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A Processible Poly(phenyleneethynylene) with Strong Photoluminescence: Synthesis and Characterization of Poly[(*m*-phenyleneethynylene)-*alt*-(*p*-phenyleneethynylene)]

Yi Pang* and Juan Li

Department of Chemistry & Center for High Performance Polymers and Composites, Clark Atlanta University, Atlanta, Georgia 30314

Bin Hu and Frank E. Karasz

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003

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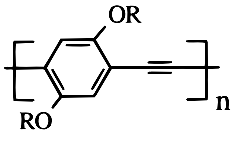
Introduction. Recent research activity has shown significant interest in the luminescent properties of π-conjugated polymers following the initial report of a polymer-based light-emitting diode (LED)[1] in 1990. Current efforts in developing π-conjugated materials of high luminescence are aimed at tailoring their spectral characteristics and improving their processibility and long-term stability. The 2,5-alkoxy-substituted poly(phenyleneethynylene)s (PPE) (**1**) are a special class of π-conjugated polymers that have exhibited high PL, some EL, and liquid crystalline properties.[2−7] The linear rigid-rod structure of **1**, however, renders the polymer difficult to process. Modification of PPE is desirable to improve the processibility while preserving the good PL and EL properties. Previous efforts to improve the solubility of PPE are based on the attachment of long alkyl side chains[4,8] and chain length control.[4]



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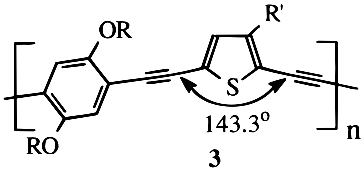

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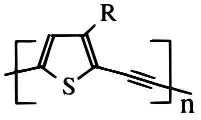

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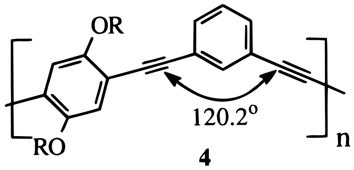

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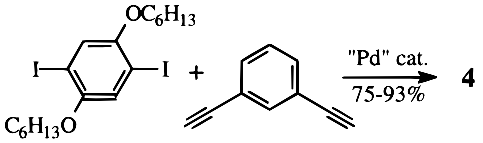
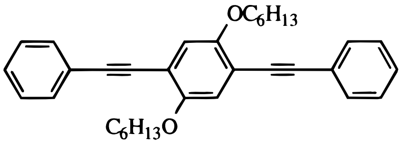
Our recent study[9] of PPETE **3** (R = n-C_8H_{17}; R′ = H or n-C_6H_{13}) shows that the incorporation of a 2,5-thienylene unit into PPE significantly modifies the rodlike molecular conformation[8] of PPE (Mark-Houwink constant $\alpha \approx 0.9$ for **3** versus $\alpha \approx 1.92$ for **1**). The PL quantum efficiencies of **3** are as high as 0.48, which is comparable with the values for PPE homopolymers.[2,3] In other words, PPETE **3** combines both the high PL efficiency of PPE **1** and the good processibility[10] of poly(thienyleneethynylene) **2** into a single chain. Deviation of **3** from a linear rodlike conformation of PPE clearly originates from the bent bond angle (less than 180°) at the 2,5-thienylene unit. A molecular modeling study[11] indicates that the bond angle at the 2,5-thienylene unit in **3** is about 143.3°; this may be compared with the bond angle of 120.2° at the *m*-phenylene unit in **4**. Thus the presence of *m*-phenylene units in PPE could further reduce the rigid-rod conformation and improve the proessibility[12] of the material. In addition, deviation from a rigid-rod conformation will have a large impact on molecular packing and may improve the amorphous solid state of PPE. It is known that a π-conjugated polymer in the amorphous state exhibits higher EL efficiency[14] than the polymer of significant crystallinity. Therefore, inclusion of *m*-phenylene in PPE **1** could simultaneously improve the processibility and luminescence behavior of the material. In this contribution we report some results of the synthesis and characterization of **4**.

Results and Discussion. Polymer Synthesis. The synthesis[15] of **4** was accomplished at room temperature via a Heck-type coupling[16] of 2,5-bis(hexyloxy)-1,4-diiodobenzene with 1,3-diethynylbenzene in the presence of $PdCl_2(PPh_3)_2/CuI/Et_3N$ catalyst. Similarly, a model compound **5** and the PPE **6** (a *p*-phenylene isomer of **4**) were prepared for comparison.[17] In sharp contrast to **6**, which had low solubility, PPE **4** (a pale yellow solid) was quite soluble in common organic solvents (up to 0.1 g/mL in chloroform). Uniform thin films could be readily cast from the polymer solution. ^1H and ^{13}C NMR (Figure 1) measurements detected no trace of terminal acetylenic groups, indicating complete polymerization.





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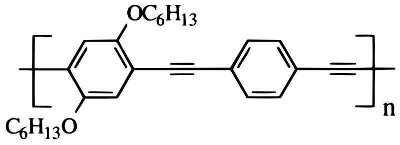

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Molecular Weight and Chain Stiffness. The weight-average molecular weights were about 77 900 for **4** and 25 600 for **6**. Combination of the high molecular weight, normal polydispersity (about 2.4), and monomodal distribution of **4** suggested that cyclic products were not formed during the polymerization. The Mark-Houwink exponent α for **4** was measured to be 0.65 in THF from the on-line viscometer detector, smaller than that for **3** ($\alpha \approx 0.9$)[9] and even comparable to that for poly(thienyleneethynylene) **2** ($\alpha \approx 0.68$).[10] The observed low α for **4** can be rationalized in terms of the bond angle at the *m*-phenylene (120.2°), which is significantly smaller than that of 143.3° at the 2,5-thienylene unit in **3**. In comparison with 3, the smaller bond angle at the *m*-phenylene unit in 4 permits the polymer backbone to deviate even more from the rigid-rod conformation of PPE and to effectively adopt a coil-like confor-

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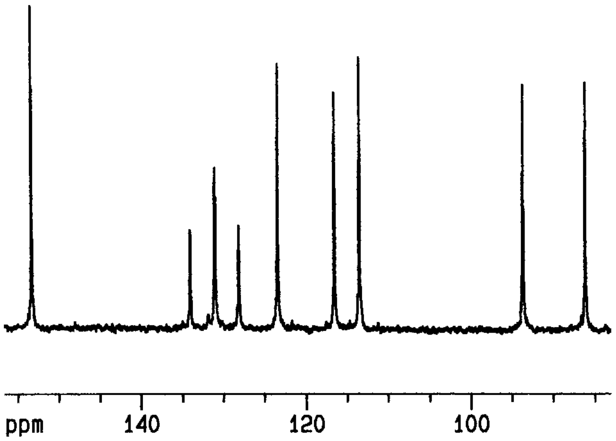

Figure 1. ^{13}C NMR spectrum of polymer **4** in $CDCl_3$ (alkyl region is not shown).

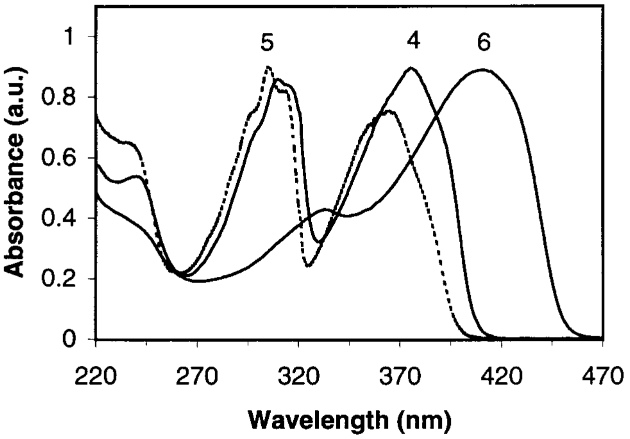

Figure 2. UV–vis spectra of **4**, **5**, and **6** in THF at room temperature.

mation in solution. Thus the presence of the *m*-phenylene unit indeed has a significant impact on the chain stiffness of PPE.

Photoabsorbance and Photoluminescence. UV-vis absorption spectra were obtained from dilute THF solutions of the polymers (Figure 2). Two major absorption bands of similar intensity were observed from PPE **4** with λ_{max} at 310 and 375 nm, while for **6** only one major absorption band was found with $\lambda_{max} = 411$ nm. The lower λ_{max} value for **4** indicates that the *m*-phenylene units interrupt the conjugation and thereby affect the energy band gaps of the corresponding PPE. Effective interruption[18] of π-conjugation of PPE at the *m*-phenylene linkage was further confirmed by spectroscopic comparison with the model compound **5**, which showed nearly an identical absorption spectrum to **4** with slightly shifted λ_{max} values at 305 and 366 nm.

Figure 3 shows the fluorescence spectra of the respective PPEs measured in dilute THF solutions. The emission λ_{max} of **4** is about 40 nm lower than that of **6**, attributed to the π-conjugation interruption in the former. It is also noticed that the emission spectrum of **4** is very similar to that of **5**, indicating the presence of similar pathways for radiative decay. The similarity in both absorption and emission characteristics of **4** and **5** suggests that the chromophore in PPE **4** has essentially the same $\pi \rightarrow \pi^*$ energy band structures as **5**. The solution PL quantum efficiencies,[20] determined in THF relative to a quinine sulfate standard, were 0.44 for **4**, 0.66 for **5**, and 0.45 for **6**. It is noted that the PL efficiency of **4** is comparable to that of **6**, although the conjugation length of the former is significantly shorter than that of the latter.

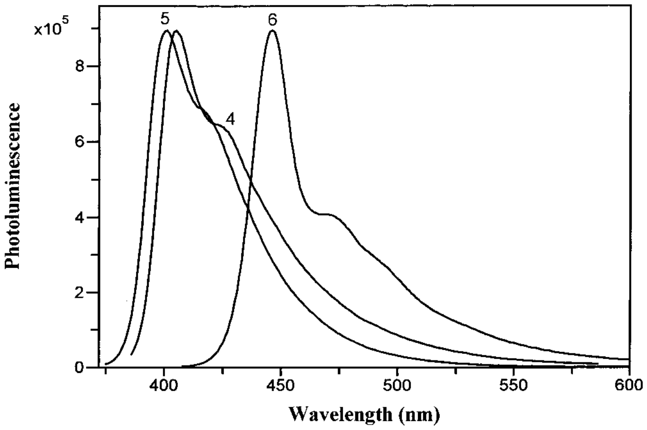

Figure 3. Normalized fluorescence spectra of PPEs in THF at room temperature.

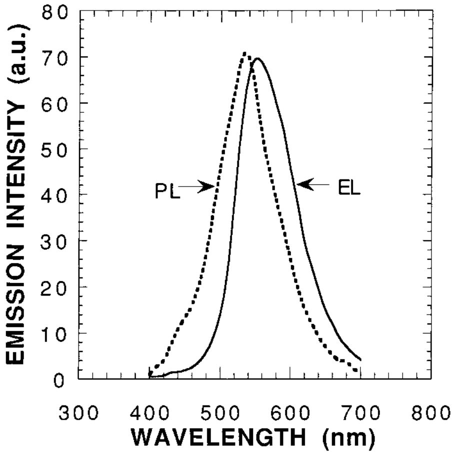

Figure 4. EL (dashed) and PL (solid) spectra of **4** from the ITO/polymer/Ca configuration.

The absorption spectra of the polymer films were slightly red-shifted from the solution to the film states, with λ_{max} values of about 387 nm and 428 nm for **4** and **6** respectively. Both films of **4** and **6** exhibited high solid state luminescence. Direct comparison[21] under identical experimental conditions showed that the PL intensity of PPE **4** was about five times stronger than that of **6**. Clearly, PPE **4** has a superior PL efficiency in the solid state than the isomer **6**. Comparison between **4** and poly(*p*-phenylenevinylene)[22] showed that the PL efficiency of the former was about twice as high as that of the latter from the films. Preliminary results indicated that electroluminescence (EL) could be obtained in a single layer device from **4** (Figure 4) though the EL spectrum is slightly red-shifted with respect to the PL spectrum, indicating perhaps the presence of a second electro-optically active species.

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(11) Bond angles were calculated for 2,5-bis(phenylethynyl)thiophene and 1,3-bis(phenylethynyl)benzene at their respective energy minima, by using Molecular Simulation Insight II software.

(12) Introducing *m*-phenylene into PPEs to improve the processibility has been briefly described in literature.[13] Quantitative characterization of *m*-phenylene on the chain rigidity of PPEs, however, has not been reported.

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(15) PPE 4 was synthesized by using the same procedure[9] for PPETE **3** and had the following spectral characteristics. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.70 (s, 1H), 7.48 (d, $J = 7.3$ Hz, 2H,), 7.32 (t, $J = 7.6$ Hz, 1H), 7.01 (s, 2H), 4.03 (t, $J = 6.1$ Hz, 4H), 1.85 (m, 4H), 1.54 (br, 4H), 1.35 (br, 8H), 0.88 (t, $J = 6.4$ Hz, 6H). ^{13}C NMR (CDCl$_3$, 100MHz, δ): 153.25, 133.98, 130.98, 128.09, 123.37, 116.53, 113.47, 93.66, 86.13, 69.23, 31.23, 28.92, 25.38, 22.29, 13.70. Anal. Calcd for $C_{28}H_{32}O_2$: C, 83.96; H, 8.05; O, 7.99. Found: C, 83.16; H, 8.02.

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(17) ^{1}H NMR and ^{13}C NMR data of the model compound 5 match the literature values.[7] Anal. Calcd for $C_{34}H_{38}O_2$: C, 85.32; H, 8.00; O, 6.68. Found: C, 85.29; H, 8.03. PPE **6** had the following spectral characteristics. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.49 (s, 4H), 7.00 (s, 2H), 4.03 (br, 4H), 1.84 (br, 4H), 1.53 (br, 4H), 1.35 (br, 8H), 0.89 (br, 6H). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 153.2, 130.9, 122.7, 116.4, 113.5, 94.3, 87.4, 69.2, 31.1, 28.8, 25.2, 22.1, 13.5.

(18) Interruption of conjugation by a *m*-phenylene unit in π-conjugated polymers has been previously observed, for example, in poly[*m*-(phenyleneethynylene)-*alt*-(oligothienyleneethynylene)]s.[19]

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(20) The sample solutions were excited at 376, 364, and 410 nm for **4**, **5**, and **6**, respectively. The absorbances of all samples were kept between 0.05-0.06 at the corresponding excitation wavelength. The ϕ_{fl} values given here were averaged from over at least three independent measurements with a standard deviation below 0.03.

(21) Films **4** and **6** were excited at 373 and 396 nm respectively. Photoabsorbances of the films were 0.83 for **4** and 0.84 for **6** at the corresponding excitation wavelength. Emissions were detected at 90° from the incident beam by the front face fluorescence method.

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