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Effect of Ultrasonication on Optical Properties and Electronic States of Conjugated Polymer MEH-PPV

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Abstract Poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene](MEH-PPV) solutions with different concentrations were prepared in chloroform for different ultrasonication times. The ultraviolet absorption and photoluminescence(PL) spectra of the MEH-PPV solutions were measured, and the electronic states of the polymer chains under different experimental conditions were studied. The results showed that the effects of ultrasonication on the dilute and concentrated solutions were different. After ultrasonication, the intensity of the absorption peak at 280 nm significantly decreased, relative to the absorption peak at 500 nm for both dilute and concentrated solutions, indicating that the proportion of the two excited states in the polymer chains had changed. For dilute MEH-PPV solutions, the blue-shifted absorption(at about 500 nm) and PL spectra show that ultrasonication also led to polymer chain degradation and thus shortened the effective conjugation length. For concentrated solutions, however, the peak positions of the absorption spectra remained unchanged. In addition, the effects of the solution temperatures on the optical spectra for the MEH-PPV solutions were also discussed.

Keywords MEH-PPV; Optical property; Electronic state; Ultrasonication

1 Introduction

Conjugated polymers as organic semiconductive and electroactive materials have attracted a great interest in science and technology in the past decades. The ease of processing, in combination with many desirable mechanical properties of plastics, makes conjugated polymers quite attractive for a wide variety of applications including field-effect transistors[1], light-emitting diodes[2], photocells[3,4], and lasers[5]. To realize the full potential of conjugated polymers, researchers have investigated their molecular parameters, which dictate photophysical behavior, by comparing the experimental data with the theoretical models. However, it is still not very clear whether the description of electronic excitations in those materials is most appropriately formulated within a molecular(localized) or semiconductor(delocalized, band-theory) picture. Köhler *et al.*[6] studied the electronic states associated with optical excitations in the visible and ultraviolet ranges for conjugated polymers, by means of photocurrent measurement and quantum-chemical calculations. They found that the mixing of delocalized valence-band states with localized states on the molecular units produced a sequence of excited states in which positive and negative charges could be further separated at higher energies.

Being an important kind of conjugated polymer, poly(1,4-phenylene vinylene)(PPV) and its derivatives are widely studied because of their excellent semiconductor and luminescent properties[7—12] Within the class of PPVs, poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene](MEH-PPV) exhibits characteristics that make it particularly favorable for photoelectric device fabrication. The chemical structure of MEH-PPV[shown in Scheme 1(A)] is comprised of an aromatic backbone with slightly polar alkoxy side chains in the repeating units. It has eight conjugated atoms in one unit cell and is hence expected to have eight π-electron energy bands. As indicated in the schematic band structure in Scheme 1(B)[13], four of those bands are occupied in the ground state(among which three π bands are delocalized and labeled as d_1,

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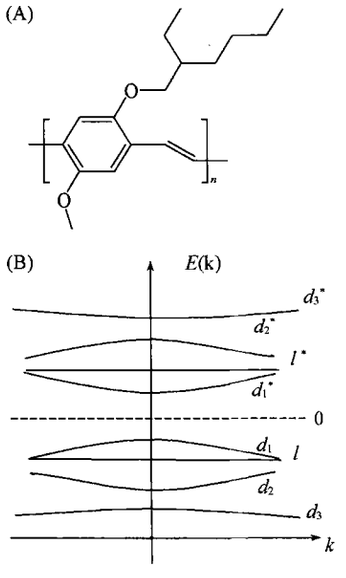
d_2, and d_3, and another localized π band is labeled as l); and the other four bands are unoccupied(i.e., three delocalized π^* bands are labeled as d_1^*, d_2^*, and d_3^* and another localized π^* band is labeled as l^*). Theoretical studies of the electronic structure of PPV and its derivatives, such as the band theory models[14,15] and the quantum chemical methods[6,16], are successful in accounting for the observed optical spectral features in some aspects. On the other hand, some spectroscopic data are also helpful in understanding the electronic states of PPVs. Miller *et al.*[17] have proved two kinds of the electronic distributions on MEH-PPV main chains using the polarized ultraviolet absorption experiments: one electronic distribution has been polarized in the direction parallel to MEH-PPV main chains; the other was polarized in the direction perpendicular to the chain axis. Despite a large number of photophysical studies, the nature of the excited states of PPVs still remains controversial, and there are few reports that discuss whether and how the environmental factors, such as temperature, intermolecular interactions or external forces, influence and change the distribution of the electronic and excited states in conjugated polymer chains.



Scheme 1 Chemical structure of MEH-PPV(A) and schematic electron band structure of PPV[13](B)

Ultrasonication is a commonly used method to prepare polymer solutions as well as achieve homogeneous dispersion of nanofillers in the polymer matrix[18—20]. At the same time, however, ultrasonication also has strong effect on the polymer chains at high temperatures and high pressures because of the formation, growth, and rapid collapse of microscopic bubbles during the ultrasonic process[21]. In this study, the authors investigated the effect of ultrasonication on the optical excitations in the visible and ultraviolet ranges for MEH-PPV solutions by means of ultraviolet(UV) absorption and photoluminescent(PL) spectra measurements. In addition, the effect of temperature on the optical properties of MEH-PPV solutions was also discussed.

2 Experimental

MEH-PPV used was purchased from Sigma-Aldrich Co. The number-averaged molecular weight of the polymer was determined to be 56000 g/mol by gel permeation chromatography(GPC) with polystyrene standard. The concentrated solutions with a concentration of 3 mg/mL and the dilute solutions with a concentration of 0.005 mg/mL were prepared by dissolving an appropriate amount of MEH-PPV into chloroform. The MEH-PPV solutions with different concentrations in sealed vials were then ultrasonicated at a frequency of 59 kHz and a power of 160 W for 1, 3 or 5 h in water-bath with the aid of an ultrasonic instrument(Model SK3300LH, from Kudos Co.) at room temperature.

UV-Visible absorption spectra of MEH-PPV solutions were recorded on a SHIMADZU UV-3150 spectrophotometer with tungsten and deuterium lamps as light sources and 1 mm thick cuvette at room temperature. The variable temperature UV absorption measurements were performed with a double-beam spectrophotometer(JASCO V-500) in which the temperature controller was connected to the sample holder and the temperature measured directly from solution could be controlled with an accuracy of about ±0.5 °C *via* a water circulation system. The PL emission spectra were measured at room temperature on a single-beam spectrophotometer(SHIMADZU RF-5310pc) with a xenon lamp as the excitation source.

3 Results and Discussion

Both the dilute and concentrated MEH-PPV solutions were used to investigate the effect of ultrasonication on the optical properties. After ultrasonication treatment, the concentrated(3 mg/mL) MEH-PPV solution was diluted to 0.005 mg/mL for the subsequent UV absorption and PL measurements, whereas, the dilute(0.005 mg/mL) MEH-PPV solution was used

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