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A Binaphthyl-Based Conjugated Polymer for Light-Emitting Diodes

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Recently, there has been considerable interest in the optical properties of conjugated polymers.[1−5] They are attractive materials for electroluminescent (EL) devices due to the ease of processing and their tunable electronic and optical properties. In particular, they offer considerable advantages over small molecule systems in large area display applications.[6] While organic EL polymers possess numerous advantages, there are still several critical areas that need to be improved for them to be used in highly efficient EL devices,[7] such as the tailoring of spectral characteristics and improvement in processability and stability under use conditions.

In this paper, we present preliminary results of synthesis and light-emitting properties of a conjugated polymer based on the binaphthyl structure. The principal concept in designing binaphthyl-containing polymers is to introduce a large dihedral angle binaphthyl unit into a polymer for manipulating its conjugation length. This may provide an effective approach to tailoring the spectral characteristics and improving solubility and thermal stability of the polymers. It has been found that the angle between two adjacent naphthalene rings can range from 60° to 120°,[8] therefore, the conjugation length of a polymer could be fine-tuned by interrupting its space configuration instead of using a nonconjugated spacer group.[9−13] As a result, this kind of polymer will have a higher concentration of fluorophores. In addition, these binaphthyl-containing polymers may have lower interchain interactions which may help to prevent polymer chains from packing. This, in turn will improve both the fluorescent quantum efficiency and solubility. Moreover, by virtue of restricting rotation between the bond that joins the aromatic ring systems, these polymers should have a higher glass-transition temperature (T_g) than the biphenyl-based analogues.

Recently, binaphthyl-containing polyarylenes or poly(arylene-ethynylenes) and their corresponding chiral polymers, both (*R*) and (*S*) configurations, have been synthesized using either the Suzuki coupling reaction or the Palladium-catalyzed cross-coupling reaction.[14] Although their optical activities, nonlinear optical properties, and uses in chiral catalysis have been reported,[15] light-emitting properties of these polymers have not yet been studied extensively.[16] In our work, the binaphthyl-based poly(arylene-vinylene) polymer was prepared via the Wittig−Horner condensation reaction. The key starting material, 2,2′-dibutoxyl[1,1′-binaphthyl]-6,6′-dicarbaldehyde was readily prepared from 1,1′-bi-2-naphthol **1** (Scheme 1). Bromination of **1** gave 6,6′-dibromo-1,1′-binaphthol **2** in 99% yield. Alkylation of **2** with 1-bromobutane using anhydrous K_2CO_3 as base in acetone produced 6,6′-dibromo-2,2′-dibutoxy-1,1′-binaphthyl **3** in 80% yield. Lithiation of **3** with *n*-BuLi (4 equiv) at −78 °C, followed by quenching with *N*,*N*-dimethylformamide (DMF) gave 2,2′-dibutoxy[1,1′-binaphthyl]-6,6′-dicarbaldehyde **4** in 85% yield. The polymer, poly(binaphthyl vinylene-1,4-phenylene vinylene) (PBVPV), was prepared by the Wittig−Horner condensation reaction between the dialdehyde **4** and xylene tetraethyl disphosphonate **5**[17] in tetrahydrofuran (THF).[18]

PBVPV was a yellow powder and could be dissolved readily in common solvents such as methylene chloride, chloroform, and THF. Its chemical structure was confirmed by ^{1}H NMR. The molecular weight of PBVPV was determined by gel permeation chromatography (GPC) using polystyrene as the calibration standard. The number-average (M_n) and the weight-average (M_w) molecular weight of the polymer was 5780 and 24 270, respectively. Uniform and pinhole-free thin films of the polymer could be obtained by spin-coating from its chloroform solution.

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(18) The mixture was then allowed to react at room temperature for 2 h. THF was removed by distillation, and the residual polymer was washed with a mixed solvent of acetone/methanol/water (3:3:1), filtered, dried, and redissovled in CH_2Cl_2 then precipitated into methanol. The collected yellow solid was further purified by Soxhlet extraction with acetone for 24 h and dried at 60 °C overnight to offer 0.43 g yellow powder, yield 78%: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07−7.87 ppm (m, 10 H), δ 3.89−3.95 ppm (br, 4H), δ 1.50−1.59 ppm (br, 4H), δ 1.35−1.40 ppm (br, 4H), δ 0.95−1.03 ppm (br, 6H).

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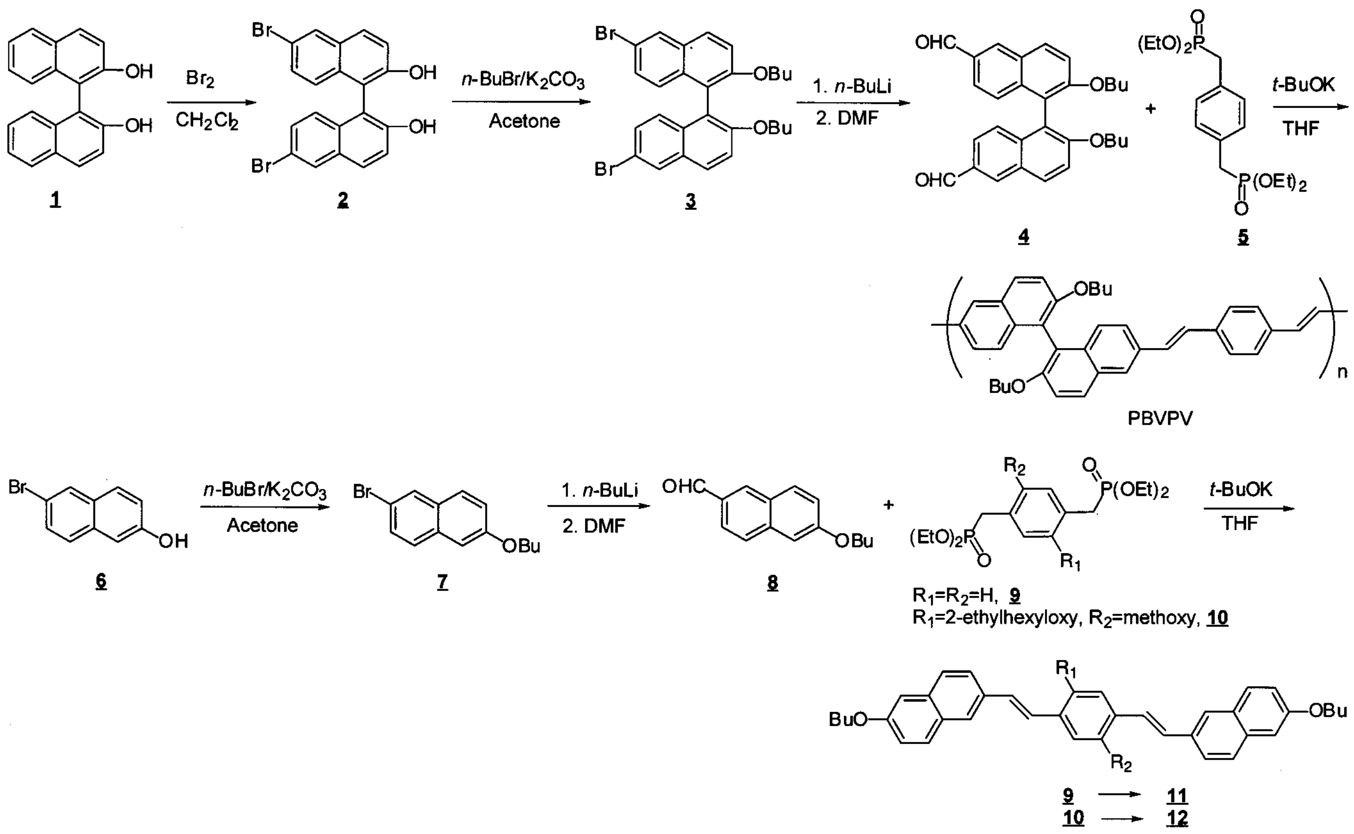
Scheme 1. Synthesis of Poly(binaphthylenevinylene-1,4-phenylenevinylene) (PBVPV)



The thermal properties of PBVPV were analyzed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. PBVPV demonstrated a high thermal stability, up to 320 °C with a heating rate of 10 °C/min. Recently, Tokito et al.[19] found that the operating lifetime of the EL device was directly related to the glass-transition temperature (T_g) and the thermal stability of the materials used. PBVPV has a much higher T_g (226 °C) when compared to those of the soluble polymer MEH–PPV (65 °C) or polyfluorenes (75–125 °C). This indicates that the incorporation of the binaphthyl moiety into the polymer chain significantly enhances the rotational barrier of the polymer chains, and thus increases the T_g of the polymer.

The cyclic voltammogram of a PBVPV-coated indium tin oxide (ITO) glass was measured in a conventional three-electrode cell configuration with a Pt gauze counter electrode, an Ag/Ag$^+$ reference electrode, and 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile as the electrolyte. Figure 1 shows an onset reduction peak at −1.86 V and an onset oxidation peak at 1.1 V. Therefore, the band gap of the polymer was estimated to be 2.70 eV, close to the band gap obtained by extrapolating the band edge of its absorption spectrum (2.82 eV). The onset of the reduction peak in Figure 3 was measured to be −1.86 eV which is smaller than that of MEH–PPV (−1.95 eV).[20] This implies that the polymer is a slightly better electron acceptor than MEH–PPV.

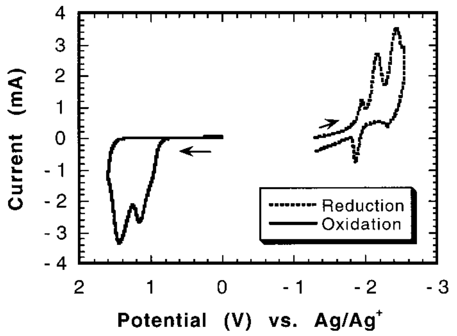


Figure 1. CV of PBVPV in a MeCN solution of $[NEt_4][BF_4]$ (0.10 M) at 100 mV s^{-1}.

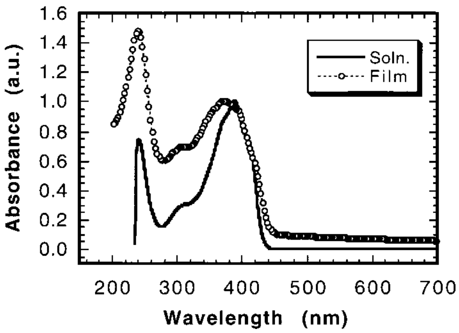


Figure 2. UV–vis absorption spectra of PBVPV.

UV–vis spectra of the polymer are shown in Figure 2. The π–π* transition maximum and the band edge of the polymer appear to be at 395 and 440 nm. The polymer emits a strong blue fluorescence under UV irradiation in a dilute $CHCl_3$ solution and shows three photoluminescent (PL) peaks at 447, 462, and 500 nm, which are the typical features of dialkoxy-substituted

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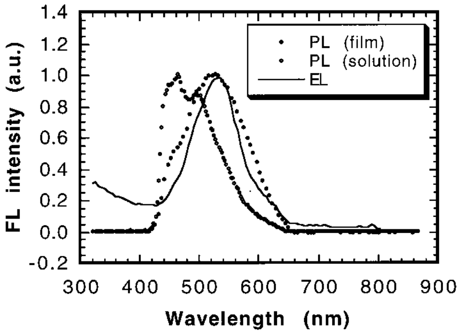

Figure 3. Photoluminescent and electroluminescent spectra of PBVPV.

PPVs (Figure 3), but much more blue shifted. Although there is no red shift in absorption spectrum of the polymer film compared to the dilute solution, PBVPV had a broad red-shifted emission peak at 525 nm in the solid film (Figure 3). This may be due to the intrachain interactions from the very crowded and rigid backbone segments that may change the diheral angles between two naphthyl units in the binaphthylene, and eventually change the conjugation properties of the polymer.

To prove that the effective conjugated length in the polymer could be truly confined within the region between the two binaphthyl moieties, a model compound **11** was synthesized as the repetitive conjugated unit of the polymer. However, compound **11** could not be dissolved in any solvents. This phenomenon indirectly verified that the solubility of PBVPV was greatly increased by introducing the twisted binaphthyl unit into its structure. Nevertheless, a modified analogue compound **12** showed a $\lambda_{\max}$ of 410 nm which was in full agreement with the $\lambda_{\max}$ of its corresponding polymer (413 nm).[21] It implies that the effective length of the conjugated polymers could be tailored by using the binaphthyl unit.

To study the EL property of the polymer, a single-layer LED device (with 2 mm diameter dots) was made by spin-coating a thin layer of the polymer (~100 nm) onto ITO-coated glass substrates from its chloroform solution (2% w/w). A layer of aluminum (~200 nm) was then deposited under a vacuum (2×10^{-6} Torr). The active area of the resulting device was 7.07 mm^2. The current–voltage and light–voltage curves of this device (Figure 4) showed a typical diode behavior with an external quantum efficiency of 0.1% and a relatively low turn on voltage (the first point that light was detected) of 6 V.

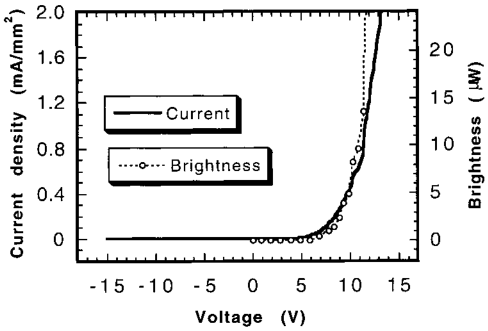

Figure 4. Current–voltage and light–voltage characteristics of an ITO/polymer/Al device.

In summary, a binaphthyl-based conjugated polymer (PBVPV) was synthesized by the Wittig–Horner reaction. It demonstrated that good thermal stability, solubility, and effectiveness in controlling the conjugation length could be achieved by incorporating the twisted binaphthyl unit into the polymer main chain. A. blue-green light emission under a forward bias potential was obtained in an LED made with this polymer, which further demonstrated the concept of controlling the conjugation length through space configuration. Further work, including the synthesis of binaphthyl blue light-emitting polymers with higher efficiency by minimizing intrachain interactions of the polymers via suitable side chains on the polymers, is in progress.

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