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One-step electrochemical synthesis of pure poly(2,5-dicyano-*p*-phenylenevinylene) films

Abstract In this communication we describe the electrochemical synthesis of poly(2,5-dicyano-*p*-phenylenevinylene) (DCNPPV) polymer films on indium tin oxide substrates. We investigate the purity, morphology, absorption and emission properties of the film. The purity was checked by infrared spectroscopy. The film formed presented spectroscopic purity equivalent to the chemically prepared PPV that was dialyzed for one week. Scanning electron microscopy of the surface revealed a grain-like morphology. The absorption and emission spectra showed absorption and emission bands at 420 nm and 575 nm, respectively, with the absorption onset at 422 nm, which corresponds to an energy gap of 2.25 eV. The electrochemical determination of the energy gap gives 2.05 eV, thus quite close to the optical energy gap at the onset of absorption. The EA and IP were determined by electrochemical measurements and are 3.46 eV and 5.51 eV, respectively.

Keywords Conducting polymers · Poly(2,5-dicyano-*p*-phenylenevinylene) · Electrochemical synthesis · Poly(*p*-phenylenevinylene)

Introduction

The increasing interest in organic light-emitting diodes has been the driving force for the research and application of PPV-type conducting polymers. Presently, different research groups and private companies are producing light-emitting devices based on PPV-type polymers at a commercial level [1]. However, a lot of improvements are still needed for large-scale application, especially concerning the metal/polymer interface in order to decrease the two charge injection barriers [2]. A better balance between the work functions of the electrodes and the polymer HOMO and LUMO levels is expected to increase the light-emitting efficiency of such devices. Ordinarily, it has been found that electron injection is more difficult than hole injection, compelling the use of low work-function metals for electron injection such as calcium or magnesium, which are unstable under atmospheric conditions [2]. This fact stimulated the search for PPV derivatives presenting larger electron affinity in order to enable the use of metals with higher environmental stability such as aluminum.

In the last decade a series of theoretical studies [3, 4, 5, 6] suggested that the addition of a cyano group to the vinyl or phenyl moieties of the polymer backbone could produce an increase in the energy edges of the quasi-bands due to its electron acceptor nature. However, efforts to synthesize this kind of polymer via the Wessling route have been unsuccessful so far. Usually, as described by Sarker [7], the synthesis of poly(2,5-dicyano-*p*-phenylenevinylene) (DCNPPV) using the Wessling method yields a very low molecular weight cyano polyelectrolyte, presenting particular problems in its conversion to the final PPV form. The cause of this difficulty was attributed to a rather slow tetrahydrothiophene elimination, which does not occur in other PPV derivatives, causing appreciable level of structural defects.

Recently, using a different approach, some cyano-based PPV syntheses have been reported with the cyano group linked to the vinylene moiety [8, 9, 10, 11]. Alternatively, cyano-PPVs with the cyano group linked to the phenylene moiety were obtained in copolymeric structures [12, 13, 14]. Even in these cases, only low molecular weight polymers were obtained. An alternative route, not explored for cyano-PPV derivatives, but which can avoid tetrahydrothiophene elimination, is electrochemical synthesis. Although it is expected that

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insoluble polymers yield low molecular weight oligomers by electrochemical synthesis, it is interesting to explore the overall quality of the polymer films obtained, since the electrochemical synthesis bypasses the high-temperature conversion step of Wessling's route, especially when the polymers are insoluble.

The electrochemical synthesis of PPV-type polymers was first described by Nishihara et al. [15]. Later the method was further developed by Utley et al. [16]. Electrochemical synthesis is particularly appropriate for polymers with labile side groups that cannot survive high temperatures or strong alkaline or acid solutions [17, 18, 19]. However, the soluble polymers obtained by this method showed either low molecular weight or large dispersion of their sizes.

In the present study we describe a suitable electrochemical method for the synthesis of DCNPPV uniform films on indium tin oxide (ITO) transparent electrodes. The morphology, chemical structure and electronic characteristics of the films were characterized by microscopy, spectroscopy and electrochemical measurements.

Experimental

Solvents and electrolyte

Acetonitrile (ACN) (Aldrich, 99.9%) was heated under reflux over phosphorus pentoxide for 24 h before distillation. It was stored, under a dry nitrogen atmosphere, over freshly baked 4 Å molecular sieves. Dichloromethane (Aldrich, 99.9%) was treated as ACN. Tetraethylammonium bromide (TEAB) (Merck, 99%) was baked at 120 °C overnight before use. All other chemicals were commercial grade and used as received.

Equipment

^{1}H NMR FT spectra (200 MHz) were recorded on a Bruker AC-200 spectrometer using deuterated chloroform/TMS (Aldrich) as solvent/reference. FTIR spectra were recorded as a KBr pellet, on a Perkin-Elmer 1750 series grating. For film characterization, IR spectra were obtained on a Bomem MB-102 spectrophotometer with a Spectra Tech 500 reflectance accessory. UV-Vis spectra were obtained by transmission on a Hitachi U-3501 spectrophotometer. Emission spectra were recorded on a Hitachi F-4500 fluorimeter. Scanning electron microscopy (SEM) images were obtained on a LEO 440 microscope. Electrochemical experiments were carried out using a FAC 2001 potentiostat/galvanostat.

Starting material

The starting material for the electropolymerization process, α,α,α′,α′-tetrabromo-2,5-dicyano-p-xylene (DCNPX), was prepared from p-xylene in three steps, as described below.

2,5-Diiodo-p-xylene

This was obtained from p-xylene in 82% yield, following a method described in the literature [25]. Mp 101–102 °C (lit. 102–103 °C [25]). ^{1}H NMR (200 MHz, CDCl$_3$/TMS, δ): 2.40 (s, 6H), 7.64 (s, 2H). FTIR (KBr, cm^{-1}): 2967 and 2939 (v_{C-H}), 1464, 1429 and 1370 ($v_{C=C}$), 1307 (δ_{C-H}), 1037 (γ_{C-H}), 874 (v_{C-I}).

2,5-Dicyano-p-xylene

A mixture of 2,5-diiodo-p-xylene (11.2 mmol), CuCN (26.0 mmol) and N,N-dimethylformamide (DMF, 8 mL) was refluxed for 6 h. After cooling, water was added (20 mL) and the obtained solid was filtered, washed with 3×20 mL of warm aqueous EDTA solution and with 3×20 mL of chloroform. The combined organic filtrate was dried over magnesium sulfate, filtered and the solvent removed by evaporation. After recrystallization from ethanol, 9.63 mmol (86%) of white crystals were obtained. Mp 208–210 °C (lit. 209–210 °C [26]). ^{1}H NMR (200 MHz, CDCl$_3$/TMS, δ): 2.55 (s, 6H), 7.56 (s, 2H). FTIR (KBr, cm^{-1}): 3035 and 2920 (v_{C-H}), 2220 ($v_{C≡N}$), 1492 and 1443 ($v_{C=C}$), 1389 (δ_{C-H}), 905 (γ_{C-H}).

α,α,α′,α′-Tetrabromo-2,5-dicyano-p-xylene

This compound (DCNPX) was obtained from 2,5-dicyano-p-xylene in 36% yield, following a method described in the literature [16] for similar compounds. Mp 219–223 °C (lit. 221 °C [27]). ^{1}H NMR (200 MHz, CDCl$_3$/TMS, δ): 6.84 (s, 2H), 8.30 (s, 2H). FTIR (KBr, cm^{-1}): 3040 and 3005 (v_{C-H}), 2220 ($v_{C≡N}$), 1482 ($v_{C=C}$), 1388 (δ_{C-H}), 903 (γ_{C-H}), 605 (v_{C-Br}).

Film preparation and electrochemical characterization

DCNPPV films were obtained on ITO as the working electrode, polarizing the metallic substrate at −0.2 V in a solution of 0.1 mol L^{-1} of TEAB in ACN with 0.05 mol L^{-1} of DCNPX. A graphite sheet was used as the counter electrode and Ag/AgBr as the reference electrode.

Cyclic voltammetry measurements were performed by the same electrochemical approach using CH$_2$Cl$_2$/LiClO$_4$ as the solvent/electrolyte system. N$_2$ was bubbled through the system, shortly before measurements, in order to remove any dissolved O$_2$.

Results and discussion

The DCNPPV films were obtained from the electrochemical reduction of DCNPX at constant potential on an ITO electrode. To establish the preparative potential, a cyclic voltammogram (CV) was recorded, which shows in the first cycle a cathodic peak centered at −0.2 V vs. Ag/AgBr (see Fig. 1). This result contrasts with the CV obtained for the reduction of α,α,α′,α′-tetrabromo-
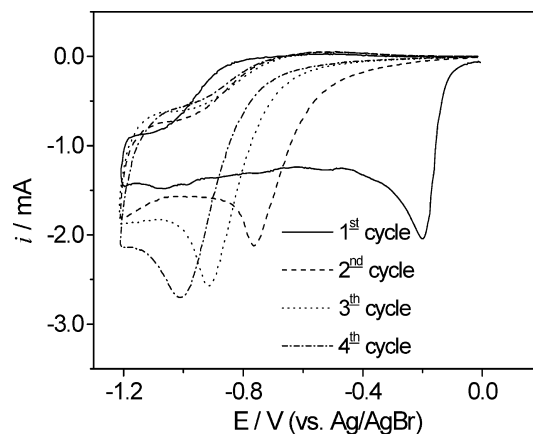

Fig. 1 Cyclic voltammograms of ITO substrate in a solution of 0.1 mol L^{-1} of TEAB in ACN with 0.05 mol L^{-1} of DCNPX

p-xylene [20], where two peaks were observed at −0.80 and −1.30 V. The less negative reduction threshold of DCNPX is related to the strong electron-withdrawing character of the cyano groups that changes dramatically the energy levels of the molecule, facilitating the electrochemical reduction of this polymer precursor (see below). The absence of the oxidation peak in the reverse scan indicates that the solid film formed is stable and it is not oxidized back to the precursor molecule. In subsequent cycles, the reduction peak was strongly shifted to more negative potentials due to the semiconductive nature of the deposited film, which is also responsible for the absence of an oxidation peak of the formed film in the reverse scans. The oxidation of the film takes place only at much more positive potentials (see below).

The IR spectra of the DCNPPV films obtained at −0.25 V is shown in Fig. 2, together with the spectra of unsubstituted PPV obtained by the Wessling route. Clearly the spectra are quite similar. The electrochemically synthesized DCNPPV presents the typical C≡N band at 2232 cm^{-1}. The bands at ca. 3043 and 963 cm^{-1} are assigned to the *trans*-vinylene C–H stretching and deformation, respectively. This band clearly ensures formation of the vinyl groups in the film. In Table 1 we show the band assignments for DCNPPV in comparison
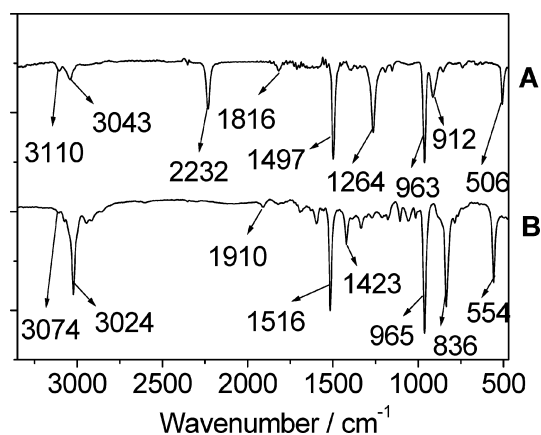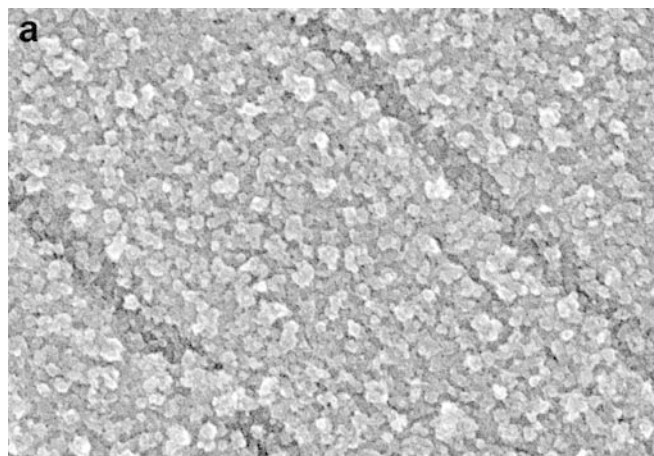
to those observed for PPV. The IR spectrum of the DCNPPV film clearly indicates that its purity is similar to that of PPV, synthesized by the Wessling route, whose soluble precursor was dialyzed for one week before the conversion step carried out by pyrolysis under an oxygen-free environment. The long-term dialysis is required to produce a high-purity precursor for the PPV, free from small oligomers and the low molecular weight byproducts produced during polymerization of the precursor. Therefore the converted PPV is assumed to be of high purity in this case. A previous report on electrochemical synthesis of PPV [20] shows the presence of many other bands due to either incorporation of ions from the solution and over-reduction of the film formed. In the present case, only the bands due to the DCNPPV are visible, indicating formation of a pristine film without incorporation of the supporting electrolyte components. In this sense, we will assume that the film formed is of high purity, according to the purity standards for PPV films. This result shows a clear advantage of the electrochemical synthesis over the Wessling route, since the former is a one-step procedure to generate the active film on the transparent substrate (ITO). IR and UV-Vis intensities in the spectra, recorded during the polymerization process, show that after 10 min at −0.25 V the polymer growth almost stops, probably due to the semiconductive nature of the film which precludes further growth after a certain thickness owing to the increased ohmic drop across the film. Typical thickness of the film obtained was 4.0 μm (the thickness was measured from a lateral view of SEM image as shown in Fig. 3b).
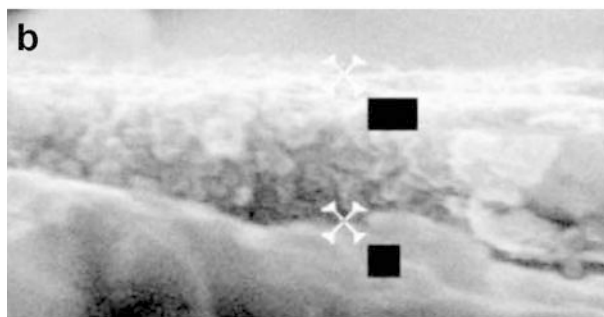
SEM images (Fig. 3) showed the film to be uniform with a grain-like structure at the surface, suggesting that its follows a nucleation and growth mechanism. In fact the current transient at constant potential shows a typical pattern for this kind of mechanism [21]. Further information obtained from the lateral view of the SEM image (see Fig. 3b) is that the film surface is relatively smooth, although the morphology shows a granular film very clearly.

The absorption and emission spectra of a DCNPPV film, obtained at −0.25 V, are depicted in Fig. 4. These spectra are red shifted compared to unsubstituted PPV. Previous molecular modeling calculations [3, 4, 5, 6] suggest that the CN group attached to the polymeric backbone causes a stabilization of both the valence and conduction band edges, the latter being more stabilized. As a result, the energy gap (E_g) of DCNPPV is 2.20 eV, which is 0.23 eV lower than the one for PPV. The emission spectrum shows a relatively sharp, but poorly defined, pattern with a tail on the low-energy side, probably related to a distribution of different conjugation lengths along the chains [22].

The CV of conjugated polymers in an appropriate electrolyte has been frequently used to estimate both the ionization potential and the electron affinity. The method was introduced by Brédas et al. early in 1983 [23] and consists in recording the threshold reduction

Fig. 2 Infrared spectra of DCNPPV synthesized electrochemically on an ITO substrate (**A**) and of unsubstituted PPV synthesized via the Wessling route (**B**)

Table 1 Main IR bands observed for DCNPPV and literature values for PPV solid films

DCNPPV band (cm^{-1})	Data for PPV from the literature (cm^{-1}) [20, 21]	Assignment[a]
912	837	$\delta_{C-H \text{ arom}}$ o-o-p
963	965	$\delta_{C-H trans\text{-vinylene}}$ o-o-p
1497	1519	$\nu_{C=C \text{ arom}}$
2232	–	$\nu_{C\equiv N}$
3043	3024	$\nu_{C-H trans\text{-vinylene}}$
3110	3074	$\nu_{C-H \text{ arom}}$

[a] o-o-p = out-of-plane

Fig. 3 (**a**) SEM image of the surface of the DCNPPV electrochemically synthesized on an ITO substrate. (**b**) SEM image of the lateral view of the DCNPPV film deposited onto an ITO electrode. The *lower part* of this figure indicates the roughness of the ITO substrate. The thickness of the film is indicated by the *two crosses*

Fig. 4 UV-Vis and fluorescence spectra of a DCNPPV film electrochemically synthesized on an ITO substrate
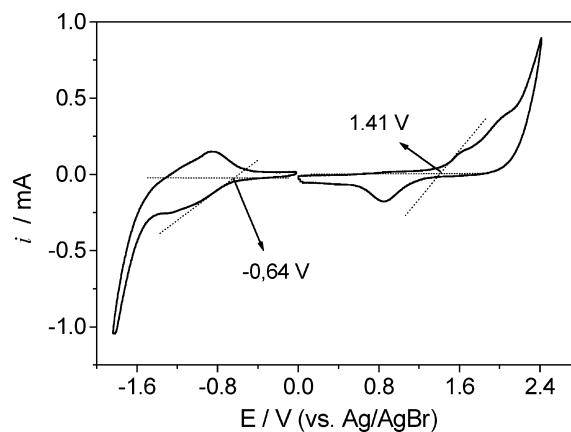
Fig. 5 Cyclic voltammetry of DCNPPV films electrochemically synthesized on ITO substrates

and oxidation potentials of the polymer. The former is associated with the electron affinity and the latter with the ionization potential. Obviously, upon charge transfer, the polymer must keep its chemical nature for the method to be valid. Relaxation effects are expected to be minimized, since only the threshold is considered.

The CV of DCNPPV is shown in Fig. 5, which was recorded in two steps employing two polymer samples: one for reduction and the other one for oxidation. At negative potentials a reduction/oxidation wave is observed at −1.26/−0.86 V, respectively. At the oxidation portion, a more complex process can be visualized. There are two oxidation waves, and one reduction peak. The cathodic peak at 0.85 V corresponds to the reduction of the oxidized polymer into its pristine form. It should be mentioned that on changing the scan rate (between 2 and 10 mV/s) the peaks are slightly affected, but not the threshold potential; therefore, we believe that up to the threshold potential the process occurs under equilibrium conditions and can be used as a good estimation of the IP and EA.

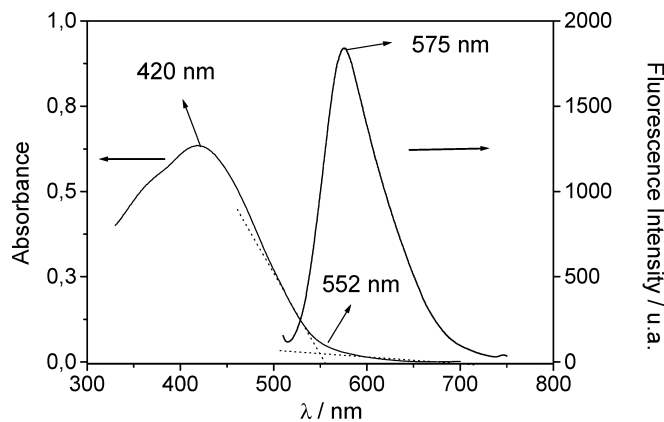The thresholds for the reduction and oxidation were taken as −0.64 and +1.41 V, respectively. The reference

electrode potential[1] in the vacuum scale is 4.1 V [24]. Thus, the estimated values for the EA and IP are 5.51 and 3.46 eV, respectively. These values are in good agreement with the predicted ones [5], which are 5.21 and 3.17 eV. The difference between IP and EA is 2.05 eV, which is in good agreement with the threshold of the optical absorption, shown in Fig. 4, which is 2.25 eV, and the theoretically predicted E_g of 2.04 eV [4]. The relatively good agreement between the E_g values obtained from the electrochemical measurements and the optical absorption spectrum is an indication that the former method can be used to estimate the electronic properties of the polymer film. The main uncertainty for the EA and IP associated with the method is the determination of the reference electrode potential in the vacuum scale.

The estimated IP and EA confirm the prediction that the cyano groups bonded to the polymer backbone

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[1]The potential of the quasi reference Ag/AgBr electrode immersed in the solution was measured against a saturated calomel electrode in the same solution and the value referred to the calomel electrode was then calculated in the vacuum scale

stabilize the conduction band and valence band edges of the film and that the former is more stabilized, thus suggesting that this material may be very interesting for device construction, since the barrier for electron injection is strongly decreased with respect to unsubstituted PPV.

Conclusions

Careful electrochemical synthesis can be used to obtain pure DCNPPV films (typical thickness of 4 μm) on ITO electrodes. The film obtained is at least an oligomer of DCNPPV, as shown by the IR *trans*-vinylene signatures at ca. 3043 and 963 cm^{-1}.

The low absorption energy suggests that the oligomers are at least as large as the conjugation length. There is an overall good agreement between the calculated IP, EA and E_g for DCNPPV and the experimental data obtained in this work using electrochemical estimation of these parameters. The cyano groups attached to the phenyl units stabilize both the conduction and valence band edges in comparison with unsubstituted PPV.

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