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The influence of PPV chain aggregated structure on optical properties

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Abstract

A comparison has been made on the fluorescence of the poly (*p*-phenylenevinylene) (PPV) that without filtering the low molecular weight molecules (sample A) with the PPV of the low molecular weight molecules filtered (sample B). Although there is no obvious difference found in the FT-IR and Raman spectra between two samples, in the photoluminescence spectrum of the sample A, the peak at 510 nm is not appeared and the fluorescence intensity for the peak at 550 nm is increased. Under the high pressure condition the fluorescence peak at 520 nm, which corresponds to the peak at 510 nm of the usual PPV, is observed. Applying high pressure to the sample A or by filtering the low molecular weight molecules, the chain aggregated structure is modified, resulting in a change in the PPV chain distortion degree.

Keywords: PPV; Fluorescence; Aggregated structure; Pressure

1. Introduction

In the early 1990s, Burroughes et al. [1] found the conjugated polymer poly-(*p*-phenylenevinylene) (PPV) being as a good fluorescence material. PPV is regarded as a promise optic–electronic application material because of easy processability and cheap cost. However, it is a material with low luminescence efficiency as well as weak intensity. That is why the optical property of PPV needs to be improved. The PPV/CdSe composite emits blue fluorescence and improves the luminescence intensity [2,3]. PPV blend with TiO_2 results in improving the luminescence efficiency [4]. By adjusting the conjugated length of PPV, the luminescence wavelengths can be varied. Recent studies have indicated that the luminescent properties of conjugated polymer are highly dependent on processing conditions [5,6]. The aim of this work is, therefore, to investigate the differences in photoluminescence (PL) between the two kinds of PPV with low molecular weight molecules filtered (sample B) and without filtering low molecular weight molecules (sample A).

Generally, PPV emits fluorescence in yellow–green range. The yellow is attributed to 0–1 transition at 550 nm wavelength, while the green is 0–0 transition at 510 nm. The two peak intensities are related with the distortion degree and chain aggregated structure of PPV [7]. With the high pressure technique applied to the PPV and MEH–PPV, it has been found the red

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shifting and loss of photoluminescence (PL) efficiency with increasing pressure [8,9]. But no convincing explanation has yet been given. So there have much interest to deepen study of the PPV.

In this work, two kinds of PPV samples (A and B) are investigated by FT-IR, Raman, PL spectroscopy and high pressure PL spectroscopy. We have found the fluorescence peak at 520 nm, which is not exist at ambient pressure for sample A, is appeared with the increasing pressure.

2. Experimental

2.1. Preparation of PPV

The precursor polymer to the PPV (Fig. 1) is prepared following the standard polyelectrolyte Wessling route [10], using α,α-dichloro-*p*-xylene and tetrahydrothiophene as the starting reactants. Polymerization is carried out in methanol, with tetrabutylammonium hydroxide as a base catalyst. At the end of the polymerization, the reaction is quenched by neutralizing the basic reaction mixture with dilute HCl (aq) (0.5 M) to a pH of ~4–6. The precursor polymer solution is divided into two parts. The one part is used for preparing the sample A which is not purified and the other one for the sample B which is purified by dialysis (molecular weight cut-off, MWCO of 4000) against methanol over a period of 3 days, with a daily change of fresh solvent. The two kinds of PPV are heat-treated at 200 °C in vacuum ($\sim 10^{-5}$ MPa).

2.2. Measurement

The Fourier transform infrared spectrometer (MAGNA-IR750) and the Confocal Laser MicroRaman Spectrometer (LABRM-HR) are used for obtaining FT-IR and Raman spectrum for both samples. The HITACHI fluorescence spectrophotometer (M850) is used to record the PL spectrum. But the high pressure PL spectrum of the sample A is measured by LABRM-HR. A diamond anvil cell is used for high pressure experiment. The samples are filled into a hole of diameter 0.2 mm in a stainless gasket of the thickness of 0.28 mm. The gasket is pre-indented by the diamond anvils to give an initial sample thickness of about 0.18 mm, and diameter of 0.2 mm. A few grain of ruby powder are introduced in the cell to allow in situ pressure measurements, using the well known fluorescence technique [11]. From the shift of the R_1 line of the ruby fluorescence, the pressure can be determinated.

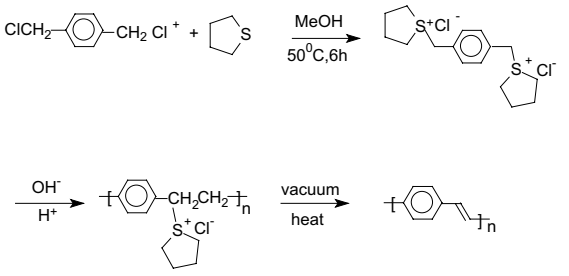

Fig. 1. Synthetic pathways of PPV.

3. Results and discussion

3.1. FT-IR and Raman

Fig. 2 shows the FT-IR spectra for sample A and sample B. Both spectra have similar characteristic absorption peaks [12]. The absorption band at 964 cm^{-1} is due to C–H out-of-plane bending of the *trans*-configuration of the vinylene group. The band at 3024 cm^{-1} is assigned to the *trans*-vinylene C–H stretching mode. The absorption band at 837 cm^{-1} and 1515 cm^{-1} is assigned to *p*-phenylene C–H out-of-plane bending and C–C ring stretching, respectively. These absorption peaks have shown styrene structure units in the two polymers.

Fig. 3 illustrates Raman spectra of the sample A and sample B. It is seen that there is no obvious difference in the spectra between the two samples. The peak positions of the bands forming the triplet are, respectively, 1542, 1579 and 1623 cm^{-1}. The first two are attributed to the phenyl group (stretching of C=C and C–C), whereas the last one and the peak at 1326 cm^{-1} are the vinyl one (C=C stretching and the CC–H bend vibration). Elongation of symmetrical cycle is at 1414 cm^{-1}. The above data are consistent with the literature [13].

Therefore, both the FT-IR and Raman spectra have indicated that there are no differences in molecular structure of PPV among the two samples.

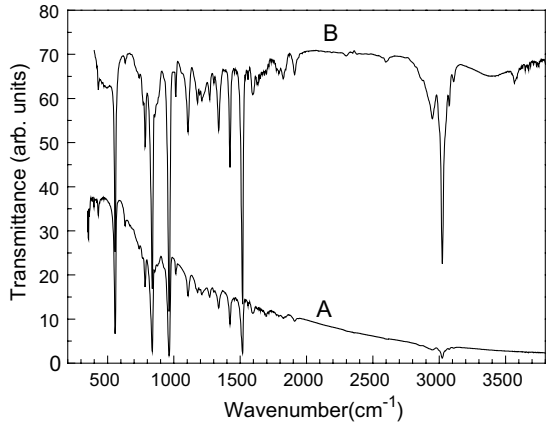

Fig. 2. FT-IR absorption spectra of the two kinds of PPV, sample A and sample B.