# Synthesis and Electrochemical Characterization of Soluble Poly(*p*-phenylene vinylene) Derivatives Containing Olefinic Bonds at the Side Chain

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Received 31 August 1998; accepted 15 January 1999

**ABSTRACT:** A new kind of soluble poly(*p*-phenylenevinylene) (PPV) derivative containing free olefinic bonds at the side chain is prepared and studied by electrochemical measurement. The electrochemical investigations reveal that the free olefinic bonds in these polymers are electroactive; a new redox reaction occurs prior to the oxidation of PPV backbone in the cyclic voltammetry. The lower oxidation potential of the olefinic bonds hints that it is possible for these olefinic bonds to react with oxygen, which is desirable to remove the harmful oxygen in the light-emitting polymer devices. The merits and possibility of such polymers containing olefinic bonds in the fabrication of the light-emitting devices are discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2535–2539, 1999

**Key words:** conjugated polymer; poly(*p*-phenylenevinylene) derivative; olefinic bonds; synthesis; electrochemical characterization

#### INTRODUCTION

Polymer light-emitting devices have become attractive due to their potential application in large flat-panel display.<sup>1,2</sup> The active layers used in the device are mainly poly(p-phenylene vinylene)(PPV) and soluble PPV derivatives, which are more processable than PPV. Different kinds of PPV derivatives have been synthesized,<sup>3-7</sup> and the performance of the light-emitting devices have been improved dramatically in recent years.

The polymer light-emitting electrochemical cells (LEC) show a promising way for one to operate a light-emitting device at lower bias.<sup>8,9</sup> When the operating voltage of LEC is greater

than the band gap of its luminescent polymer (such as PPV), the electrochemical *p*-doping on the anode and *n*-doping on the cathode take place, and a *p*-*i*-*n* junction will be created in situ.<sup>10,11</sup> The *p*-type charge carriers and *n*-type charge carriers move inside and recombine to give off light. The phase separation in the PPV/ion-conducting polymer blend due to thermodynamic instability is a factor that affects the performance of LEC.<sup>12</sup> In practice, the lifetime of both LEC and polymer light-emitting diodes (LED) could be affected by oxygen, water, and other impurities existed in the devices<sup>1,8,9,12</sup>; however, no proper solutions are available until now.

We currently focus on the fabrication of LEC, thereby, new conjugated conducting luminescent polymers (particularly PPV derivatives) that own particular characteristics are desired, such as good solubility, uniform film-forming property with PEO polymer electrolyte, and good stability. In this paper, new polymers containing olefinic bonds at the side chain of PPV and its electro-

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Contract grant sponsor: NSFC; contract grant number: 29673051.

Contract grant sponsor: CAS; contract grant number: KJ951-A1-501-01.

Journal of Applied Polymer Science, Vol. 73, 2535–2539 (1999)

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chemical behaviors are reported. The results show that the PPV backbone of such polymers may be stabilized by avoiding the reaction with the oxygen and other impurities.

## **EXPERIMENTAL**

1,4-Bis(chloromethyl)-2-boromoheptyloxy-5-methoxybenzene (1) was synthesized by a literature procedure.<sup>3</sup> To a CH<sub>3</sub>OH solution of 1,10-diboromoheptane (0.30 mol) was added the mixed solution of CH<sub>3</sub>ONa (0.24 mol)/CH<sub>3</sub>OH and methoxyphenol (0.23 mol) dropwise. The mixture was refluxed for 2 h under Ar atmosphere. The mixture was filtered after it was cooled to room temperature (RT). White solids were recrystallized (the yield was 70%). These solids were mixed with hydrochloric acid, formaldehyde, and dioxane. The reaction mixture was heated to 95°C and kept for more than 5 h; then it was cooled to RT. The resulting white solids were recrystallized and dried in vacuum. The yield is 51%. <sup>1</sup>HMR[CDCl<sub>3</sub>, tetramethylsilane (TMS)] δ: 6.9(1H, s), 6.8(1H, s),  $4.6 \sim 4.7(4H, d), 3.7 \sim 3.9(2H, t), 3.8 3H, s), 3.3$  $\sim 3.5(2H, t), 1.2 \sim 1.8(20H, m)$ . Mass spectroscopy (electron ionization): 342(3.9%), 124(100%), 109(11.5%).

1,4-Bis(chloromethyl)-2-heptyloxy-5-methoxybenzene (3) was prepared by the similar method as mentioned above.

1,4-Bis(chloromethyl)-2, 5-bis(allyloxy)benzene (4) was synthesized by the following procedure. To an acetone solution of NaOH (0.30mol) were added allyl bromide (0.29mol) and biphenol (0.136mol). The mixture was refluxed under Ar for 4 h; then 400 mL water was added into the cooled mixture solution. Ether was used to extract the product. The residue, after the ether was evaporated, was distilled at reduced pressure to afford colorless crystal, which was used to prepare monomer 4 according to the above method. The yield of monomer 4 is totally 30%. <sup>1</sup>HMR(C-DCl<sub>3</sub>, TMS)  $\delta$ : 6.85(2H, s), 5.95 ~ 6.15(2H, m), 5.2 ~ 5.5(4H, m), 4.6(4H, s), 4.3 ~ 4.5(4H, d).

Poly[2-(1-heptyleneoxyl)-5-methoxy-phenylene] vinylene (2) and copolymer poly[(2-heptyloxy-5methoxy-phenylene) vinylene-co-(2, 5-bis(allyloxy)phenylene) vinylene] (5) were obtained by the same method according to the reported route.<sup>3,4</sup> A solution of potassium *tert*-butoxide in tetrahydrofuran (THF) was added to the solution of monomer (1 or 3/4) in THF dropwise. This mixture was stirred at room temperature overnight, and precipitated with ethanol/THF to afford the polymer. Fourier transform infrared (FTIR) shows the absorption at 3060, 2927, 2854, 1766, 1605, 1503, 1464, 1414, 1353, 1253, 1205, 1037, and 960 cm<sup>-1</sup>. The absorption at 1605 cm<sup>-1</sup> is ascribed to the olefinic bond at the side chain, the absorption at 1766 cm<sup>-1</sup> is due to the oxidation of olefinic bond, and the 960 cm<sup>-1</sup> absorption indicates the *trans*-vinylene formation (identical absorption of PPV backbone).

The absorption and photoluminescence spectra were obtained on the Jasco V-550 spectrometer and Perkin-Elmer LS 50B luminescence spectrometer, respectively. The electrochemical measurements were carried out on the EG&G PARC370 system. A Pt disk (0.00196cm<sup>2</sup>), a Pt wire, and a Ag wire were used as the working electrode, counter electrode, and quasi-reference electrode respectively. The potentials reported in this paper are all referenced to the Ag wire electrode. All chemicals used were analytical grade.

## RESULTS

There are two methods to introduce olefinic bonds at the side chain of PPV: one is to introduce the olefinic bonds directly to the PPV monomer, the other is keeping the halohydrocarbon group at the side chain of the monomer, and eliminating the hydrogen halide to obtain the olefinic bonds in the polymerization. Figure 1 shows the synthesis route. Homopolymer 2 was prepared directly by eliminating the HBr at the side chain in the process of polymerization with excessive potassium tert-butoxide conveniently. The parallel experiments on polymerization of monomer 4 showed that the content of Cl is undetectable from the elemental analysis, so the halogen content in polymer 2 should be attributed to Br content, which enables us to deduce the proportion of olefinic bonds in the eliminating reaction. The analysis result shows the content of Br is 3% in the polymer; this means that at least 80% of HBr was eliminated, and then 80% olefinic bonds at the side chain was produced. The existence of newborn olefinic bonds is confirmed by the absorption at 1605 cm<sup>-1</sup> in FTIR. Monomer 4 contains olefinic bonds originally; however, the homopolymer from this monomer is insoluble. Copolymer 5, which is soluble, then is prepared. The absorption and photoluminescence spectrum of these polymers shows no pronounced different properties with the normal PPV and its derivatives, as shown in Figure 2 (e.g., polymer 2). The band gap



Figure 1 Synthesis of free olefinic bonds contained soluble PPV derivatives.

is determined as 2.1 eV from the absorption spectrum. The maximum photoluminescent intensity locates at 555 nm with excitation at 470 nm. It had been shown that the band gaps of almost all alkyloxyl-PPVs are ca. 2.1 eV.<sup>13–15,16</sup> These results confirm that the introduction of end olefinic bonds at the side chain of PPV does not affect the alkyloxyl-PPVs electronic structure concerning with the optoelectronic application.

Electrochemical experiments on the polymers were conducted to investigate the electrochemical



**Figure 2** Absorption/photoluminescence spectrum of polymer **2** in CHCl<sub>3</sub>.

behavior of the polymers, particularly on the effect of olefinic bonds on the electrochemical behaviors. In the *n*-doping potential range, only one doping/dedoping peak is found at the potential of -1.6 V for polymer 2 (or more negative as -1.65V for polymer **5**). The potential of this peak shifts due to the instability of the *n*-doping of the polymer. As found in other PPV systems, 13-17 the *n*-doping/dedoping process is electrochemically quasi-reversible. The onset potentials of *n*-doping are -1.35 and -1.45 V for polymer 2 and polymer 5, respectively. No obvious effect from the olefinic bonds on *n*-doping was found in the experiments. The electrochemical oxidation of the polymers gave three peaks in the cyclic voltammetry. Figure 3 presents an example of polymer **2**. It can be observed clearly that three oxidation peaks locate



**Figure 3** Cyclic voltammogram of polymer **2** coated electrode in 0.1M (Bu)<sub>4</sub>NPF<sub>6</sub>/CH<sub>3</sub>CN solution. The scan rate is 20 mV/s.



**Figure 4** Cyclic voltammogram of *p*-doping of polymer **2** coated electrode in 0.1M (Bu)<sub>4</sub>NPF<sub>6</sub>/CH<sub>3</sub>CN solution. The scan rate is 100 mV/s.

at 0.63, 0.85, and 1.28 V. The oxidation peak at 1.28 V, which is electrochemically irreversible, is undoubtedly attributed to the overoxidation of PPV.<sup>14,18</sup> The evidence that used to distinguish the oxidation of olefinic bonds from PPV oxidation is the onset potential, because the band gaps of polymer 2 and 5 had been estimated to be 2.1 eV from the absorption spectra, with which the band gap from cyclic voltammetries should match. The band gap from the onset potential of 0.55 V with the oxidation peak at 0.65 V and the *n*-doping onset potential does not meet 2.1 eV, while the use of onset potential of ca. 0.75 V with the oxidation peak at 0.85 V meets. Thus, we think that the oxidation peak at 0.65 V is from the olefinic bonds and the oxidation peak at 0.85 V is from PPV itself. Either peak at 0.63 or 0.85 V is quasireversible, which is shown in Figure 4 clearly. It is easy to find that the redox reaction of olefinic bonds is diffusion controlled via the change of the scan rate in cyclic voltammetry (see Fig. 5). The cyclic voltammetric curves assemble that of the conventional conducting polymer such as polypyrrole and polyaniline, etc.<sup>19</sup>

### DISCUSSION

This paper only presents the preliminary results of two PPV derivatives containing olefinic bonds at the end of side chain. There are also other routes to prepare the olefinic bond contained PPV derivatives, e.g., precursor route.<sup>7</sup> The precursor route enables one to obtain the blend with PEO very easily in the fabrication of LEC. This homogeneous blend can be kept even after heating to eliminate HCl in the PPV backbone, because the olefinic bonds are free and photo-polymerizable!<sup>20</sup> One can photopolymerize the olefinic bonds in the homogeneous blend of PPV precursor/PEO beforehand, and then eliminate the HCl by heating. Such crosslinking from photopolymerization results in the interpreted network, which is critical to the performance of LEC.<sup>12</sup> The PPVs reported here are soluble in organic solvents, thereby the photocrosslinked blends of such polymers with PEO are prospectable to be kept for a long time without phase separation due to thermodynamics stability.

The cyclic voltammetric results indicate that the oxygen effect could be avoided in such LEC and LED based on the polymer, because the oxidation potential of olefinic bonds make the olefinic bonds react with oxygen easily, which protects the PPV backbone somewhat.

#### **CONCLUSIONS**

New polymers containing free olefinic bonds at the side chain are prepared. The introduction of such olefinic bonds does not affect the performance of the polymer in the light-emitting devices. The free olefinic bonds are electroactive. The lower oxidation potential of olefinic bonds



**Figure 5** Cyclic voltammograms of olefinic bonds in polymer **2** coated electrode in 0.1M (Bu)<sub>4</sub>NPF<sub>6</sub>/CH<sub>3</sub>CN solution. The number denotes the scan rate in mV/s.

means that the oxygen effect or other impurities in the active layer of light-emitting devices will be reduced, and the stability of the PPV backbone of the polymer will be increased. Such free olefinic bonds contained PPV derivatives are proposed to be useful to form a homogeneous interpreted network with ion-conducting materials (e.g., PEO) in the fabrication of LEC. Further work on the fabrication of LED and LEC based on such new polymers is underway in our laboratory.

This work was supported by the NSFC (29673051) and key projects of CAS (KJ951-A1-501-01).

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