5162 *Macromolecules* **1999,** *32,* 5162−5164

New Poly(*p*-phenylene vinylene) Derivatives Exhibiting High Photoluminescence Quantum Efficiencies

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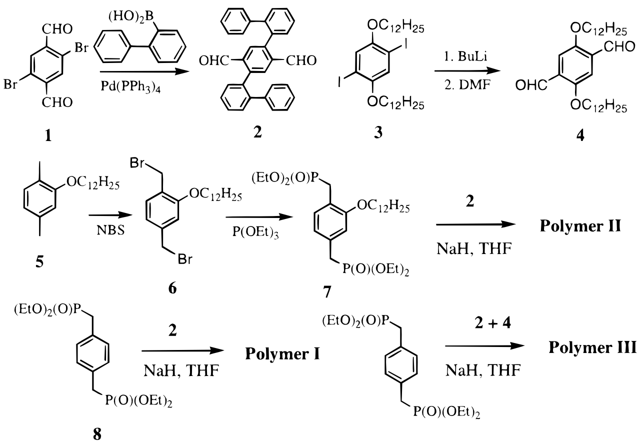
Received February 17, 1999
Revised Manuscript Received May 19, 1999

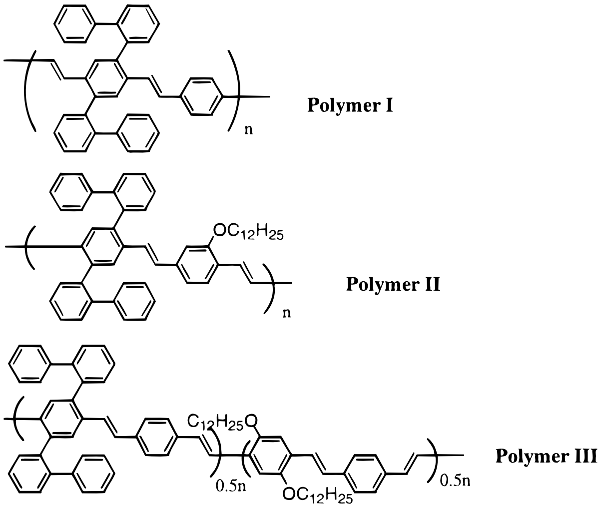
Poly(*p*-phenylene vinylene) (PPV) and its derivatives are the most extensively studied conjugated polymers for light-emitting diode (LED) applications.[1,2] Light emission from such a device comes from the radiative decay of excitons generated in the emissive polymer layer by the recombination of electrically injected electrons and holes. The excitons generated electrically are believed to be the same as those generated by optical excitation.[3] Thus, an ideal LED polymer must possess high photoluminescence (PL) quantum efficiency. While a wide variety of PPV derivatives has been synthesized and applied in LED applications, very few show high PL efficiencies in solid states.[4−7] The major reason is that conjugated backbones tend to stack cofacially with each other due to the favorable interchain $\pi-\pi$ interactions, which lead to a self-quenching process of excitons.[8,9] Introducing appropriate substituents to the PPV backbone to prevent its close packing should therefore increase its PL efficiency. Indeed, Hsieh et al. recently reported 2,3-diphenyl substituted PPVs that exhibit PL efficiency as high as 65% in the solid state.[10] In this communication, we report new highly luminescent processsable PPV derivatives (polymers **I**−**III**) which contain 2-biphenyl subsitituents.

The syntheses of the above PPVs are described in Scheme 1. The key monomer, compound **2**, was synthesized by the Suzuki coupling reaction[11] of 2,5-dibromo-1,4-benzenedicarboxaldehyde and 2-biphenylboronic acid,[12] both synthesized in one step from commercially available starting materials.[13] Other monomers (compounds **4**, **7** and **8**) were also synthesized in good yields.[14]

Scheme 1. Syntheses of the Monomers and the Polymers



All three polymers were synthesized by the Horner−Wittig−Emmons (HWE) reaction[15] with over 90% yields. The polymerization process for polymers **II** and **III** was stopped when the reaction solution became viscous. For polymer **I**, it was stopped when the polymer started to precipitate out. The structures of the polymers are confirmed by ^{1}H NMR and elemental analysis.[16]



Both polymers **II** and **III** are highly soluble in organic solvents such as chloroform, dichloromethane, tetrahydrofuran (THF), and so on. Interestingly, polymer **I**, which does not possess any solubilizing alkyl or alkoxy substituents, exhibits good solubility in some organic solvents such as tetrachloroethane. The solubility of these polymers is apparently due to the steric interactions of biphenyl subsitituents which disrupt the chain−chain interactions.

The molecular weights of these polymers were measured by gel permeation chromatography (GPC), using polystyrene as standards and THF as eluent. Both polymers **II** and **III** possess high molecular weights and narrow molecular weight distribution. The weight-average molecular weight (M_w) and polydispersity (PD) for polymers **II** and **III** are 151K, 2.5, and 235K, 2.8, respectively. Tough free-standing films can easily be cast from polymer solutions. Elemental analyses for these two polymers (polymer **II**. Anal. Calcd for $C_{52}H_{52}O$: C, 90.13; H, 7.56. Found: C, 88.74; H, 7.32. Polymer **III**. Anal. Calcd For $C_{80}H_{88}O_2$: C, 88.84; H, 8.20. Found: C, 87.22; H, 7.83) are in relatively good agreement with their respective repeating units,[16] indicating a reasonable high purity for both polymers. Polymer **I**, on the other hand, is only partially soluble in THF; the molecular weights measured by GPC (M_w of 4500 and PD of 1.5) reflect only the soluble parts of the polymer. The ^{1}H NMR spectrum of polymer **I** clearly shows the signals from end-group protons. Integration ratio of aldehyde protons/OCH$_2$ protons/aromatic protons is found to be 1:1:110. Calculation based on this ratio reveals that polymer **I** has about 6 repeating units (14 to 15 phenyl rings in the backbone). The relatively low molecular weight of this polymer (oligomer), which is also reflected in the elemental analysis, is apparently due to its limited solubility in the reaction solvent (THF). Nevertheless, the improvement in solubility by

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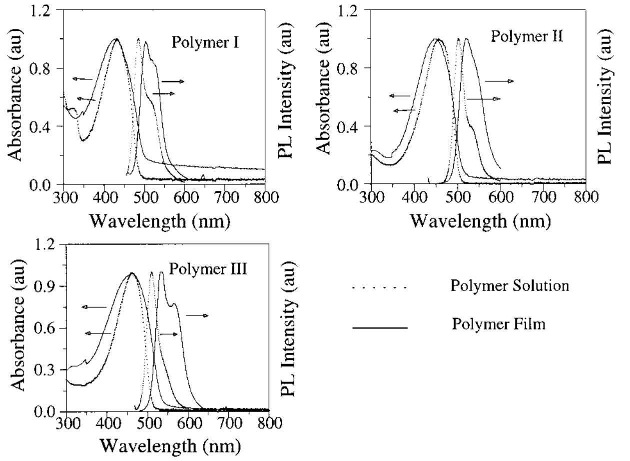

Figure 1. UV/vis and photoluminescence spectra of dilute polymer solutions (in THF) and polymer films.

Table 1. Optical Properties of the Polymers

	absorption		fluorescence			
	in THF	film	in THF		film	
polymer	λ_{max} (nm)	λ_{max} (nm)	λ_{max} (nm)	Φ_{pl}	λ_{max} (nm)	Φ_{pl}
I	432	428	488	0.77	504	0.82
II	457	450	503	0.73	520	0.61
III	462	460	510	0.53	522	0.77
DO−PPV	445	435	507	0.32	546	0.103

incorporating 2-biphenyl subsitituents is still significant, considering the fact that an oligo-PPV with five phenyl rings in the backbone tends to be insoluble in organic solvents.

Figure 1 shows the UV/vis and fluorescence spectra of these polymers in solution and as solid film. The wavelengths of absorption and emission maxima are listed in Table 1. The absorption maxima of the films are slightly blue-shifted compared to the maxima in solutions, consistent with other poly(*p*-phenylene)-related polymers.[17] With alkoxy subsitituents, the absorption maximum of the polymer film shifts from 432 nm for polymer **I** to 462 nm for polymer **III**. As a result, polymers **I** and **II** are bright yellow, and polymer **III** is brownish yellow.

These new PPV polymers are highly fluorescent in both solution and as solid film. The fluorescence spectra of these polymers were measured by a Perkin-Elmer LS50 photoluminescence spectrometer. Quantum efficiencies of each polymer in solution were determined twice using a dilute quinine sulfate solution in 1 N H_2SO_4 (assume PL efficiency of 0.546 at 365 nm excitation) and a dilute dichloroanthracene solution in hexane (assume PL efficiency of 0.54 at 365 excitation) as standards.[18] The measurements were averaged. The film PL efficiencies were measured using an optically dense configuration and diphenylanthracene (dispersed in PMMA film with concentration less than 10^{-3} M, assuming PL efficiency of 0.83) as the standard.[18,19] As shown in Figure 1, compared to solutions, PL spectra of films are slightly red-shifted by less than 20 nm for polymers **I**−**III**, in contrast to a nearly 40 nm red-shift for PPV polymer **IV** [poly(2,5-dioctyloxy-1,4-phenylene vinylene) (DO−PPV)]. Both polymer film and solution show similar vibronic features in the PL spectra.

All three polymers exhibit very high PL efficiencies (>50%) in both solution and as solid film, as shown in Table 1. These PL efficiencies are among the highest ever reported for PPVs. For comparison, the PL efficiencies of DO−PPV were measured under the same conditions. Its PL efficiencies in dilute solution and as solid film are both significantly lower than those of polymers I−III. The high PL efficiency of these new PPVs is believed to be the result of the unlikely close interaction of PPV chains. The steric effect of biphenyls with the PPV backbone forces the pendant phenyl ring to point away (one up and one down) from the conjugated plane. Such a three-dimensional structure prevents PPV stacking in any dimension.

In summary, we have synthesized three new soluble PPV derivatives by the HWE reaction. These polymers exhibit some of the highest PL efficiencies for any conjugated polymer in both solution and as solid film, making them promising candidates for electroluminescence studies.

Acknowledgment. This work was supported by the University of Missouri−Kansas City through a Faculty Research Grant. Partial support from the University of Missouri Research Board is also acknowledged. The authors thank Prof. Timothy F. Thomas, Prof. Thomas P. Johnston, Prof. Zhe Wu, and Mr. John Whitchurch for their kindly help in some of the characterizations.

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(12) Compound **2**: mp: 234−235 °C; ^{1}HNMR ($CDCl_3$) δ 9.71 (s, 1H, CHO), 9.70 (s, 1H, CHO), 7.79 (s, 1H, Ar−H), 7.75 (s, 1H, Ar−H), 7.35−7.60 (m, 8H, Ar−H), 7.10−7.30 (m, 6H, Ar−H), 6.95−7.10 (m, 4H, Ar−H). Anal. Calcd for $C_{32}H_{22}O_2$: C, 87.65; H, 5.06. Found: C, 87.29; H, 4.84.

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(14) Compound **3** was synthesized according to the following reference: Bao, Z.; Chen, Y.; Cai, R. B.; Yu, L. *Macromolecules* **1993**, *26*, 5281. Compound **4**. Anal. Calcd for $C_{32}H_{54}O_4$: C, 76.44; H, 10.83. Found: C, 76.37; H, 10.96. ^{1}H NMR ($CDCl_3$) δ 10.52 (s, 2H, CHO), 7.43 (s, 2H, Ar−H), 4.07 (t, J = 6.61 Hz, 4H, OCH_2), 1.82 (m, 4H, CH_2), 1.47 (m, 4H, CH_2), 1.26 (br, 32H, CH_2), 0.88 (t, J = 6.39 Hz, 6H, CH_3). Compound **7**. Anal. Calcd for $C_{28}H_{52}O_7P_2$: C, 59.77; H, 9.25. Found: C, 59.96; H, 8.75. ^{1}H NMR ($CDCl_3$) δ 7.25 (d, J = 8.50 Hz, 1H, Ar−H), 6.83 (s, 1H, Ar−H), 6.79 (d, J = 8.50 Hz, 1H, Ar−H), 3.90−4.10 (m, 10H, OCH_2), 3.23 (d, J = 22.0 Hz, 2H, CH_2P), 3.11 (d, J = 22.0 Hz, 2H, CH_2P), 1.79 (m, 2H, CH_2), 1.00−1.50 (m, 30H, CH_2 and CH_3), 0.88 (t, J = 7.25 Hz, 3H, CH_3).

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(16) Polymer **I**. Anal. Calcd for $C_{40}H_{28}$: C, 94.45; H, 5.55. Found: C, 88.61; H, 5.41. ^{1}H NMR ($CDCl_3$) δ 7.50 (br, 16H, Ar−H), 7.26 (br, 12H, Ar−H and vinyl protons). Polymer **II**. Anal. Calcd for $C_{52}H_{52}O$: C, 90.13; H, 7.56. Found: C,

88.74; H, 7.32. ^{1}H NMR (CDCl$_3$) δ 7.48 (br, 16H, Ar−H), 7.14 (br, 11H, Ar−H and vinyl protons), 3.86 (br, 2H, OCH$_2$), 1.65 (br, 2H, CH$_2$), 1.29 (br, 18H, CH$_2$), 0.86 (br, 3H, CH$_3$). Polymer **III**. Anal. Calcd for $C_{80}H_{88}O_2$: C, 88.84; H, 8.20. Found: C, 87.22; H, 7.83. ^{1}H NMR (CDCl$_3$) δ 7.49 (br, 20H, Ar−H), 7.26 (br, 18H, Ar−H and vinyl protons), 4.06 (br, 4H, OCH$_2$), 1.87 (br, 4H, CH$_2$), 1.55 (br, 4H, CH$_2$), 1.26 (br, 32H, CH$_2$), 0.86 (br, 6H, CH$_3$).

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MA990217H