

Synthesis and EL Properties of Blue Light-emitting Poly(arylenevinylene)s

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Abstract

A series of fully conjugated polymers containing new arylenevinylene units were synthesized and their light-emitting properties were investigated. A bisphosphonate containing tetraphenyl group was made to react with three different dialdehyde monomers to produce fully conjugated alternating copolymers. The photoluminescence (PL) and the electroluminescence (EL) peak wavelengths of the polymers were varied from 500 nm to 460 nm depending on the polymer structure. Single layer EL devices using the polymers as an emissive layer have been fabricated. The single layer EL devices became visible between 12–22 V and emitted blue light.

Keywords : arylenevinylene, alternating copolymer, blue light-emitter, EL device

1. Introduction

Conjugated polymers have attracted much attention among researchers in science and technology in the past few decades as semiconductors for diverse applications such as transistors [1], photo-voltaic devices [2], nonlinear optical devices [3], and light-emitting diodes (LEDs) [4,5]. In particular, interests in conjugated polymers as an emissive layer (EML) in electroluminescent (EL) devices have increased in recent years since poly(1,4-phenylenevinylene) (PPV) was first employed in a polymer EL device in 1990 [4]. Polymer light-emitting diodes have many advantages in flat panel displays because of their good processibility, low operation voltage, fast response time, and easy color tunability over the full visible range by controlling HOMO–LUMO band gaps of the emissive polymers. A large number of light-emitting polymers have been

developed and their EL properties have been investigated over the last 10 years. PPV [4], PPV derivatives [5], poly(p-phenylene) (PPP) [6], PPP derivatives [7], polyfluorenes [8], polythiophenes [9], polypyridines [10], and conjugated-nonconjugated block copolymers [11] have been reported for a blue light-emission. But blue light-emission from poly(arylenevinylene)s has been seldom reported.

In addition, light-emitting materials containing fluorine atom have been reported to affect photoluminescence (PL) and EL efficiencies. A fluorine containing PPV derivative, poly(2-fluoro-1,4-phenylenevinylene) (PFPV) showed a highly improved quantum efficiency in EL device compared with PPV [12]. The enhanced EL efficiency of the PFPV is due to the decrease in the band offset between polymer and electron injection electrode.

In this article, we report of the synthesis and properties of fluorine containing new blue light-emitting poly(arylenevinylene)s. The synthetic schemes of the monomers and polymers are shown in Schemes 1 and 2.

2. Experiments

Synthesis of monomer. 1,22-Dimethyl-8, 9, 11, 12, 14, 17, 18-octafluorotetraphenyl (1). A solution of

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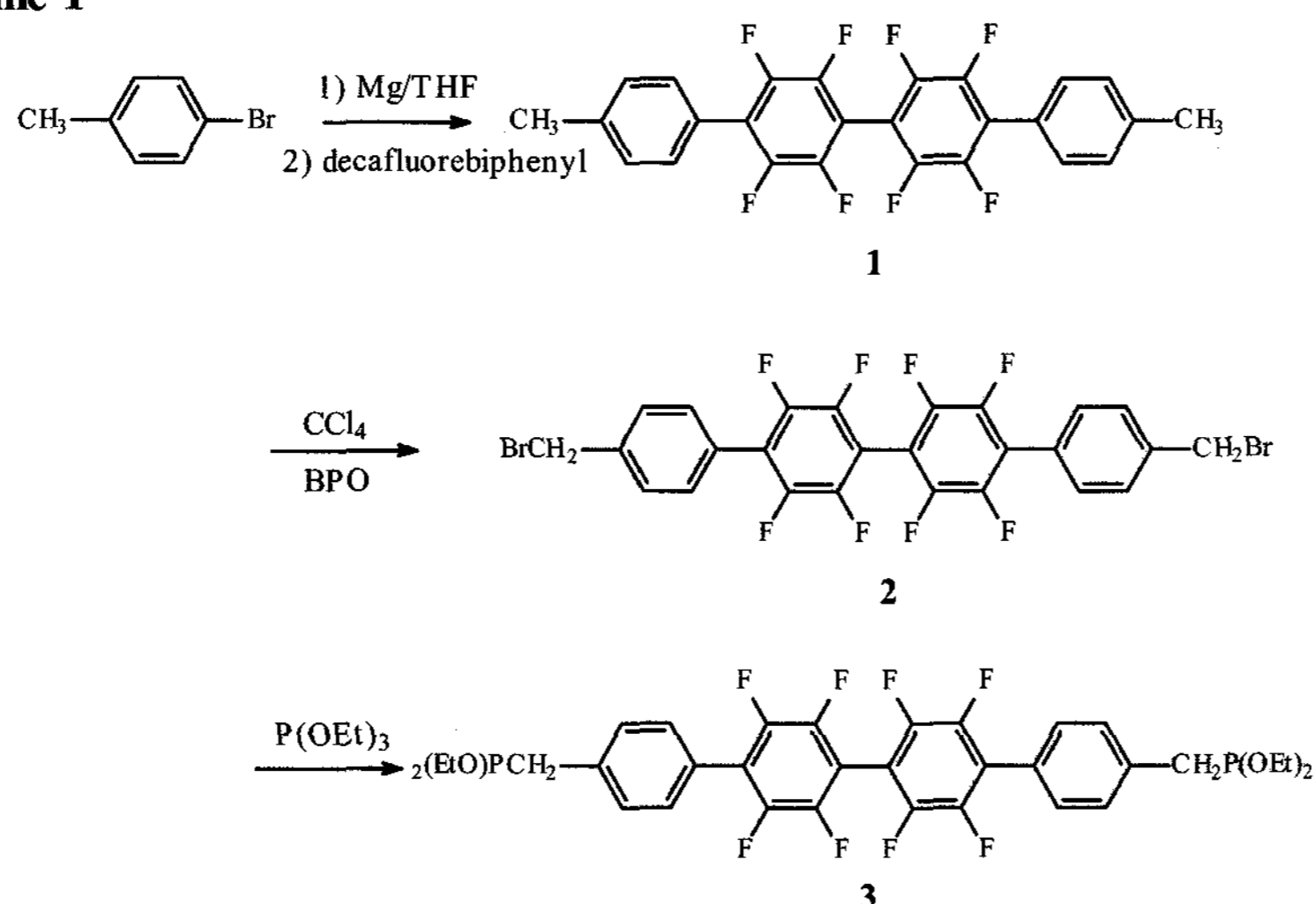
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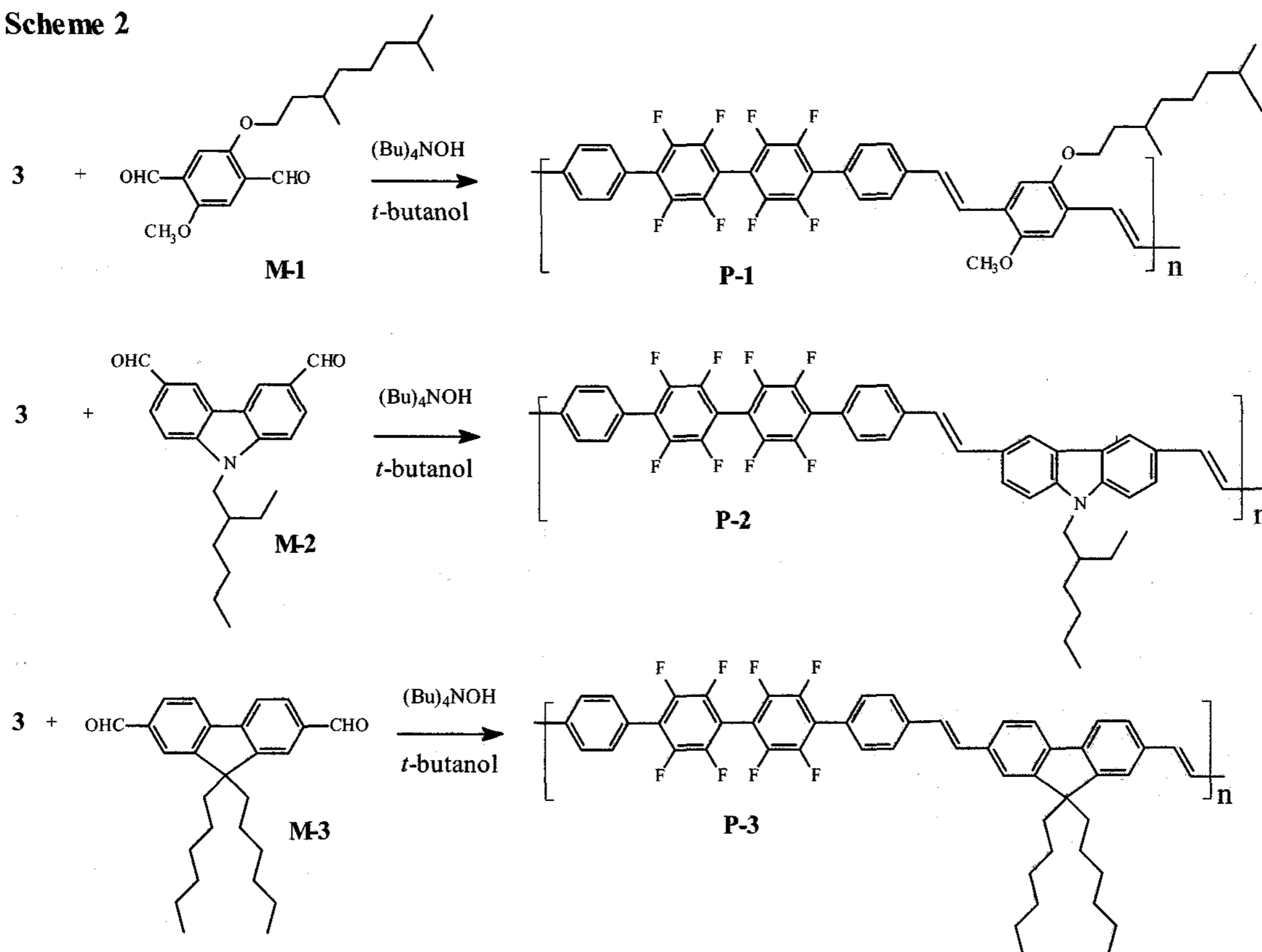
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Scheme 1



Scheme 2



15.4 g (90 mmol) of 4-bromotoluene diluted in 30 mL of anhydrous THF was added to 3.3 g (135 mmol) of clean magnesium turnings after initiation by 5 mol % of dibromoethane. Then, this solution was refluxed for 30 mins under nitrogen atmosphere. When the magnesium was completely consumed, the solution was poured in to

a different flask containing 10.0 g (30 mmol) of decafluorobiphenyl dissolved in 100 mL of anhydrous THF. The reaction mixture was refluxed for 24 h and then the solution was added into water/methanol (1/1) co-solvent to precipitate the reaction products. The precipitate was washed with methanol, filtered and dried

in vacuum oven. The product yield was 90% (12.9 g). $^1\text{H-NMR}$ (CDCl_3 , ppm): δ 2.42 (s, 6H), 7.37 (m, 8H).

1,22-Bis(bromomethyl)-8, 9, 11, 12, 13, 15, 17, 18-octafluorotetraphenyl (2) was prepared by reacting 9.3 g (19.4 mmol) of compound 1 with 7.3 g (40.8 mmol) of N-bromosuccinimide (NBS) in 40 mL of carbon tetrachloride. A small amount of benzoyl peroxide was added to act as a radical initiator. The reaction mixture was refluxed at 90 °C for 3 h under nitrogen atmosphere. The appearance of succinimide on the surface of the solution indicated the completion of the reaction. A yellow solution was obtained after filtration of succinimide and the solution was concentrated and poured into methanol. After filtration and vacuum drying, 7.9 g of white solid was obtained. The product yield was 64%. $^1\text{H-NMR}$ (CDCl_3 , ppm): δ 4.54 (s, 4H), 7.53 (m, 8H).

{4-[4-(4-{4-[(Diethoxyphosphino) methyl] phenyl} - 2, 3, 5, 6-tetrafluorophenyl)-2, 3, 5, 6-tetrafluorophenyl] phenyl} methyl diethoxyphosphine (3). 7.9 g (12.41 mmol) of compound 2 and excess amount of triethylphosphite was made to react at 100 °C for 24 h, and then the reaction mixture was cooled to room temperature. The reaction mixture was dissolved in 10 mL of diethylether and precipitated into petroleum ether. After filtration and vacuum drying 9.0 g of white solid was obtained. The product yield was 90%. $^1\text{H-NMR}$ (DMSO-d_6 , ppm): δ 1.25 (t, 12H), 3.22 (d, 4H), 4.01 (q, 8H), 7.47 (s, 8H).

2-Methoxy-5-(3',7'-dimethyloctyloxy)benzene-1,4-dicarbaldehyde (M-1), 9-(2-ethylhexyl)carbazole-3,6-dicarbaldehyde (M-2) and 9,9-Di-*n*-hexylfluorene-2,7-dicarbaldehyde (M-3) were synthesized according to the procedures outlined in the literature [13].

Synthesis of polymer. The fully conjugated polymers were prepared by Horner polycondensation reaction. The mixture of the equimolar phosphonate monomer 3 and the corresponding dialdehyde monomer dissolved in tert-butanol was reacted with equimolar 1.0 M tetrabutylammonium hydroxide in methanol as a base at room temperature for 24 h. Reaction mixture was precipitated into methanol, filtered, and dried in vacuum oven. The obtained polymer yield was 60-70 %.

Characterization. $^1\text{H-NMR}$ spectra were measured

using a Bruker AM 200 spectrometer. The UV-visible spectra were obtained with a Shimadzu UV-3100S. Thermogravimetric analysis (TGA) was performed on a DuPont 9900 analyzer at a heating rate of 10 °C/min under nitrogen atmosphere. Photoluminescence spectra were obtained by exciting the polymer film at 350 nm from a Xenon lamp. The polymer film with 100 nm thickness was obtained by spin coating the filtered polymer solutions on the substrates and drying in vacuum oven at 100 °C for 1 h. Aluminum was vapor deposited for the top electrode at a pressure of below 1×10^{-6} Torr, yielding an active area of 3.14 mm². EL spectra were measured using a monochromator (Jobin-Yvon HR320) with the photomultiplier tube (Hamamatsu R928). Voltage-light intensity (V-L) characteristics were measured with the current/voltage source (Kethley 238) and the calibrated silicon photodetector (Newport 818SL).

3. Results and Discussion

The synthesized polymers were soluble in common organic solvents such as chloroform and toluene, and formed a smooth thin film after spin coating. The molecular weights of the polymers were determined by GPC. GPC measurement of the polymers with polystyrene as the calibration standard showed a M_w of 6,000–20,000 and polydispersity index of 1.20–1.45 depending on the polymer structures. The synthesized polymers showed no significant weight loss up to 300 °C in TGA thermograms, which are not presented in this paper.

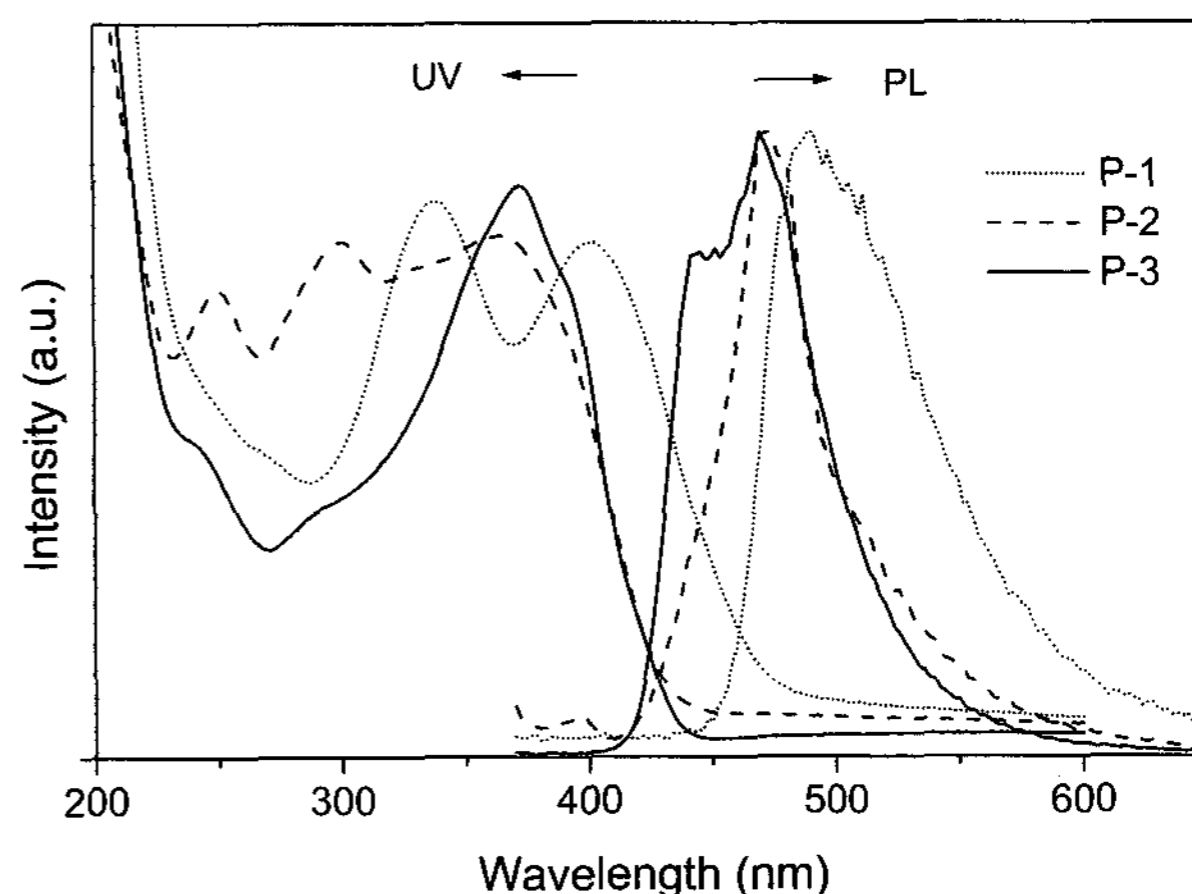


Fig. 1. UV-visible and PL spectra of the polymers.

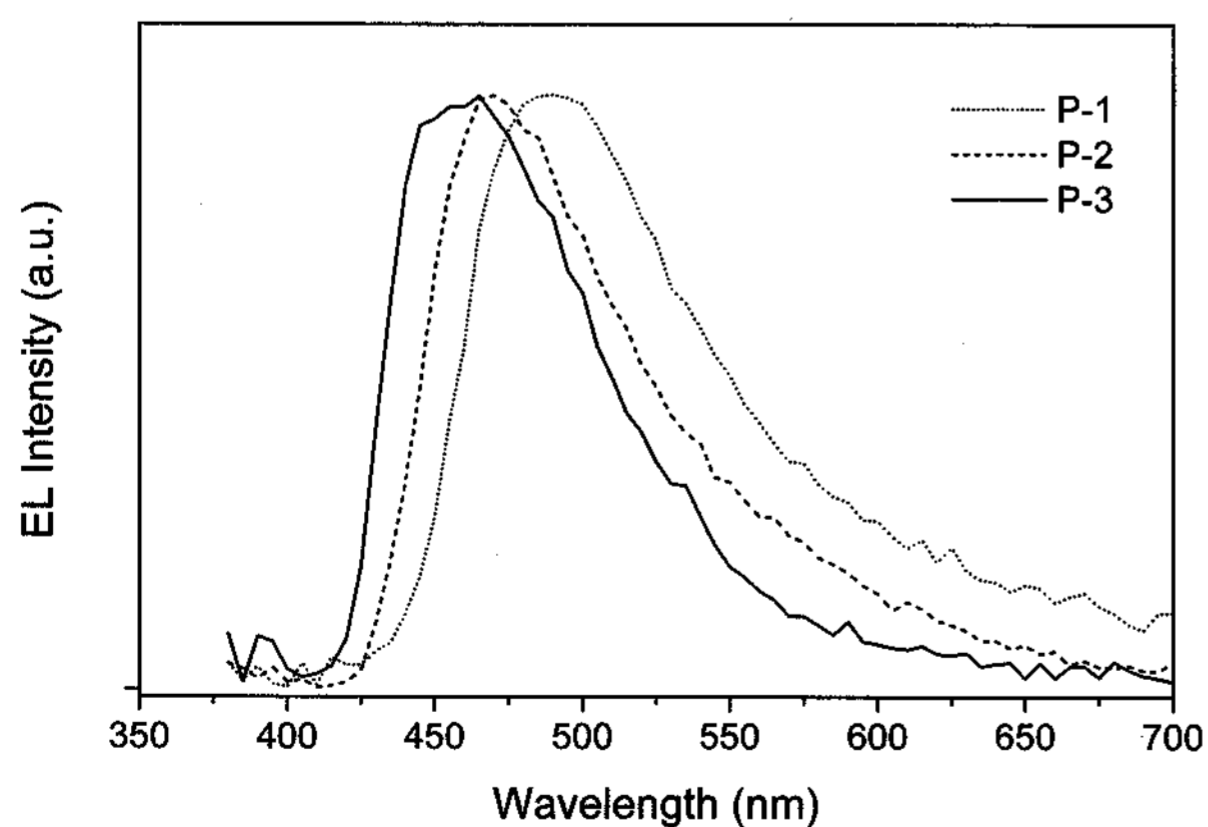
Table 1. Molecular weights, polydispersity indices, and peak positions of UV absorption and PL of the polymers.

	P-1	P-2	P-3
Mw	20,000	8,000	6,000
PD	1.24	1.20	1.45
UV _{max} (nm)	338	367	372
PL _{max} (nm)	490	470	468

Table 2. Turn-on voltage, maximum brightness and peak EL of the single layer devices.

	ITO/P-1/Al	ITO/P-2/Al	ITO/P-3/Al
V _{turn-on} (V)	12	15	22
Maximum brightness(cd/m ²)	100	50	30
EL _{max} (nm)	490	468	465

Fig. 1 shows the UV-visible absorption and PL spectra of the polymer films. P-1 shows the absorption maximum at 338 and 402 nm and the absorption edge at 480 nm. P-2 and P-3 show the absorption maxima at 367 and 372 nm, respectively. P-1 shows PL emission in the greenish-blue region (PL_{max}=490 nm), and P-2 (PL_{max}=470 nm) and P-3 (PL_{max}=468 nm) in the blue region. Table 1 summarizes average molecular weights, polydispersity indices, and peak positions of UV absorption and PL emission of the polymers.

**Fig. 2.** EL spectra of the single layer devices with ITO/polymer/Al configuration.

Single layer electroluminescent devices were fabricated with the polymers as emitting layer and

aluminum and ITO as cathode and anode, respectively. The EL spectra from the single layer devices were similar with those of the PL spectra of the polymers, as shown in Fig. 2.

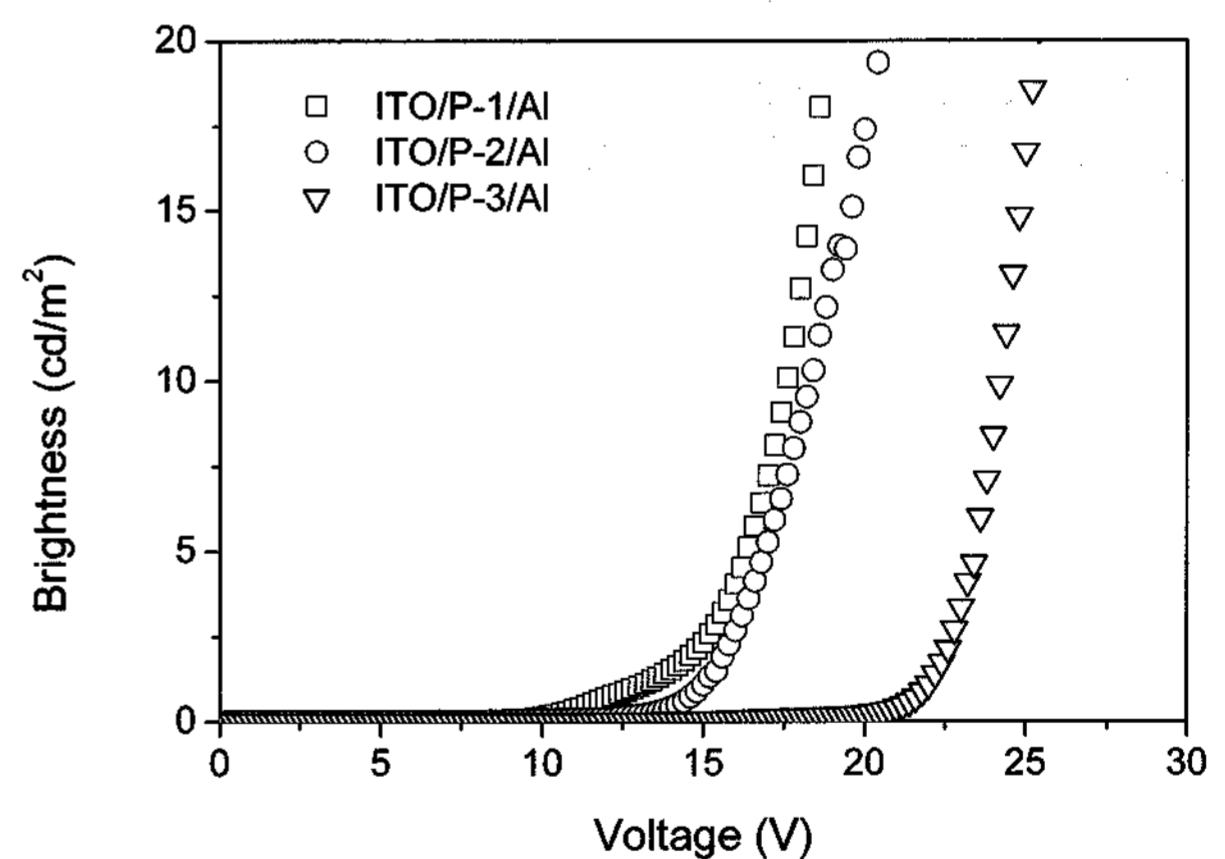
**Fig. 3.** L-V curves of the EL devices with an ITO/Polymer/Al configuration.

Fig. 3 shows the L-I curves of the single layer devices with ITO/polymer/Al configuration. The forward current of the devices increased with increasing forward bias showing typical diode characteristics. The turn-on voltages of the single layer devices of P-1, P-2, and P-3 were 12, 15, and 22 V, respectively. The maximum brightness of the single-layer devices was measured to be

between 30–100 cd/m². Table 2 summarizes EL data of the single layer devices. The efficiencies and brightness of the devices may be improved by using a low work-function metal electrode as a cathode and also by using charge-transporting layers.

4. Conclusion

Summary, fully conjugated blue light-emitting polymers containing new arylenevinylene units were synthesized by using Horner condensation polymerization, and their light-emitting properties were characterized. All the synthesized polymers showed their photoluminescence in blue or greenish blue region. The single layer EL devices using the polymers with ITO/polymer/Al configuration has been fabricated and the light-emission from the devices have become observable at a bias voltage of 12–22 V.

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