEHPV) was red-shifted, even in the case of having a small amount of MEH−PPV via intramolecular and intermolecular energy transfer. The maximum EL emission peaks of poly(FV) and poly(FV-*co*-MEHPV) were at 507 and 585 nm, respectively, which corresponded to a greenish-blue and an orange-red color. Efficient energy transfer in poly(FV-*co*-MEHPV) systems are expected to occur by a Förster type mechanism, due to the remarkable overlap between the emission spectrum of the poly(FV) and absorption spectrum of the MEH−PPV units. Further intramolecular exciton transfers from poly(FV) to MEH−PPV segments are energetically favorable and might occur efficiently through transfers of holes and electrons. Poly(FV-*co*-MEHPV) showed improved device performance compared to poly(FV) and MEH−PPV. The luminescence efficiency of poly(FV-*co*-MEHPV) was much higher than that of MEH−PPV. The maximum brightness and luminescence efficiency of the present EL polymers were 1350 cd/m^2 and 0.51 cd/A at 5.9 V.

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