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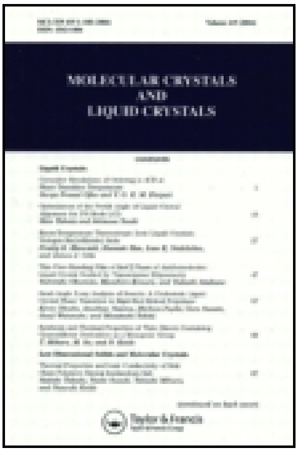

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Synthesis and Light Emitting Properties of Poly (Biphenylenevinylene) Derivative with Bulky Substituent

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Synthesis and Light Emitting Properties of Poly (Biphenylenevinylene) Derivative with Bulky Substituent

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Poly[4,4-biphenylene-α-(4'-t-butylphenyl)vinylene] (PBBPV) was synthesized by nickel catalyzed coupling reaction. The single layered device prepared from the PBBPV by using aluminum as cathode, and ITO as anode showed a turn-on voltage of 11 V (0.012 mA/cm^2).

Keyword: photoluminescence; electroluminescence; turn-on voltage; PPV; PPP; cathode; blue

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INTRODUCTION

Efficient thermally stable blue light emitting materials are needed both to complete the color spectrum and to serve as energy transfer media for incorporated fluorophores [1]. 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), 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 derivatives have also been extensively investigated for light emitting materials because they are thermally and oxidatively stable polymers [2]. 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. PPP is, however, highly insoluble, limiting the molecular weights and processability. We designed the new blue electroluminescent polymer having advantages both of PPP and PPV [3]. In this article, we describe the synthesis and luminescent properties of a new soluble blue-light-emitting PBPV derivative, poly[4,4-biphenylene-α-(4'-t-butylphenyl) vinylene] (PBBPV).

EXPERIMENTAL

1,2-bis(bromophenyl)-1-(4'-t-butylphenyl)ethene(BPBPE). In a two-necked flask equipped with reflux condenser, a mixture of (4-bromobenzyl)triphenylphosphonium bromide (7.42 g, 14.5 mmol), sodium hydride (1.16 g, , 48 mmol), toluene (70 ml) was refluxed for 8 h. After cooling, 4-bromobenzo-4'-*t*-butylphenone (4.56 g, 14.5 mmol) was added and refluxed for 48 h. The mixture was worked up with ice water, and then was extracted with ether. The extract was dried over $MgSO_4$, and filtered. The solvent was removed by evaporation. The residue was dissolved in *n*-hexane, and then purified by chromatography to remove side products. After removal of *n*-hexane, recrystallization from ethanol afforded pure BPHFE. The product was collected by filtration and dried under vacuum. Yield : 2.8 g, mp: 139 ^{o}C. ^{1}H-NMR ($CDCl_3$, ppm): δ 7.53-7.51 (m, 3H), 7.45 (d, 1H), 7.39-7.38 (d, 2H), 7.33-7.31 (d, 2H), 7.26-7.25 (d, 2H), 7.11-7.10 (d, 2H), 6.96-6.94 (d, 3H), 1.36 (s, 9H).

Poly[4,4-biphenylene-α-(4'-t-butylphenyl)vinylene](PBBPV). Into a 10 mL three-necked flask equipped with a nitrogen inlet, we added BPBPE (0.35 g, 0.75 mmol), nickel choloride (9.5 mg, 0.75 mmol), zinc (0.2256 g, 3.45 mmol), triphenylphosphine (0.295 g, 1.125 mmol), bipyridine (11.7 mg, 0.075 mmol), and N,N-dimethylformamide(DMF)

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(2.0 ml) under nitrogen. The reaction mixture was stirred at 90 °C for 6 h. The products were precipitated into a large excess of 20 % hydrochloric acid/methanol solution. The white-green solid was filtered and washed with methanol, water, and methanol sequentially. The polymer collected and dried under vaccum. The yield of the polymer after complete workup was 0.16 g (63 %). ^{1}H-NMR ($CDCl_3$, ppm): δ 7.73-6.94 (m, 13H), 1.36 (s, 9H).

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RESULTS AND DISCUSSION

The PBBPV was synthesized through the Yamamoto coupling reaction of corresponding dibromide, BPBPE.(Figure1)

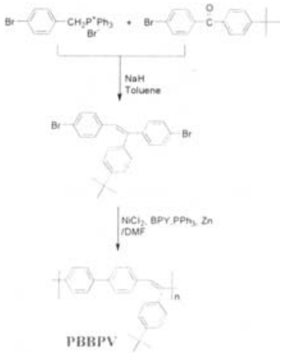

FIGURE 1. Reaction scheme of PBBPV

The aromatic and vinyl protons of PBBPV appeared at the range of 6.8–7.5 ppm and methylene protons of polymer showed at around 1.2 ppm. It was found that PBBPV is readily soluble in common organic solvents solvents such as THF, toluene, chloroform, etc. The molecular weights of the polymer, as determined by size-exclusion chromatography using polystyrene standards, are Mn = 4,200 and Mw = 6,420 (PDI = 1.53). It was found that PBBPV had high thermal stability as weight loss was less than 5 % on heating to about 370 °C under nitrogen atmosphere.

Figure 2 shows the UV absorption and photoluminescence spectra of the PBBPV in chloroform solution and solid film. As shown in the absorption spectrum of the PBBPV solution, the wavelengths of the absorption maximum(λ_{max}) of the polymer solution and polymer film had strong absorption bands at around 360 nm and 362 nm, which is attributed to the π - π^* transition of the conjugated segment. The UV spectrum of the polymer thin film showed the absorption maximum and

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the absorption edge of PBBPV at about 363 and 430 nm, respectively, which is 50-60 nm blue shifted as compared with those of PPV. This shift is a result of ineffective conjugation because of the strong steric hindrance between large side chain, (4'-t-butylphenyl group) and phenylene ring.

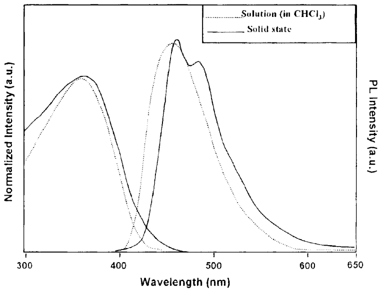

FIGURE 2. UV visible and PL spectra of PBBPV

Upon UV excitation at 360 nm, the photoluminescence of the polymer solution and polymer film has maxima emissions at 458 and 462 nm with shoulder peak at 485 nm, respectively, indicating blue emmision. As mentioned previously, this blue emission may be explained by short conjugation length due to steric hindrance. The introduction of bulky side group, t-butylphenyl, into vinyl bridge led to disturb the coplanarity, which reduced the effective conjugation length.

Electroluminescence device prepared from the PBBPV by using aluminum as cathode, and ITO as anode showed a turn-on voltage of 11 V (0.012 mA/cm^2), and peak brightness of 42 cd/m^2 (24.7 V).

Acknowledgements

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