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Regina M.Q. Mello · José P.M. Serbena
Adriano R.V. Benvenho · Ivo A. Hümmelgen

Electrochemical preparation of poly(*p*-phenylene) thin films

Abstract We report the electrochemical preparation of poly(*p*-phenylene) (PPP) thin films with a polymerization degree of approximately 20 using biphenyl as starting material. The PPP films are prepared directly on a tin oxide electrode, presenting a positive charge carrier mobility of 5×10^{-7} cm^2 V^{-1} s^{-1}.

Keywords Electrochemical synthesis · Light emitting diodes · Poly(*p*-phenylene) · Thin films · Tin oxide electrode

Introduction

Since the first report on polymer light emitting diodes (LEDs) in 1990 [1], large efforts have been devoted to the development of these devices, improving efficiency and durability and producing materials with new emission colors. Among different conducting polymers, poly(*p*-phenylene) (PPP) is an interesting material for LED applications since it is stable under ambient atmosphere even at high temperatures and presents electroluminescent emission in the blue region of the spectrum. In spite of these distinguishing properties, the use of PPP in several applications has been limited by processability constraints due the insolubility of PPP.

Owing to the impossibility of production of PPP films from solution by spin casting, these have mainly been obtained by vacuum evaporation of pure oligomers. There is, however, another possibility, which is the synthesis and simultaneous deposition of the PPP film through an electrochemical process. The advantages of the latter are: (1) direct deposition of the polymer on the desired substrate material; (2) formation of a well adsorbing and mechanically tough film; and (3) the possi-bility to control different parameters during the polymerization (e.g. film thickness). Additionally, if desired, the electrochemical setup also can be used to dope PPP via anion (p-doping) or cation (n-doping) [2, 3] insertion.

Blue LEDs are important because the emission can be converted into other emission colors either by an external color-conversion technique (ECCT) or an internal conversion technique (ICCT), necessary for full color display applications [4].

Electrolytic synthetic methods for PPP preparation have been reported. Most of them involve the electrolysis of benzene, which forms the polymer by anodic oxidation through the use of severe chemical conditions. Another strategy reported in the literature is PPP synthesis using biphenyl as the starting material [5, 6, 7, 8, 9, 10, 11, 12, 13], which presents a lower oxidation potential than the monomer benzene. Furthermore, if biphenyl is used as the starting material, as is the case in this contribution, milder anodic conditions can be used. Besides being a potentially less toxic process than those involving benzene, biphenyl oxidation only requires the use of aprotic solvents. Furthermore, this method yields PPP with a generally longer chain length and a lower degree of cross-linking than PPP electroformed from benzene [5, 6, 7, 8, 9, 10, 11, 12, 13].

Most polymers, when in the solid phase, are randomly oriented as in cooked spaghetti, with strong consequences on energetic disorder and charge transport properties. To improve the molecular orientation and crystal domain size in semi-crystalline polymers, thermal annealing is often employed as a post-synthesis treatment [14].

In this work we report on the electrochemical synthesis of PPP films onto a tin oxide (TO) coated [15] glass substrate using biphenyl as the staring compound, determining the charge carrier mobility of positive charge carriers in these films. TO is transparent to light in the visible range of the spectrum and electrically conductive, so that TO/PPP structures are potentially interesting for applications in optoelectronic devices.

R.M.Q. Mello (✉) · J.P.M. Serbena · A.R.V. Benvenho
I.A. Hümmelgen
Departamento de Física, Universidade Federal do Paraná,
Caixa Postal 19044, 81531-990 Curitiba, PR, Brazil

Experimental

A conventional three-electrode electrochemical cell was used for the preparation of the PPP films. The film deposition was carried out in a one-compartment cell containing 0.05 mol L^{-1} biphenyl, 0.1 mol L^{-1} lithium perchlorate and perchloric acid in the following concentrations, depending on the specific batch: 0.0, 0.55 or 5.5 mol L^{-1}. A TO-coated glass was used as the working electrode (electrode area: 1 cm^2) and graphite as the counter electrode. The potentials in the synthesis experiments were measured using Ag/AgClO$_4$ as the reference electrode.

PPP was electrodeposited by the potential pulse technique. The solution was purged with nitrogen before polymerization and during the additions of perchloric acid. This addition was a strategy necessary to grow PPP onto a resistive working electrode because the acid increases the ionic strength of the electrolytic solution and decreases the anodic polymerization potential, in agreement with the results of Goldenberg et al. [16]. The same strategy was used in polythiophene synthesis, resulting in moderately concentrated HClO$_4$ (5 M) being particularly suitable for carrying out the electropolymerization of thiophene at a low potential (0.9 V vs. SCE instead of 1.6 V in acetonitrile) [17].

Voltammetric experiments were used, at different conditions than those used to prepare the films, to estimate the polymer highest occupied molecular orbital (HOMO). The HOMO was estimated via oxidation onset using a gold plate (surface area = 1 cm^2) as the working electrode, Ag/Ag$^+$ as the reference electrode and 0.1 mol L^{-1} LiClO$_4$ in acetonitrile as the electrolyte solution.

The PPP films were obtained in the doped state. The dedoping was electrochemically made in a solution of 0.1 mol L^{-1} in acetonitrile through polarization of the working electrode at 0 V vs. Ag/Ag$^+$ during the time necessary to suppress the current (~10 min). In the sequence, the PPP films were washed with methanol and thermally annealed during 12 h at 300 °C in a nitrogen atmosphere. In order to produce TO/PPP/Ag devices, Ag was evaporated onto these TO/PPP samples. The TO/PPP/Ag devices were handled in air and measurements performed in a nitrogen atmosphere.

The current-voltage (I vs. V) characteristics of the devices were determined in dark conditions. After setting the zero, the applied voltage was increased stepwise (steps of 0.01 V) at a rate of 0.01 V s^{-1} up to the maximum value.

Results and discussion

Figure 1 shows only the first scan of the anodic polarization curves of 0.05 mol L^{-1} biphenyl in acetonitrile/0.1 mol L^{-1} LiClO$_4$ mixed with various concentrations of HClO$_4$. It can be observed that the oxidation potential of biphenyl decreases with increasing acid content. Further additions, leading to higher HClO$_4$ concentrations, were impossible owing to precipitates forming in the solution. The 5.5 mol L^{-1} HClO$_4$ solution was used for the experiments described in the sequence.

To perform the electropolymerization, the potential was square-wave modulated from a base potential without observable faradaic reaction (0.0 V) to a potential at which anodic oxidation of biphenyl occurs (1.8 V for TO as the working electrode and 1.35 V for Au as the working electrode). The potential modulation frequency was 0.5 Hz. This technique allows a continuous film buildup in perchlorate electrolytes, in agreement with earlier reports [5, 6, 7, 8, 9, 10, 11, 12, 13].
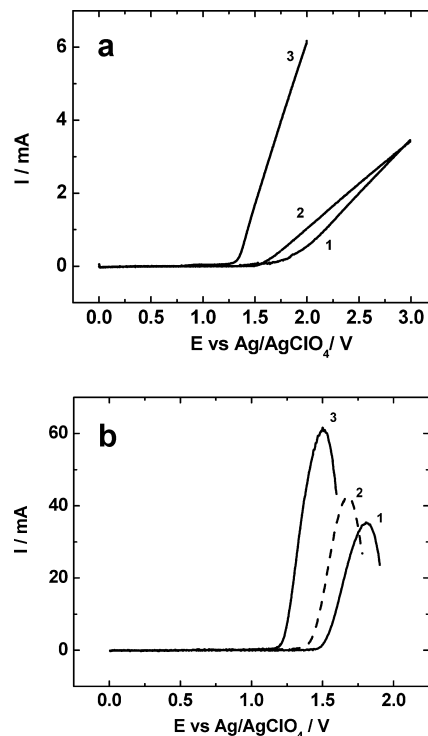

Fig. 1a, b Anodic polarization curves of 0.05 mol L^{-1} biphenyl in acetonitrile/0.1 mol L^{-1} LiClO$_4$ mixed with various concentrations of HClO$_4$: *1*, 0.00 mol L^{-1}; *2*, 0.55 mol L^{-1}; *3*, 5.5 mol L^{-1}. Voltage scan rate: 50 mV s^{-1}. **a** TO working electrode; **b** Au working electrode

Figure 2 shows the IR absorption spectra of PPP, which were performed from a powder of KBr + PPP in its p-doped or undoped state (after an electrochemical reduction, washed with methanol and annealed). The dedoping process leads to the disappearance of the ion (lithium and perchlorate) related vibrational lines of the spectrum. Their characteristic IR absorption lines are located around 650–900 cm^{-1} [18]. The band around 810 cm^{-1} is characteristic of the C-H out-of-plane vibration for adjacent hydrogen atoms on a *p*-disubstituted ring. The two bands located between 699 and 752 cm^{-1} are typical of C-H out-of-plane deformation vibrations of the monosubstituted benzene ring (the
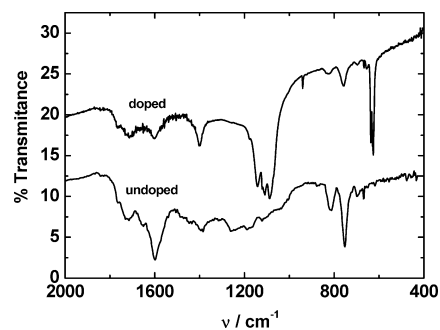

Fig. 2 IR absorption spectra of PPP produced from a powder of KBr + PPP in its p-doped and undoped states

terminal phenyl ring). In this spectrum, no strong Figure 3 shows the UV-vis absorption (left) and photoluminescence (PL; right) spectra of a PPP film electrodeposited onto TO and excited by monochromatic light ($\lambda = 340$ nm). The photoluminescence was clearly observed in the range 400–520 nm (3.10–2.38 eV), with two peaks located at 418 and 440 nm (2.96 and 2.82 eV), corresponding to violet-blue.

Leising and co-workers [19] observed a linear dependence between the position of the first absorption peak and the inverse of the chain length. Using their E_{peak} vs. $1/n$ data (E_{peak} is the energy of the first peak of absorbance in eV, n is the degree of polymerization), the PPP synthesized in this work [E_{peak}(339 nm) = 3.66 eV] corresponds to $n \approx 20$.

The same problem was also investigated by Seoul et al. [20]. Curiously, our absorption and PL data do not present the same shifts as observed by Seoul et al. This shift difference implies that different n values are obtained if our data are compared with those of Seoul et al., depending if PL or absorption spectra are used as reference, leading to an apparent inconsistency. For this reason, we use the data of Leising and co-workers [19] in our analysis.

The cyclic voltammogram (Fig. 4) was used to estimate the PPP HOMO energy level [21, 22]. Using the procedure reported by Micaroni et al. [22], taking the energy corresponding to the oxidation onset, $\sim 0.5 \pm 0.1$ eV, and making the conversion from the reference electrode to vacuum level, we estimate the ionization potential of PPP as IP = $(0.5 \pm 0.1) + 4.4 \approx 4.9 \pm 0.1$ eV. It is important to stress that it is only an estimate, considering that even the onset is not well defined in Fig. 4, probably due to the high energetic disorder present in the formed PPP film. At ~ 0.5 V (Fig. 4) there is a stronger current increase, which may be associated with a major contribution of the HOMO energy levels, representing most of the macromolecules or macromolecular segments of the film, despite the fact that a non-zero current is observable at lower oxidation potential values.

The optical energy gap E_g was determined following a procedure reported by Morita et al. [23]. From analysis of the absorption edge and assuming direct transition, the gap can be calculated with help of the $(h\nu \times \eta)^2$ vs. $h\nu$ plot (where η is the absorption coefficient, h is Planck's

Fig. 4 Cyclic voltammogram recorded in 0.1 mol L^{-1} LiClO$_4$/acetonitrile. Working electrode: gold plate with PPP film; counter electrode: graphite; reference electrode: Ag/Ag$^+$. Scan rate: 10 mV s^{-1}

constant and v the frequency), as presented in Fig. 5, leading to $E_g = 2.8$ eV. Assuming the validity of Koopman's theorem [24], we estimate the electroaffinity (χ) of PPP as:

$$\chi = IP - E_g = 2.1 \text{eV} \tag{1}$$

If the potential energy barrier ϕ at the electrode/conjugated polymer interface is so that $\phi >> kT$ (k is Boltzmann's constant and T the absolute temperature), the transport is injection limited up to a certain applied voltage (dependent on material and device parameters [25]). Thermionic injection into low mobility semiconductors, as is the case for several conjugated polymers, predicts that [26, 27]:

$$J = qN_v\mu F \exp\left(-\frac{\phi}{kT}\right)\exp\left(\frac{\beta F^{1/2}}{kT}\right) \tag{2}$$

where N_v is the effective density of states in the semiconductor, μ is the charge carrier mobility, F is the electric field strength and β is a constant given by:

$$\beta = \left(\frac{q^3}{4\pi\varepsilon}\right)^{1/2} \tag{3}$$

where q is the elementary electronic charge and ϵ is the permittivity of the material.

It can be seen from Eq. 2 that a linear dependence between $\ln(J/V)$ and $V^{1/2}$ is expected when the charge carrier transport is limited by thermionic injection into
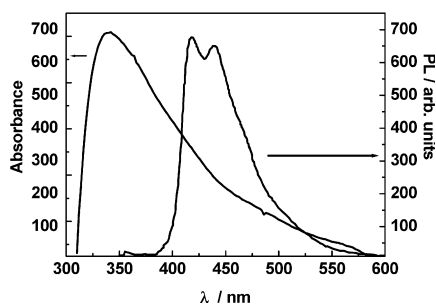

Fig. 3 UV-vis absorption and photoluminescence spectra of PPP film electrodeposited onto TO and excited with light of wavelength 340 nm

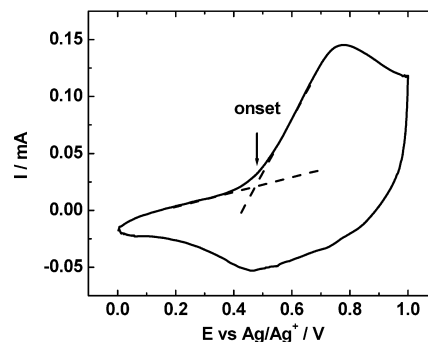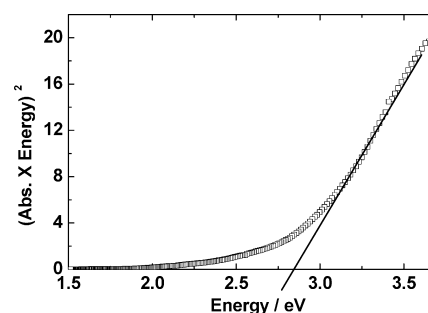**Fig. 5** Absorption spectrum of PPP film electrodeposited onto TO

low-mobility materials, dependence followed by the electrical characteristics of a TO/PPP/Ag device, as can be seen in Fig. 6.

The temperature dependence of the current for these devices is presented in the inset of Fig. 6. From Fig. 6:

$$\left[\frac{\partial \ln I}{\partial T^{-1}}\right]_{V=\text{constant}} = \frac{\beta d^{1/2} V^{1/2} - \phi}{k} \quad (4)$$

can be calculated. Knowing V and T, it is possible to determine ϕ. Applying this procedure, we have obtained $\phi \approx 0.1$ eV.

We have determined μN_v using our data. Assuming $N_v = 2.5 \times 10^{19}$ cm^{-3} [28], a positive charge carrier mobility $\mu = (4.7 \pm 0.6) \times 10^{-7}$ cm^2 V^{-1} s^{-1} is then calculated for PPP.

The value adopted for N_v needs some comments. This value of N_v was used to fit the results for poly(dialkoxy-p-phenylenevinylene) by Blom et al. [28] and further applied to analyze results obtained on poly(4,4'-biphenylenevinylene) by Ma et al. [29], leading to a good agreement between mobility values obtained applying Eq. 2 and those determined from samples presenting space-charge-limited transport [29]. In spite of a N_v value dependence on the specific polymer, the presence of chemical and conformational defects in the polymer chain and even in the sample preparation process, our assumption is reasonable for a first estimate, considering the order of magnitude. This is relevant since a direct determination of actual N_v is quite difficult, so that only estimates are frequently possible. Essentially, only the μN_v product can be determined from Eq. 2. However, if a space-charge-limited current regime is achieved at higher applied voltages, before device degradation, which is not always the case, there is an independent way to determine μ and, consequently, to calculate N_v. This, however, was not the case in our devices.

The average value of the positive charge carrier mobility obtained in this work is approximately one order of magnitude lower than that reported by Lee et al. [30] for vacuum-deposited PPP thin films, estimated using ITO/PPP/Al devices and electroluminescence delay-time measurements.
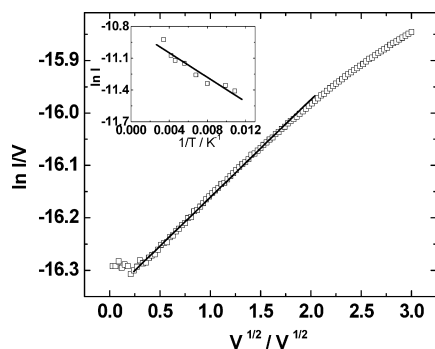
It is important to stress that different models have been used to explain the experimental data in conjugated polymer devices. Equation 2 is not generally obeyed for organic semiconductors, as is the case, for example, in poly(dialkoxy-p-phenylenevinylene) [31] or some poly(p-phenylenevinylene) and poly(p-phenylene) derivatives [32], but in the case of polythiophene derivatives (poly-methylthiophene [33], polyhexylthiophene [34] and polyoctylthiophene) it correctly describes the experimental data. The weak temperature dependence of the current in the PPP devices and the low barrier height value, significantly lower than the difference between PPP ionization potential and electrode work function ($\sim$4.3 eV for both TO [15] and Ag [35]), suggests a high contribution of polarization at the interface to barrier lowering or a large distribution of HOMO level states due to high energetic disorder. Assuming a HOMO energy distribution of the gaussian type, the injection would preferentially occur through energetically more favorable sites, which may be localized out of the center of the distribution, leading to lower barrier heights. This latter possibility is consistent with the ill-defined oxidation onset observed in the cyclic voltammogram (Fig. 4) and in the low-energy tail of the absorption spectrum (Fig. 3).

Conclusion

The electrochemical PPP synthesis described in this work allows the preparation of polymer films with $n \approx 20$ and emission in the violet-blue spectral region, which is interesting for full color display applications. This PPP films can be prepared directly on tin oxide, a transparent conducting material, and present a positive charge carrier mobility of 5×10^{-7} cm^2 V^{-1} s^{-1}.

Fig. 6 $I(V)$ characteristics of a TO/PPP/Ag sample ($d = 670$ nm). *Inset*: $I(T)$ dependence of TO/PPP/Ag sample ($d = 120$ nm); $V = 0.9$ V

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