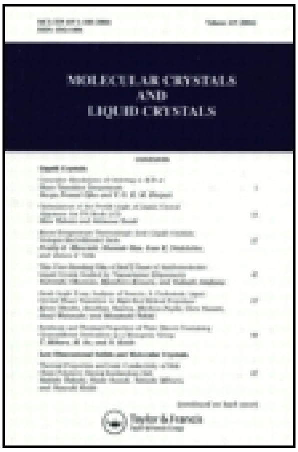

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Electrosynthesis and Optical Properties of Poly(p -phenylene) and Poly(p -phenylene-pyrrole) Films

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To cite this article: C. Eiras, M. Foschini, R. M. Faria & D. Gonçalves (2002): Electrosynthesis and Optical Properties of Poly(p -phenylene) and Poly(p -phenylene-pyrrole) Films, Molecular Crystals and Liquid Crystals, 374:1, 493-496

To link to this article: http://dx.doi.org/10.1080/10587250210493

Mol. Cryst. Liq. Cryst., Vol. 374, pp. 493-496
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1058-725X/02 $12.00 + .00

Electrosynthesis and Optical Properties of Poly(*p*-phenylene) and Poly(*p*-phenylene-pyrrole) Films

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Poly(*p*-phenylene) (PPP) and poly(*p*-phenylene-pyrrole) (PPP-Ppy) films were electrochemically polymerized on indium-tin-oxide glass (ITO) and platinum electrodes. Their optical properties were studied by UV-vis and photoluminescence spectroscopy. The influence of the final potential applied during synthesis (E_f) on the optical properties of PPP films was also studied. The PPP film prepared at 1.5 V showed an absorption band at 540 nm which was attributed to a p-doping process. Stable films with a similar emission band at 420 nm (blue region) were obtained after polymerization of *p*-terphenyl, and *p*-terphenyl/pyrrole monomers.

Keywords: poly(*p*-phenylene vinylene); poly(pyrrole); light-emitting diodes; copolymers.

INTRODUCTION

A considerable effort has been directed to the development of light-emitting diodes (LEDs) based on highly delocalized π-conjugated polymers such as poly(*p*-phenylene) (PPP) and derivatives. [1,2]. While blue LEDs are relatively difficult to obtain using inorganic semiconductors, a wide range of coloration is reached with conjugated polymers and copolymers containing short conjugated segments [3]. Among the conjugated polymers, PPP shows a blue light emission [$\lambda_{máx}$ = 459 nm (2.7 eV)] [2,4]. The electrochemical synthesis of PPP using biphenyl or *p*-terphenyl monomers has been provided to be a convenient method of obtaining absorbing and smooth films directly on the electrode surface. In this work, PPP and PPP-polypyrrole (PPP-Ppy) copolymers were obtained in a non-aqueous medium. These films were analyzed by cyclic voltammetry in a monomer-free solution and optical measurements.

EXPERIMENTAL

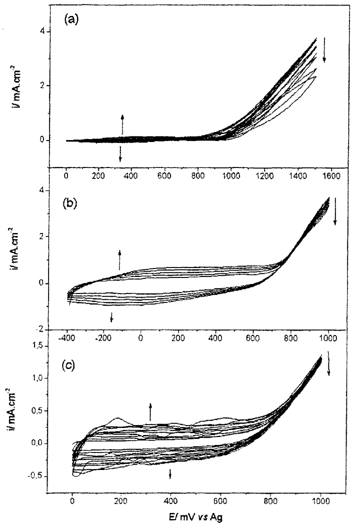

FIGURE 1: Cyclic voltammograms of Pt electrodes in ACN and TBAClO$_4$ (0.01 mol L^{-1}): (a) *p*-terphenyl (0.02 mol L^{-1}); (b) pyrrole (0.1 mol L^{-1}); (c) a *p*-terphenyl (0.02 mol L^{-1}) and pyrrole (0.01 mol L^{-1}) mixture.

The electrochemical syntheses of PPP and PPP-Ppy films were realized at 80 °C and room temperature, respectively. A platinum foil (about 1 cm^2) was used as the working electrode, and a platinum wire as the counter electrode. The reference electrode was an Ag quasi-reference electrode (Ag-QRE). The potential of Ag-QRE in acetonitrile (ACN) and 0.1 mol L^{-1} tetrabutylammonium perchlorate (TBAClO$_4$) solution was 94 mV *vs* SCE. Transparent ITO electrodes were used for UV-vis (HITACHI U-2001 spectrophotometer) and photoluminescence (PL) (Fluorometer resolved at time ISS K2) measurements. All electrochemical measurements were performed using a potentiostat/galvanostat (EG&G PAR 283).

RESULTS AND DISCUSSION

The cyclic voltammograms of Pt electrodes in medium of *p*-terphenyl, pyrrol, and a *p*-terphenyl and pyrrole mixture (2:1) are shown in Figure 1. The basic difference noticed in theses curves is that *p*-terphenyl oxidizes at a more positive value of potential (1.5 V as compared with 1.0 V for pyrrole, and 2:1 *p*-terphenyl and pyrrole). As such, two values of final potential (E_f) were used for obtaining PPP films: 1.5 V and 1.6 V.

The voltammetric responses of these films are shown in Figure 2. The PPP film shows a typical electroinactive response even after reaching a more positive final potential (curves a). The same response is noticed for the copolymer film in the first voltammetric cycles (curves c). After a stabilizing time (37 cycles), the voltammetric curve assumes the same shape as observed for Ppy films (curves b).

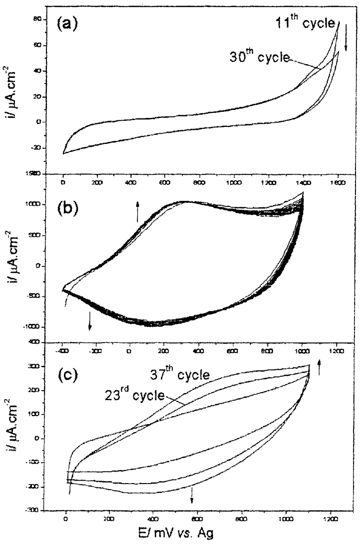

FIGURE 2: Cyclic voltammograms: (a) PPP; (b) Ppy; and (c) PPP-PPy films in ACN and 0.01 mol L^{-1} $TBAClO_4$; 50 mV s^{-1}.

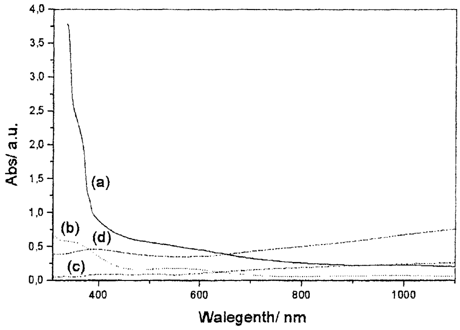

FIGURE 3: UV-vis spectra: (a) PPP at $E_f = 1.6$ V; (b) PPP at $E_f = 1.5$ V; (c) Ppy; and (d) PPP-Ppy films.

Figure 3 shows the UV-vis spectra of PPP films obtained at different values of E_f, and Ppy and PPP-Ppy films.

The UV-vis spectra of the PPP film exhibit a band at 360 nm (curves a and b). Another band was observed at 540 nm in the spectrum of PPP at 1.5 V, which can be associated with a p-doping process. In the spectrum of the copolymer film (curve d), one notices a band at 360 nm (a contribution from PPP), a broad band at 1000 nm (a contribution from Ppy) (curve c).

The photoluminescence (PL) properties of PPP and PPP-Ppy films were also investigated (Figure 4) using a 300 nm Xe lamp.

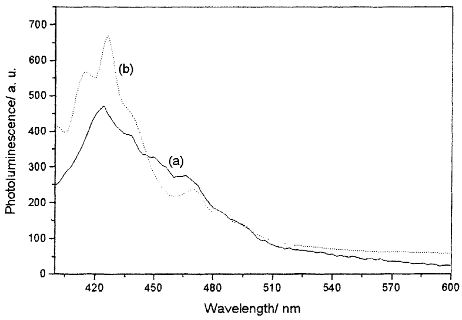

FIGURE 4: Photoluminescence spectra: (a) PPP; and (b) PPP-Ppy films.

Both spectra show an emission bands at about 420 nm (blue region). They are reproducible and in agreement with data reported in the literature for PPP obtained at similar conditions [4].

CONCLUSIONS

The PPP-Ppy films showed an electroactive response, particularly because the presence of Ppy. The UV-vis spectrum of a PPP-Ppy film exhibited two bands: at 360 nm and 1000 nm, this latter due to Ppy units. For the emission spectra of PPP-Ppy, a band at 420 nm was noticed indicating that this polymer can used as light-emitting layers of blue PL devices.

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