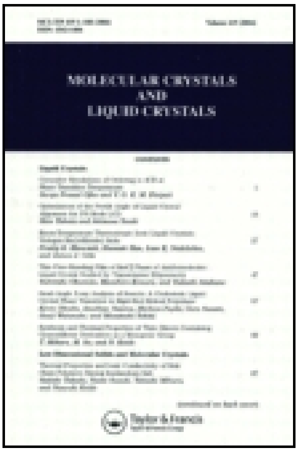

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Reversible Electrochromical Response of Thin MEH-PPV Films

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A reversible electrochromical response of thin poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) films spin-coated on ITO substrates was observed during spectroelectrochemical experiments. The polymer layer changes its coloration from reddish-orange (neutral form) to brownish-green (oxidized form) upon varying the applied potential. The oxidized form showed to be stable even after removing the film from the electrochemical cell, returning to its original form only after electrochemical reduction. The color transitions at different potentials were studied by UV-vis-NIR absorption spectroscopy.

Keywords: poly(*p*-phenylene vinylene) and derivatives; light-emitting devices; electrochromism; spectroelectrochemistry.

INTRODUCTION

The physical properties of poly(*p*-phenylene vinylene) (PPV) and its derivatives have been widely studied due to their use as active layers of electronic polymeric devices such as light-emitting diodes (LEDs) [1] and light-emitting electrochemical cells (LECs) [2]. However, optical and electrical properties of MEH-PPV when in doped states have not been so far well explored.

It is well known that the conductivity of PPV and derivatives increases drastically after chemical doping by iron chloride in solution or iodine vapor [3]. Colorations of the non-doped and the doped polymer are usually different, characteristic that indicates distinct doping levels. In this work, we studied the electrochromic properties of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) films during spectroelectrochemical measurements in a non-aqueous medium.

EXPERIMENTAL

MEH-PPV was synthesized by a modified Gilch route as similarly described by Wudl [1]. MEH-PPV in chloroform solutions were prepared at 6 mg mL^{-1} and filtered through a 0.45μm pore filter. Uniform films were obtained by spin coating the solutions on ITO-coated glass substrates, which were previously treated using a 5:1:1 (H_2O:H_2O_2:NH_4OH) solution at 80 °C for 10 min and washed with water. Typical thickness of the polymer layers varied from 100 to 300 nm.

UV-vis-NIR absorption curves were carried out using a Hitachi U-2001 spectrophotometer. A potenciostat (PAR EG&G 283) was used to perform all electrochemical experiments. The electrochemical measurements were realized using a standard glass cell and Ag, Pt and the MEH-PPV-covered ITO substrate were used as semi-reference, counter and working electrodes, respectively. The electrolyte solution was composed by tetrabutylammonium perchlorate (TBAP) in acetonitrile (ACN) in a concentration of 0.01 mol L^{-1}.

The MEH-PPV films electrochemically oxidized at different potentials were removed from the cell and dried with a stream of nitrogen before each absorption spectrum scan. To return to the neutral form, the films were immersed again in the electrolyte solution, and a potential of 0 V *vs* Ag was applied to the working electrode until stabilizing the current. Iodine vapor doping was carried out exposing the films in a closed recipient containing a small amount of iodine crystals for 10 min.

RESULTS AND DISCUSSION

Figure 1 shows the voltammetric response of a MEH-PPV film deposited on ITO in a positive range of potential. The well-defined redox couple observed between 600 and 1000 mV *vs* Ag can be attributed to a *p*-doping/dedoping process of the polymer structure in the TBAP-ACN electrolyte solution [4]. The current density for both peaks decreases slightly with the number of cycles, indicating an effect of material loss and/or degradation of the polymer. Since no color transition was noticed in the negative range of potential, and considering that a previous work reported redox reactions in this region [4], the correspondent voltammograms are no longer treated here.

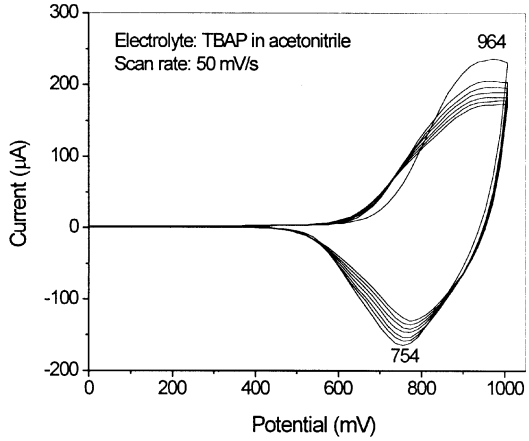

FIGURE 1 Successive cyclic voltammograms of a MEH-PPV/ITO film in 0.01 mol L^{-1} TBAP and acetonitrile.

Figure 2 depicts the absorption spectra of a MEH-PPV film at three different states. Curve *a* represents the absorption spectrum of a film in its pristine form (orange-reddish color) with a lower-energy band at 500 nm, which is associated with the excitonic transition of the delocalized π electron system, as previously described in the literature [5-7]. Upon applying +1000 mV, the absorption spectrum assumes the curve *b* shape, and the film coloration changes to green-brownish. In this latter case, the intensity of the band at about 500 nm decreases (leading to a residual shifted band at 420 nm), and a new broad band appears at about 770 nm. The resulting spectrum is similar to that obtained for an iodine-doped sample (curve *d*, normalized in comparison to the neutral form spectrum) evidencing that a *p*-doping process in fact occurs in the positive range of potential. When the potential is reduced back to zero (curve *c*), the absorption spectrum assumes the shape of the spectrum of the pristine sample (curve *a*) but with a lower intensity.

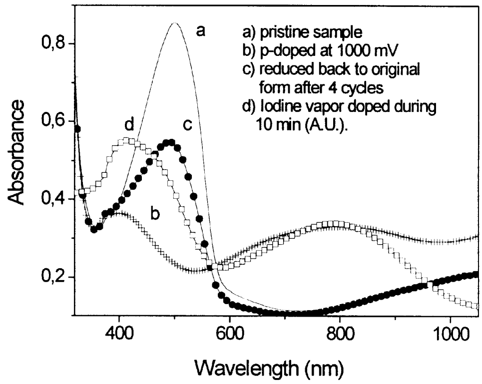

FIGURE 2 UV-vis spectra of a MEH-PPV/ITO film at different applied potentials.

One also notes that the intensity of the 500 nm band in curve *c* (obtained after 4 complete cycles from 0 to 1000 mV) is about 35 % lower than the same band in the pristine sample spectrum. After the first cycle, however, the decrease of the band intensity is less than 10 %, showing that it gradually decreases with the number of cycles, probably due to the degradation and/or material loss process already observed in Figure 1.

Figure 3 shows the spectroelectrochemical spectra of a MEH-PPV film by applying different potential steps. In between two successive steps there was a potential ramp from an initial potential (E_i) to a final potential (E_f). The values of E_i for successive steps were chosen to be exactly the value of E_f of the respective previous steps. It allows that all steps complete an entire cycle in the 0-1000 mV range.

For the sample reduced back to its neutral form, $E_i = 400$ mV, $E_f = 0$ mV, the decrease of the intensity of the absorption at 500 nm is approximately the same as observed for four complete cycles as previously mentioned, even though after a higher number of measurements. Therefore, one infers that this effect can be related to a faster degradation of the film when complete cycles are carried out, since the sample is subject to high cathodic currents for longer times.

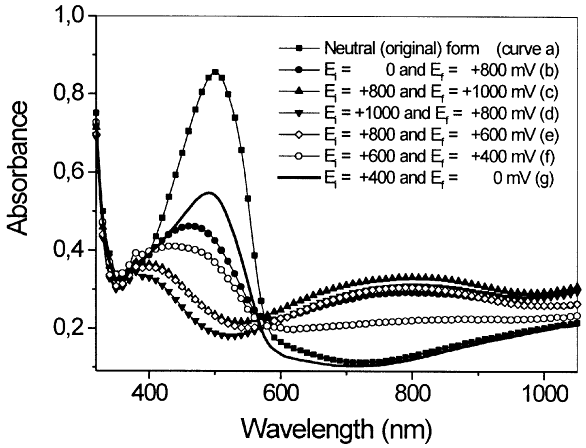

FIGURE 3 UV-vis-NIR absorption spectra at different oxidation potentials.

The crossing over region at about 570 nm in Figure 3 indicates that the increase in area under the absorption curve for wavelengths higher than 570 nm is accompanied by a correspondent decrease for values below this point, resembling an isosbestic point. This point can be associated with the value of energy in which the polymer changes its state from the non-doped to doped state.

The shape of the absorption curve also varies with the electrochemical history of the sample. Those curves obtained at a same final potential, but at different E_i values (curves *c* and *d* of Figure 3), are different since the film is in a different oxidation state for each applied potential step.

CONCLUSIONS

The reversible electrochromical response of MEH-PPV at different potentials is an excellent indicative of the oxidation and/or doping level of the polymer film, which is promissory to be applied in chemical sensors or electrically controlled optical switches. The decrease in the optical absorption of the film during measurements, as a consequence of a degradation effect, can not be considered as a technical limitation to the development of such related devices. Controlled experimental conditions and the use of different electrolyte media are procedures which probably may minimize these effects.

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