

Communication

Photophysical Properties of a Conjugated Poly(1-dodecyl-2,5-pyrrolyene vinylene)

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Abstract: Poly(1-dodecyl-2,5-pyrrolyene vinylene) (PDPV) has an extended π -conjugated structure and exhibits characteristic spectroscopic features. The PDPV we prepared has an absorption maximum at 510 nm and its long absorption tail at ca. 750 nm in methylene chloride is due to the long π -conjugated system connected to vinyl group. The large red-shift of emission was 625 nm upon excitation at 480 nm, which suggests the existence of a low emissive state. The emission of PDPV in less-polar solvents decreased markedly relative to that in the more-polar solvents; this observation was ascribed possibly to quenching by a strong vibrational mode of the dodecyl groups of PDPV in less-polar solvents. Furthermore, the emission from the high-energy side had a single decay component (0.1 ns, 49.96%), while that from the low-energy side had two components (0.6 ns, 27.1%; 2.7 ns, 22.87%). We characterized the redox properties of PDPV by cyclic voltammetry. Every redox peak showed irreversible behavior; the oxidation peaks appeared at 1.7, 0.8, and 0.6 V and the reduction peak at -0.5 V.

Keywords: PDPV, π -conjugated structure, absorption, emission, time-resolved emission spectroscopy, redox properties.

Introduction

An interesting feature of the pyrrole system is that a number of functionalized polymers can be readily prepared by polymerization of the pyrrole monomer.¹ Polypyrroles have been extensively investigated as materials for application in molecular electronic devices,² electrolytic capacitors,³ actuators,⁴ sensors,⁵ artificial muscles,⁶ and light-emitting diodes (LEDs).⁷ These polymers have been mainly focused on the control of conjugated polymer band gap, and their fundamental photophysical properties have been limitedly studied. Recently we reported synthesis, characterization and properties of low band gap conducting poly(1-dodecyl-2,5-pyrrolyene vinylene)(PDPV).⁸ In this study, Electronic,

luminescent, time-resolved emission studies and electrochemical studies of PDPV including an investigation of its conformational structure were reported for the first time.

Experimental

The absorption spectra were measured using Hitachi U-3300 spectrophotometer. Fluorescent pH titration was measured by using pH Scan BNC (Singapore).

The fluorescence spectra were measured using SLM8100 spectrofluorometer (Aminco, USA) with Xe-arc lamp light source using 4 or 8 nm band pass excitation and emission monochromators, in which the rhodamine B solution was used as a reference to correct for variation of the Xe light source with time and wavelength.

The time-resolved emission measurements were performed with an Edingburgh FL 900 and a picosecond mode-locked

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Ti-sapphire laser.

The electrochemical measurements were taken using EG & G PAR (Princeton, NJ, USA) Model 273A potentiostat/galvanostat controlled by an IBM PC with an E&G M270 software program. The cyclic voltammetry was carried out under the condition of the PDPV film on Au electrode in 0.1 M LiClO₄/CH₃CN electrolyte solution (V. vs. Ag/Ag⁺).

The computer calculation of a conformational structure of PDPV was carried out by simulated annealing methods of sybyl 6.9 program (Tripos Co., USA) under the following conditions; heat molecule at 800 K/1000fs, force field: tripos, charges: Gasteiger-Huckel. These were done in order to calculate the torsional angle.

Results and Discussion

A poly(1-dodecyl-2,5-pyrrolylene vinylene)(PDPV) was synthesized by as described in literature.⁸ The electronic spectra of PDPV (0.3 wt.-%) were investigated on solvent effect at 25 °C (Figure 1). At first, PDPV gave absorption maximum at 510 nm having the long absorption tail to about 750 nm in methylene chloride because of a long conjugated group including vinyl group. The appearance of the long absorption tail was partly supported by extended structure

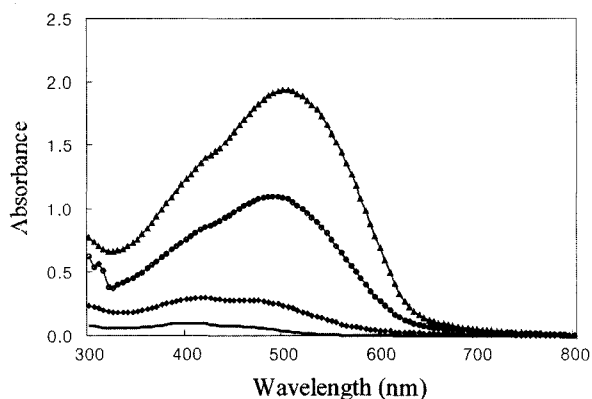


Figure 1. Electronic absorption spectra of PDPV (0.3 wt.-%) in various solvents at room temperature (▲ in methylene chloride, ○ in hexane, ◆ in ethanol, and — in acetonitrile)

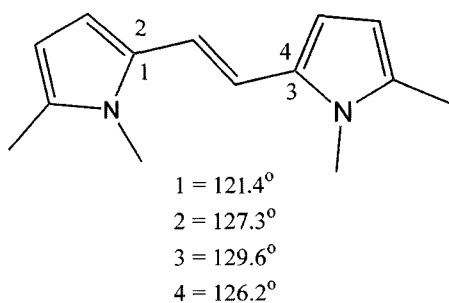
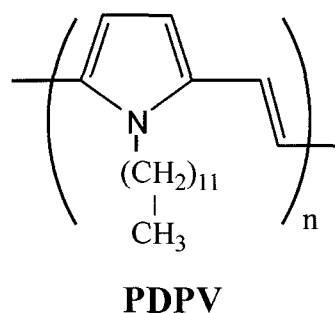


Figure 2. The torsional angles formed by two pyrrole rings connected to vinyl group



between repeating units as shown in Figure 2.

In other words, torsional angle of N-C-C between pyrrole group and ethenyl group was 121.4° and 129.6°, respectively, and that of C-C-C between pyrrole group and ethenyl group was 127.3° and 126.2°, respectively. Hence, the extended π -conjugated structure was formed between two pyrrole rings connected to the vinyl group. The electronic absorption spectra of PDPV showed a red-shift in the less polar solvent and a blue-shift in the more polar solvent, although a solubility problem occurred in acetonitrile and methanol, respectively. This absorption band could be attributed to the structureless $n-\pi^*$ and longer $\pi-\pi^*$ transition.

Figure 3 shows the emission spectra of PDPV excited by 480 nm on solvent effect. The emission spectra appeared as a symmetric pattern compared to the absorption spectra on solvent effect.⁹ The larger red-shift of emission to 625 nm occurred in methylene chloride, which supported the existence of a low emissive state. The emission of PDPV in the less polar solvent such as methylene chloride decreased markedly than that of PDPV in the more polar solvent such as acetonitrile and ethanol. It was assumed that this was ascribed to quenching by strong vibrational mode of dodecyl group of PDPV in the environment of the less polar solvent as a possible reason.

The decay time of the 520 nm emission of PDPV was measured at room temperature in acetonitrile (Figure 4).

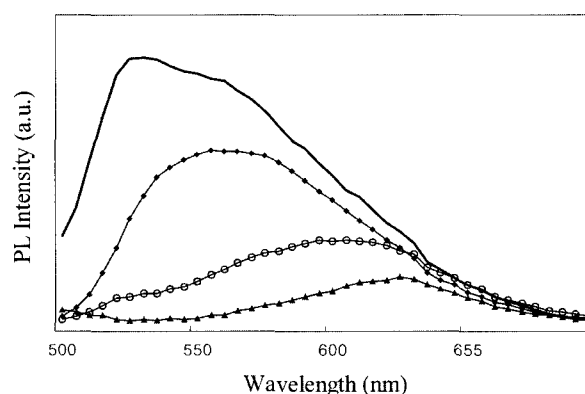


Figure 3. Emission spectra of PDPV (0.3 wt.-%) in various solvents at room temperature (▲ in methylene chloride, ○ in hexane, ◆ in ethanol, and — in acetonitrile)

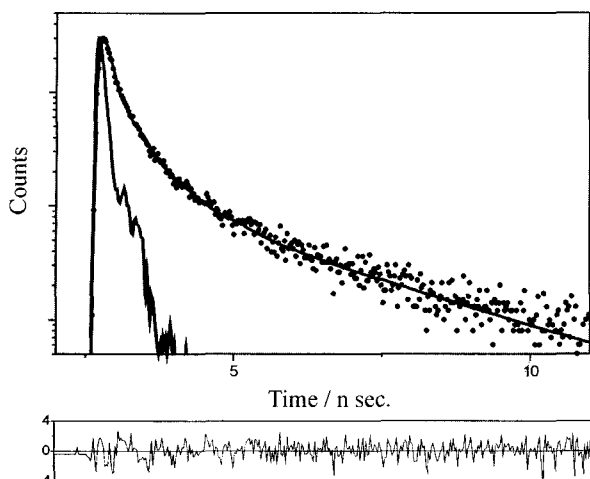


Figure 4. Time-resolved emission spectroscopy of PDPV monitored at $\lambda_{em} = 520$ nm.

The emission from the high-energy side had a single decay component of 0.1 ns (49.96%), while that from the low-energy side had two components with 0.6 ns (27.1%) and 2.7 ns (22.87%). Long-lived phosphorescence in the low-energy side emissions was not found in the emission of PDPV.

The redox properties of PDPV were characterized by cyclic voltammetry (CV).

CV measurement was carried out in the range of -1.5 V to 2.5 V vs. Ag/Ag⁺ at a scan rate of 60 mV/sec. Every redox peak showed irreversible behavior. The oxidation peaks appeared at 1.7, 0.8, and 0.6 V, respectively, and the reduction peak appeared at -0.5 V. The pattern and position of these redox peaks of PDPV were different from those of PHDP (poly(1-hexyl-3,4-dimethyl-2,5-pyrrolylene)) without vinyl group, which have oxidation peaks at 1.3 and 0.2 V, respectively, and the reduction peaks at -0.30 and -0.42 V, respectively, as reported recently.¹⁰

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