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Synthesis, spectroscopy, and electrochemical properties of a novel p–n diblock poly(*p*-phenylenevinylene)-related copolymer containing bipyridine

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Abstract

A novel p–n diblock copolymer constituted of 2,2′-bipyridylene vinylene and 2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene moieties was synthesized and characterized. The electrochemical properties of the copolymer were evaluated and the HOMO and LUMO energy levels of the polymer were estimated by cyclic voltammetry. The polymer demonstrated intrinsically balanced tendencies for injecting and transporting electrons and holes, which are essential for fabrication of light-emitting diodes. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Bipyridine-containing copolymer; Poly(*para*-phenylene vinylene); Electrochemical property

Since the discovery of electroluminescence (EL) of poly(*para*-phenylene vinylene) (PPV) [1], polymer light-emitting diodes (PLEDs) have attracted much attention because of their potential applications in display technology [2,3]. Currently one of the biggest problems for PLEDs as commercially viable displays is the low quantum efficiency [3]. To resolve this problem depends not only on the device engineering, but also on the development of highly efficient materials. In the past few years, several approaches have been exploited to obtain high efficient EL conjugated polymers [4,5]. One of the most effective and feasible ways is to design and synthesize emissive polymers with intrinsically balanced injection/mobility capabilities for holes and electrons from the opposite electrodes. It is well known that most of the conjugated polymers, such as PPV, poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV), and polythiophenes, are p-doped type polymers due to their conjugated structures being composed of electron-donating aromatic units. They have much greater tendency for transporting holes than for transporting electrons. Another series of useful EL π-conjugated polymers containing electron-withdrawing heterocycles (e.g. pyridine, 2,2′-bipyridine, and 1,10-phenanthroline ring) are typical n-dopable ones, showing greater tendency for transporting electrons [6–8]. These polymers have been extensively synthesized and employed as emissive materials for PLEDs due to their good electron affinities and thermal/oxidative stabilities [6,9,10]. All these polymers are mainly unipolar, a characteristic which may result in unbalance of injection of electrons and holes at the opposite contacts in PLEDs. If EL polymers are endowed with bipolar character, the balance between electrons and holes may be improved. Indeed, a new class of π-conjugated copolymers constituted of both electron-donating and -withdrawing units have also been reported, and these p–n diblock copolymers show unique optical and electrochemical properties [11–15]. In this communication, we report the synthesis and electrochemical study of a new p–n diblock copolymer (BPy-MEH-PPV) which consists of 2,2′-bipyridylene vinylene (BPyV) and 2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene (MEH-PV) moieties.

BPy-MEH-PPV was synthesized utilizing facile Wittig reaction between 5,5′-bis(triphenylphosphoniomethyl)-2,2′-bipyridine dibromide, which was prepared from 5,5′-bis(bromomethyl)-2,2′-bipyridine and triphenylphosphine in DMF, and 1,4-dialdehyde-2-methoxy-5-(2′-ethyl-hexyloxy) benzene (synthesized according to Ref. [14]) in the presence of sodium ethoxide (Scheme 1; the synthetic route for BPy-MEH-PPV). The structure of the polymer

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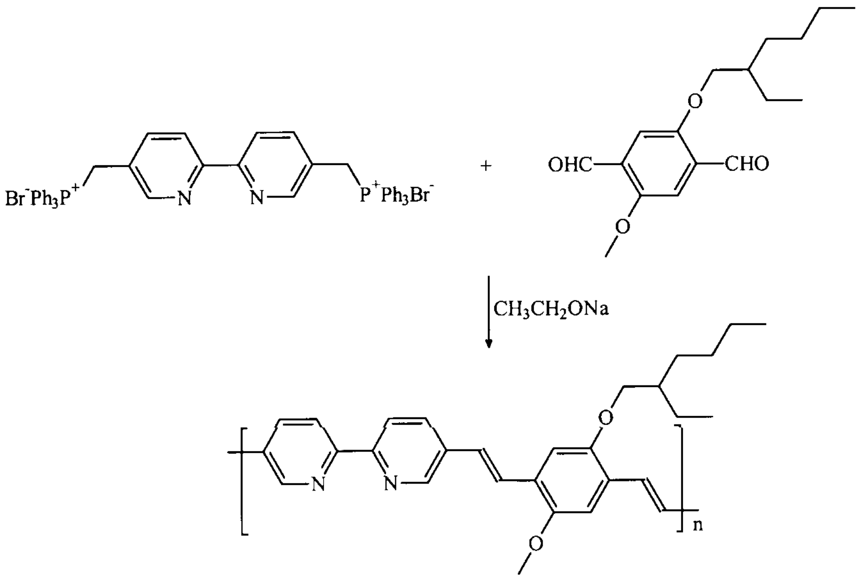

PBy-MEH-PPV

Scheme 1.

was confirmed by ^{1}H NMR spectrum (Fig. 1) and elemental analysis.[1] BPy-MEH-PPV is soluble in common organic solvents such as chloroform, THF, dichloromethane, and toluene. BPy-MEH-PPV demonstrates high thermal stability. Its starting decomposition temperature is 334°C in air according to thermogravimetric analysis (TGA). The number average (M_n) and weight average (M_w) molecular weights of the polymer, which were determined by gel permeation chromatography (GPC) using polystyrene as standard, are 6400 and 7700, respectively. Fig. 2 shows the UV–Vis absorption and photoluminescence (PL) spectra of BPy-MEH-PPV film. The absorption band corresponding to π–π^* transition along the conjugated polymer chain of BPy-MEH-PPV peaks at 460 nm. The band gap (E_g) can be estimated to be 2.35 eV from the absorption edge of the film sample. The BPy-MEH-PPV spectrum exhibits an emission peak at 610 nm, indicating an orange emission.

The redox behavior of the polymer (coated as a film on a 1 cm^2 Pt electrode) was studied by cyclic voltammetry (CV) in a CH_3CN solution containing 0.10 M Bu_4NBF_4 as the electrolyte, using a Pt wire as the counter electrode and a $Ag/AgNO_3$ (0.10 M) electrode as the reference electrode. A typical cyclic voltammogram of BPy-MEH-PPV is shown in Fig. 3. BPy-MEH-PPV exhibits a highly reversible n-doping process (reduction). The reduction peak occurred at -1.79 V with a corresponding re-oxidation peak at -1.53 V (vs. SCE), which represents a charging and discharging process. Along with the potential scan, the color of the film changed from orange to dark blue first, then back to orange after oxidation. The reduction onset potential of BPy-MEH-PPV was seen at -1.59 V. These results of the reductive behavior indicate that BPy-MEH-PPV can be easily reduced or n-doped, agreeing well with the previously reported results that poly(arylene)s containing electron-withdrawing imine nitrogen(s) such as poly(pyridine-2,5-diyl) and poly(2,2′-bipyridine-5,5′-diyl) are good for n-doping [9,15]. It could be ascribed to the enhancement of electron affinity of the polymer through introduction of the bipyridyl segment [16]. BPy-MEH-PPV also showed a fairly reversible p-doping process, which exhibited an oxidation peak at 0.89 V with a re-reduction peak at

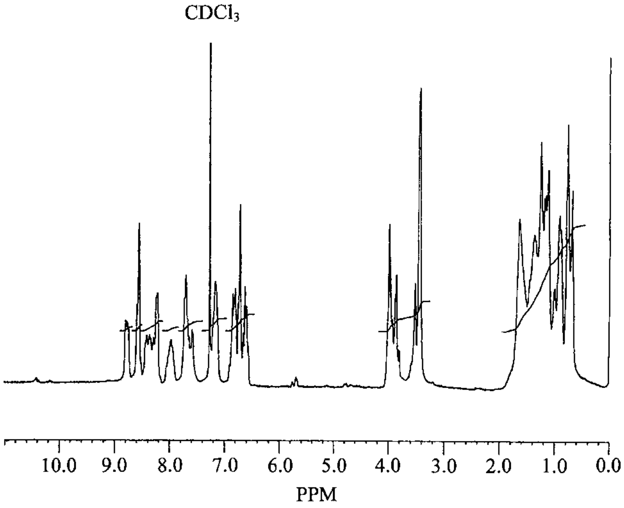

Fig. 1. ^{1}H NMR spectrum of BPy-MEH-PPV.

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[1] Selected data for BPy-MEH-PPV: ^{1}H NMR ($CDCl_3$, ppm) 0.69–1.64 (15H, C_7H_{15}), 3.43–3.98 (5H, $-OCH_2-$, $-OCH_3$), 6.59–6.84 (4H, –CH=CH–), 7.37–8.82 (8H, aromatic protons). Anal. Calcd for $C_{29}H_{32}N_2O_2$: C, 79.06; H, 7.32; N, 6.36. Found: C, 77.00; H, 7.91; N, 6.22.

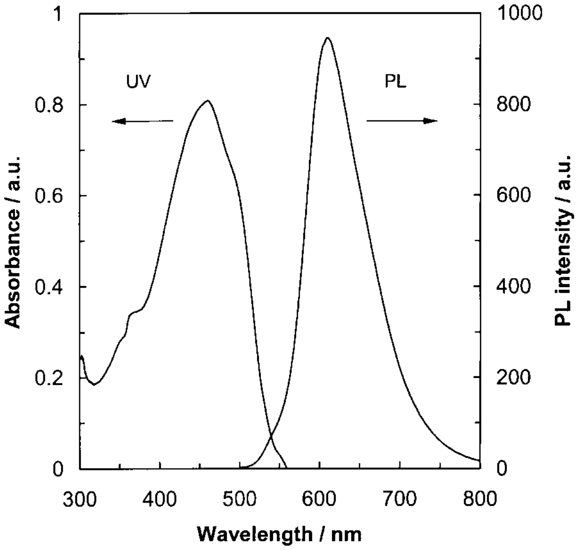

Fig. 2. The UV–Vis absorption and photoluminescence spectra of BPy-MEH-PPV film.

0.80 V, and the oxidation onset potential of the polymer was seen at 0.78 V. The reversible color changes were also observed. It may be attributed to the π-electron-excessive properties of the MEH-PV units in polymer chain because the bipyridine ring is inactive towards p-doping [9]. The redox properties of the polymer imply that BPy-MEH-PPV with both p-dopable MEH-PV moiety and n-dopable BPy moiety in the polymer chain has an intrinsically balanced tendency for injecting and transporting electrons and holes.

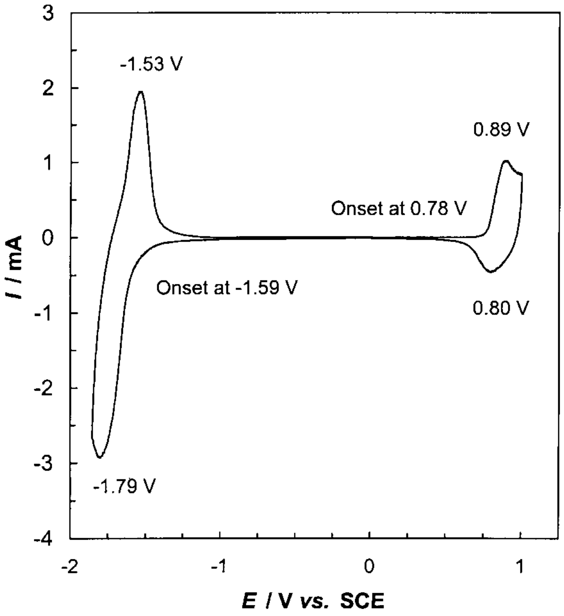

Fig. 3. Cyclic voltammogram of BPy-MEH-PPV film on a Pt electrode in CH_3CN solution containing 0.10 M Bu_4NBF_4 at a scan rate of 20 mV/s under argon.

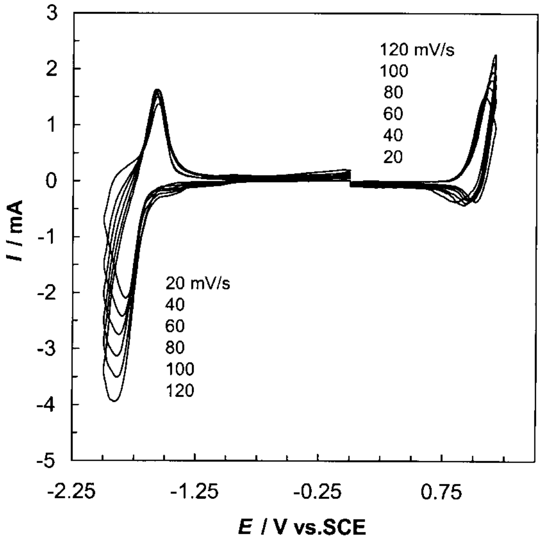

Fig. 4. Cyclic voltammograms of BPy-MEH-PPV film, taken at increasing scan rates.

BPy-MEH-PPV demonstrates excellent electrochemical reproducibility and stability. The cathodic and anodic sweeps of polymer films could be repeated at least 12 cycles without any significant change of the CV curves. Cyclic voltammograms at various scan rates for BPy-MEH-PPV are illustrated in Fig. 4. The heights of the anodic and cathodic peaks were proportional to the scan rates for $v \leq 90$ mV/s, providing evidence that the electrochemical reactions occur within the thin film on the electrode surface instead of in solution. At faster scan rates, the I_p/v value decreases, suggesting the onset of kinetic or diffusive limitations.

The redox potentials obtained from CV measurements can be used to estimate the band gap and the HOMO and LUMO energy levels on various conjugated polymers. From the onset potentials of the oxidation and reduction processes, the band gap of BPy-MEH-PPV is estimated to be 2.37 eV, which is in good agreement with the value (2.35 eV) obtained from the optical absorption spectrum. The HOMO and LUMO energy levels were calculated by assuming the energy level of E_{SCE} at −4.4 eV [17]. The HOMO and LUMO energy levels of BPy-MEH-PPV were estimated to be −5.18 and −2.81 eV, respectively. Noting that the electrochemical system is much closer to the practical LED device configuration, the above data from CV provide valuable information for the fabrication of EL devices with suitable configurations.

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