

Synthesis and Characterization of New Poly(terphenylene vinylene) Derivative as Blue Emitting Material

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Efficient thermally stable blue light emitting materials are needed both to complete the color spectrum and serve as energy transfer media for incorporated fluorophores. The extended delocalization lengths of most fully conjugated polymers, however, result in small electronic band gaps and red-shifted emissions.

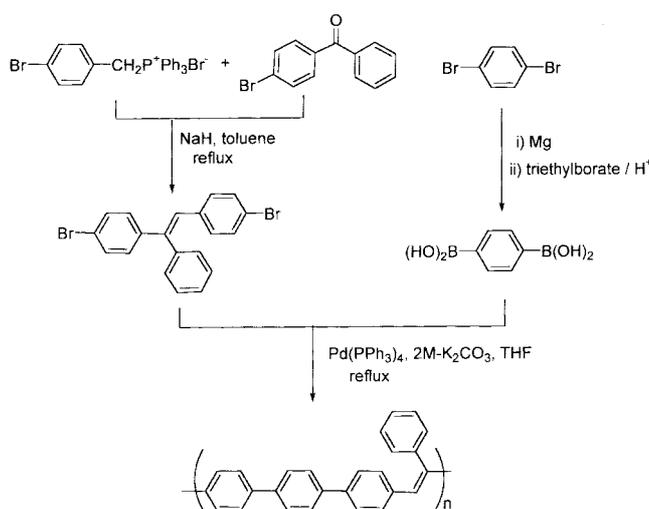
The poly(*p*-phenylenevinylene) (PPV),¹⁻⁶ which is the first reported electroluminescent polymer, and PPV derivatives have several advantages as an emitting material; high thermal stability, good film quality, suitable color tunability, etc. However, it has low oxidative stability and some difficulties in processability and emitting blue color.

Poly(*p*-phenylene) (PPP), and its derivatives⁷⁻¹² have also been extensively investigated for light emitting materials because they are thermally and oxidatively stable polymers. PPP derivatives show large band gaps since the aromatic rings are twisted to relieve unfavorable steric interactions in the backbone, which limits the effective conjugation length. Unsubstituted PPP is highly insoluble, limiting the molecular weights and processability. Large, solubilizing substituents may also be incorporated, resulting in improved processability, but this usually exacerbates the steric interactions in the polymer main chain. Thus, PPP derivatives are intrinsically violet-blue emitter to have some difficulties in color tunability.¹³

Solubility, oxidative stability, low turn-on voltage, and color tunability (especially blue emission) are desirable properties for conjugated polymers used in LEDs.¹⁴ Moreover, good thermal stability is needed because heat is generated when current passes through the device.

Thus, we tried to synthesize a blue-light-emitting polymer, which has the advantages of both PPP and PPV. Recently, we reported synthesis and properties of poly(biphenylenevinylene) (PBPV) derivatives with a controlled conjugation length of biphenylene vinylene unit, which is composed of alternating PPP and PPV units.

In this communication, we describe the synthesis and characterization of blue-light-emitting, poly(α -phenylene terphenylenevinylene) derivative. And, on the basis of poly(terphenylenevinylene), our research also involved introducing substituent into the vinyl bridge. Introducing phenyl pendant group to a vinyl bridge may expect to lead to enhanced solubility, oxidative and thermal stability, and reduced the formation of eximers owing to interchain interactions.



Scheme 1

The synthetic route of polymer was shown in Scheme 1. Benzene diboronic acid was obtained by Grignard reaction of 4,4-dibromobenzene with triethylborate. [1,2-(4',4'')-Di-bromophenyl]-1-phenyl ethylene] were synthesized by Wittig reaction of (4-bromobenzyl)triphenylphosphonium bromide with 4-bromobenzophenone. The polymerization was carried out using a typical Suzuki coupling reaction with good yield. After the polymerization, the end-capped reaction of the bromine and boronic acid end group, which hamper thermal stability and efficiency of PL, was accomplished by bromobenzene and benzene boronic acid. The polymer structure shown was consistent with the elemental analysis and the spectroscopic data from ¹H-NMR and FT-IR. The obtained polymer was readily soluble in common organic solvents such as chloroform, dichloromethane and toluene even though the polymer was composed rigid aromatic and vinyl carbons. The weight average molecular weight (Mw) of polymer, as determined by gel permeation chromatography using polystyrene standard, was Mw = 13500 (PDI = 1.6). The thermal characterization of the polymer was accomplished by DSC and TGA. The DSC thermogram obtained from the second heating of the polymer. The polymer had glass transition at around 146 °C. TGA curve showed that the weight loss of the polymer is less than 5% on heating to 430 °C. From the above results, the obtained polymer has good thermal stability.

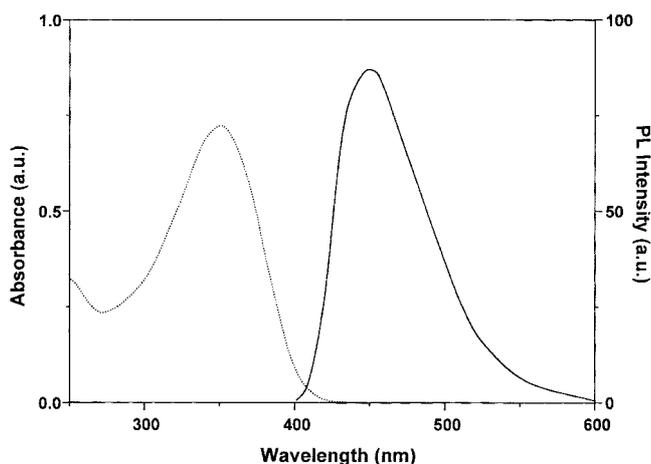


Figure 1. The optical absorption and photoluminescence spectra of the polymer in chloroform.

Figure 1 shows the optical absorption and photoluminescence spectra of a dilute solution of the polymer in chloroform. The maximum absorption of polymer showed 350 nm. The maximum absorption peak of the polymer are 70-90 nm blue shifted as compared with that of PPV, 10-20 nm blue shifted as compared with that of PBPV and 10-20 nm red shifted as compared with that of PPP. These shifts may originate from the terphenylene vinylene units composed of PPP and PPV units. The band-gap energy of the new polymer estimated from extrapolation of the low energy absorption spectra was about 2.98 eV.

The PL spectrum of the dilute solution of the polymer pumped by UV light (350 nm) has a maximum peak at 450 nm. Although the PL spectrum of a solid film of polymer shows a slight bathochromic shift from that of solution, it is blue shifted by 10-20 nm from those of poly(biphenylene vinylene) derivatives^{14,15} which were composed alternating PPP and PPV. It may be resulted from increased phenyl unit in the main chain.

From the cyclic voltammogram of a polymer, the polymer is reductive as well as oxidative electrochemically showing EA and IP values 2.96 and 5.73 eV, respectively. The π - π^* band gap of 2.98 eV is almost the same as that determined

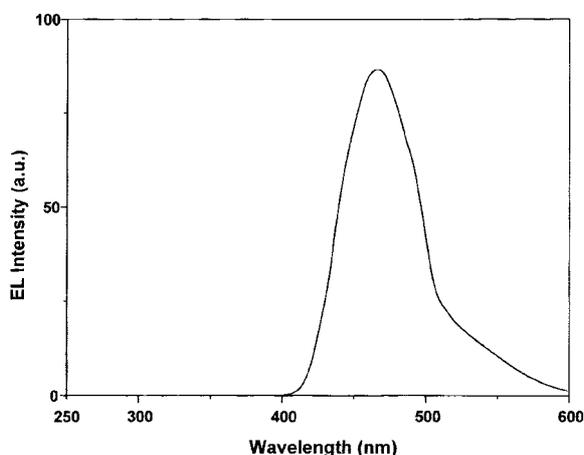


Figure 2. The electroluminescence spectrum of the ITO/polymer/Al device.

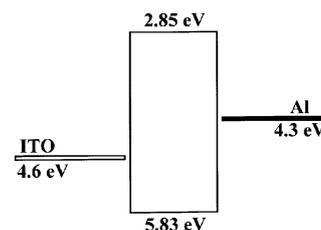


Figure 3. The position (with respect to the vacuum) of the HOMO and of the LUMO for the polymer with no field. The work functions of the indium tin oxide and Al are also reported.

from the onset of optical absorption (420 nm).

Single-layer light-emitting diode was fabricated by using ITO as the anode and an Al as the cathode. The electroluminescence spectrum of the polymer is shown in Figure 2. Blue light emission was observed from the EL device of the polymer. The EL spectrum of the polymer depicted a close correspondence to the PL spectrum, indicating that the recombination processes were the same for both cases, as often observed for polymer-based LEDs. It was also of note that tailing in the long wavelength region observed for the electroluminescence spectrum suggested that emission from some excimer states should be taken into consideration. Figure 3 shows the electronic energy band gap scheme of the new polymer as evaluated from cyclic voltammogram and UV-vis absorption spectrum. The efficient device for the obtained polymer as emitting layer is suggested that the hole injection and low work function metal are needed. Now we are pursuing the study of the optimized devices and poly(terphenylene vinylene) derivatives.

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