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New Blue Light Emitting Polymers Having the Characters of PPP and PPV

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The new blue light emitting conjugated polymers, PBPV and PTPV having advantages of both PPP and PPV, have been synthesized by Suzuki coupling reaction and nickel-catalyzed coupling reaction. The obtained polymers showed good solubility. PTPV has more good thermal stability than that of PBPV. The photoluminescence spectra of PBTV and PTPV showed the maximum at 460 nm and 450 nm, respectively. The optical energy band gap of PBTV and PTPV were 2.93 eV and 2.98 eV, respectively.

Keywords: Blue light emitting; Suzuki coupling; Nickel catalyzed coupling; UV-absorption; Photoluminescence, Optical energy band gap

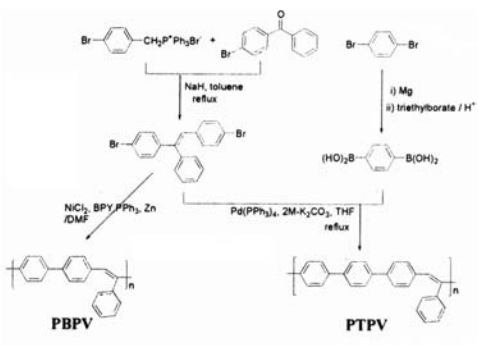
INTRODUCTION

Since light-emitting devices (LED) using conjugated polymers were first realized in the early 1990s [1], a great number of different conjugated polymers suitable for LEDs have been investigated and developed. Efficient, organic stable blue-light-emitting materials are desirable both to complete the luminescence color spectrum and to serve as a host for energy-transfer when used in conjunction with small band gap fluorophores [2].

The first report of blue emission from a conjugated polymer LED was for poly(*p*-phenylene) (PPP) [3]. Poly(*p*-phenylene) (PPP) and its

derivatives have good thermal and oxidative stability. PPP, however, exhibits low solubility and high turn-on voltage. Furthermore, the low work function metals are required for efficient carrier injection in PPP derivatives. PPP and its derivatives are intrinsically violet-blue emitter to have some difficulties in color tunability.

PPV derivatives have several advantages as an emitting material such as high thermal stability, good film quality, suitable color tunability, etc. However, the design of blue-emitting electroluminescent polymers based on PPVs with interrupted conjugation suffers from the drawback that their emission is occurred usually broadened and red-shifted from the more conjugated segments. In this article, we describe the synthesis and characterizaton of new soluble blue-light-emitting polymers, poly[4,4-biphenylene-α(phenyl)vinylene](PBPV) and poly[4,4-terphenylene-α(phenyl)vinylene](PTPV), and their application to LEDs.



SCHEME 1.

EXPERIMENTAL

Poly[4,4'-biphenylene-α(phenyl)vinylene] (PBPV). A 25 mL 3-neck, round-bottomed flask was charged with anhydrous nickel (II) chloride (0.13 g, 0.001 mol), 2,2'-bipyridine (0.15 g, 0.001 mol), triphenyl phosphine (1.0 g, 0.0038 mol), and zinc powder (3.0 g, 0.046 mol), and the flask was repeatedly evacuated and back-filled with nitrogen (ca. 20 times). Dry N,N-dimethylformamide (15 mL) was added to flask, and the mixture was heated with stirring to 50℃. After heating was continued until actived catalyst was made, 1,2-di(4'-bromophenyl)-1-phenyl ethylene (4.46 g, 0.01 mol) was added via solid dropping funnel. The reaction mixture was heated at 90 ℃ with stirring for 24 h. And then, the mixture was poured into H_2O (150 mL) and filtered solid crude product. The product was filtered and the process was repeated for

purification. The yield was 80 %.

Poly[4,4-terphenylene-α(phenyl)vinylene] (PTPV). To a stirred solution of benzene diboronic acid 0.357 g(1.786 mmol), [1,2-(4',4''-dibromophenyl)-1-pheny ethylene] (1.786 mmol) in 10 mL THF and 4 mL 2M K_2CO_3 aqueous solution was added catalysts of $Pd(PPh_3)_2$ 8.4 mg(0.6 mol %). The reaction mixture was heated at 80 °C under nitrogen atmosphere for 8 h. After bromobenzene 0.05g (0.32 mmol) was added, phenyl boronic acid 0.05g(0.41 mmol) was added with small amounts of catalysts for end-capping. After reaction, precipitation was twice repeated to methanol. (Yield= 60 %)

RESULT AND DISCUSSION

The synthetic schemes of the monomers and the polymers are outlined in Scheme 1. PBPV was obtained by a nickel-catalized polycondensation reaction of 1,2-di(4'-bromophenyl)-1-phenyl ethylene. PTPV was obtained by the polymerization of 1,2-di(4'-bromophrenyl)-1-phenyl ethylene and benzene diboronic acid using Pd-catalyzed coupling reaction. After the polymerization, the end capped reaction of the bromine and boronic acid group was also accomplished.

^{1}H-NMR and FT-IR spectra, and the results of elemental analysis agree with the proposed structures of PBPV and PTPV. The obtained polymers were readily soluble in common organic solvents. The results can be explained by pendant α-phenyl substituents. The thermal properties of the synthesized polymers were evaluated by means of TGA curve. It is found that the polymers exhibit good thermal stability. The weight loss of the PBPV and PTPV are less than 5 % until heating to 380 °C and 430 °C, respectively. The DSC measurement showed glass transition of PBPV and PTPV at around 130 ℃ and 146 °C, respectively. From the results, PTPV has more good thermal stability than that of PBPV. Figure 1 shows the optical absorption and photoluminescence spectra of a dilute solution of the polymers in chloroform. The absorption spectrum of the dilute solution of PBPV has a maximum peak of 365 nm. The maximum absorption of PTPV showed 350 nm. The maximum absorption peak of the PTPV is blue shifted (70-90 nm) as compared with that of PPV, blue shifted (10-20 nm) as compared with that of PBPV and red shifted (10-20 nm) as compared with that of PPP. It is supposed that the absorption spectrum can shift to short wavelength by the increased phenylene unit.

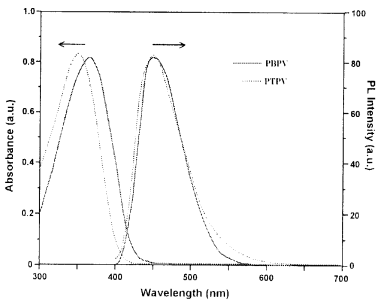


FIGURE 1. UV visible and PL spectra of polymers in chloroform

The PL spectrum of the dilute solution of the PBPV(pumped UV =365 nm) and PTPV (pumped 350 nm) have maximum peak at 450 nm and 460 nm, respectively. In order to evaluate the ionization energy and the optical energy band gap, the electrochemical analysis was carried out using cyclic voltametery. The optical energy band gap for PBPV was 2.93 eV. From the electrochemical data, the HOMO and LUMO of the polymer are 5.72 eV and 2.79 eV, respectively. The optical energy band gap, HOMO and LUMO for the PTPV were 2.98 eV, 5.83 eV and 2.85 eV respectively.

In conclusion, the new blue light emitting materials, PBPV and PTPV, were synthesized by nickel-catalyzed coupling reaction and Suzuki reaction. The obtained polymers had good solubility and high thermal stability. PTPV containing terphenylene vinylene had blue shifted in the maximum of UV absorption and PL emission compared with those of PBPV containing biphenylenvinylene.

Acknowledgments

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