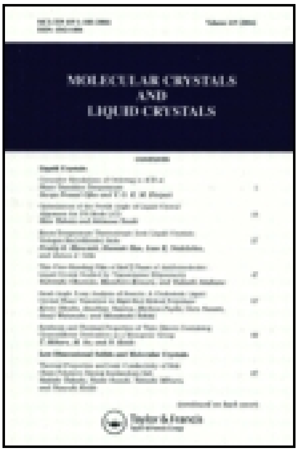

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Optical Properties of Self-Assembled Poly(p -Phenylene Vinylene) Converted at Low Temperatures

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Optical Properties of Self-Assembled Poly(*p*-Phenylene Vinylene) Converted at Low Temperatures

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Self-assembly films of poly(*p*-phenylene vinylene) (PPV) were prepared by dipping quartz substrates alternately in solutions of the PPV polymer precursor poly(xylylidene tetrahydrothiophenium chloride) (PPV-precursor) and of a sodium salt of dodecylbenzenesulfonic (DBS) acid. The advantage of introducing DBS lies in the possibility of converting films with a high conjugation length at 115 °C within only 3 min. By controlling the DBS concentration, symmetrical and non-symmetrical PPV heterostuctures can be realized with a macromolecular manipulation during the dipping direction, leading to enhanced optical proprieties.

Keywords: Self-assembly; PPV, Luminescence, absorption

INTRODUCTION

The discovery of the extremely rapid thermal conversion process into poly(p-phenylene vinylene) (PPV) by the incorporation of dodecylbenzenesulfonic counterion (DBS) [1] has opened up a number of new possibilities to molecularly engineered superstructures with improved properties. The main advantage of this novel procedure is that thermal conversion may be performed at temperatures considerably lower (80-100 °C) than those conventionally used (> 200 °C), within very short time (down to 3 minutes) and under ambient conditions. In this work, we show that DBS can be used to produce self-assembled (SA) multilayers with new special features. Rather than alternating layers provided by suitable polyanion and polycation, we adopted in this work an alternative approach based on substitution of chloride counterion in PPV precursor (poly(xylylidene tetrahydrothiophenium chloride or PTHT) by a long chain sulfonic counterion, the DBS. The internal layer structure of these PTHT-DBS films is, therefore, likely to be different from conventional layer-by-layer films, since DBS is expected to be incorporated into the PTHT chain.

EXPERIMENTAL

The PPV-precursor was synthesized using the same precursor route described in the literature [2]. PPV-precursor solution had 0.18 mg/mL and pH=5.0. The DBS solutions were prepared with concentration varying from 10^{-3} to 1 M and pH = 5.0, diluted in Milli-Q water. The PTHT-DBS films were processed by alternate immersion in the polycation solution (PTHT) and polyanion solutions (DBS), and finally dried with N_2. The films were adsorbed on hydrophilic quartz substrates treated in H_2SO_4/H_2O_2 (7:3) bath for 30 min and $H_2O/H_2O_2/NH_3$ (5:1:1) bath for 30 min. In each bilayer, the immersion times in PTHT and DBS solutions were fixed in 15 s and 10 s, respectively. SA-PPV films were obtained with a low temperature thermal treatment (80 to 120 °C) during 30 min under atmospheric conditions. The UV-Vis spectroscopy were accompanied by a Hitachi U-2001 and coupled with a closed helium cryostat in the low temperature measurements. The emission properties of these films were investigated by photoluminescence (PL) spectroscopy. Details of the PL set-up were published elsewhere [3].

RESULTS

Figure 1 shows the evolution of the UV-visible spectra depending on the number of PTHT-DBS bilayers. The absorption increases linearly with the number of bilayers. This demonstrates that layers of PPV-precursor can be adsorbed alternately after the surface substitution of Cl counterions by DBS in the tetrahydrothiophenium group. In this figure is also presented the absorption spectrum of a PPV film converted at 110 °C in air during 30 min, although saturation in the conversion process can be achieved in smaller periods of time [1].

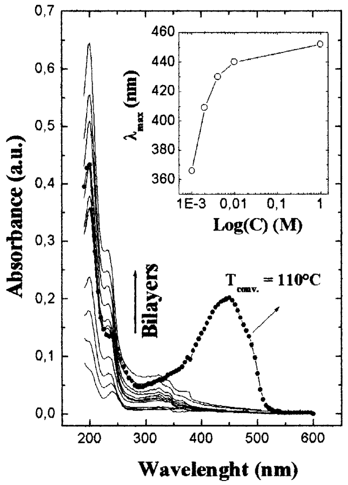

FIGURE 1. UV-Vis absorption spectra after each bi-layer of PTHT-DBS film before conversion. The doted curve represents the absorption spectrum after conversion at 110 °C by 30 min. The insert shows the band-edge wavelength ($\lambda_{max.}$) in π-π^* band for films containing different DBS concentrations.

When the concentration of the DBS solution is changed, not only the absorption ratio changes but also a shift is observed at the absorption spectra. The insert shows the dependence of the absorption band-edge wavelength ($\lambda_{max.}$) on the DBS concentration. This red shift of the non-localized band between 300 and 500 nm demonstrates that different conjugation lengths can be achieved for increasing DBS concentrations. This can be explained by the fact that, at low conversion temperatures, only the PTHT segments containing DBS are converted into PPV.

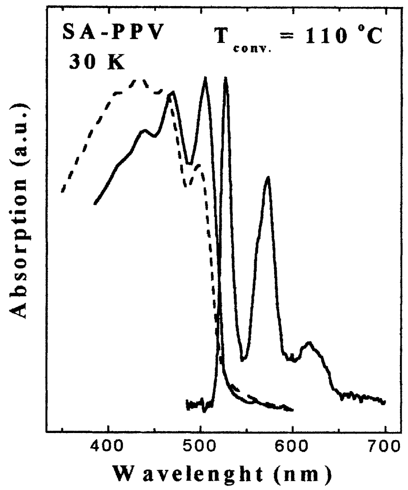

FIGURE 2. Low temperature (30K) absorption and PL spectra of a SA-PPV-film (continuous lines). The absorption spectrum at 30K of a LB-PPV film is shown for comparison (dash line).

Figure 2 shows the absorption and photoluminescence (PL) spectra (continuous line) of a SA-PPV film converted at 110 °C under atmospheric conditions. For comparison, the absorption spectrum of a Langmuir Blodgett PPV film (LB-PPV film) [3], converted in the same conditions, is also present in Fig. 2 (dashed line). One observes lower absorption intensity at higher energies and well resolved vibronic structures for SA-PPV samples converted at low temperatures. This indicates that SA-PPV films are more ordered (higher conjugation length) and present lower density of defects (see below) than for LB-PPV films. The quality of the PPV films by the SA methodology and the efficacy of the conversion procedure at low temperatures presented here are demonstrated by the very sharp and well resolved vibronic structures in the PL and absorption spectra. This new methodology has the advantage of being inexpensive and easy to be processed.

Figure 3 compares the dependence of the integrated PL intensity for samples prepared under identical conditions, but converted at 80 and 230 °C under vacuum conditions. A strong difference in the temperature dependence is observed in the emission intensity of both samples. A drastic improvement in quantum efficiency of PPV is observed when we decrease the conversion temperature from 230 to 80 °C. This effect may be explained by the decrease of extrinsic defect incorporation, such as carbonyl groups, observed by infrared measurements when the films were converted at low temperatures [4].

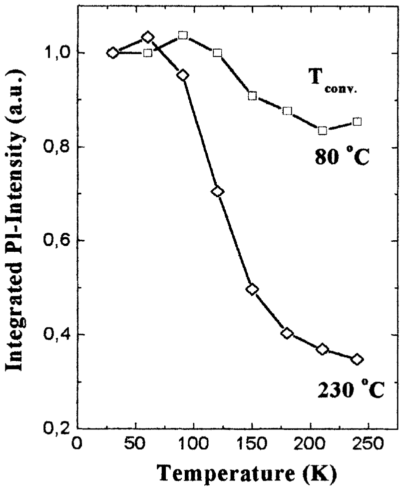

FIGURE 3. Integrated PL-intensity as a function of sample temperature for films converted at different temperatures (80 °C and 230 °C).

CONCLUSIONS

In the present work, developed an alternative approach to produce self-assembled thin films of PPV, consisting of a controlled substitution of the chloride counterion of a water-soluble PPV precursor by a long chain DBS counterion. The advantage of introducing DBS lies in the possibility of converting films with a high conjugation length at 115 °C within only 3 min. By varying the amount of DBS in the solution, we could control the conjugation length of PPV segments, what opens the possibility of producing asymmetric heterostructure in conjugated polymers. In addition, a dramatic improvement in quantum efficiency of PPV is observed when the conversion temperature is decreased form 230 to 80 °C. Such flexibility in film fabrication and efficient low temperature conversion to PPV offer an advantageous alternative to the standard conversion procedures, which may have important implications in device applications.

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