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Influence of the acidity level on the electropolymerization of *N*-vinylcarbazole: Electrochemical study and characterization of poly(3,6-*N*-vinylcarbazole)

Juan Manuel Reyna-González [a], Martha Aguilar-Martínez [a], José Antonio Bautista-Martínez [a],
Ernesto Rivera [b], Ignacio González [c], Pedro Roquero [a,*]

[a] *Facultad de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, 04510 D.F. México, Mexico*
[b] *Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Ciudad Universitaria, 04510 D.F. México, Mexico*
[c] *Departamento de Química, Área de Electroquímica, Universidad Autónoma Metropolitana – Iztapalapa,*
Apartado Postal 55-534, 09340 D.F. México, Mexico

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Abstract

Poly(3,6-*N*-vinylcarbazole) films were prepared by electrochemical oxidation of *N*-vinylcarbazole on a Pt electrode using acetonitrile as solvent and tetraethylammonium tetrafluoroborate as electrolyte. The electrosynthesis was carried out by electrical potential cycling in the presence of two different bases: tetraethylammonium benzoate (Bz^-) and tetraethylammonium phthalate (Ph^-). These salts were expected to modify the acidity level of the electrolyte since they can act as scavengers for the protons released during the polymerization, when the reaction takes place in the carbazole unit.

Products were characterized by cyclic voltammetry, scanning electron microscopy, FTIR spectroscopy, thermogravimetric analysis, differential scanning calorimetry, absorption spectroscopy and four-probe electrical conductivity measurements. Both bases influenced significantly the chemical structure and morphology of the deposited materials. The presence of Ph^- in the electrolyte decreases the cross-linking of the electrodeposited polymer, leading to a poly(3,6-*N*-vinylcarbazole) bearing a more uniform morphology, higher thermal stability and electrical conductivity compared to those of the polymers obtained in the presence of Bz^- and without acidity control.

Keywords: Electrochemical polymerization; Poly(3,6-*N*-vinylcarbazole); Acidity level

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1. Introduction

Poly(*N*-vinylcarbazole) (PVK) has been intensively studied due to its huge variety of possible applications in sensors [1], secondary batteries [2,3], electrochromic [4] and electroluminescent devices [5–17]. Electrolysis of *N*-vinylcarbazole (NVK) in acetonitrile, on a platinum electrode, generates a deposit of an electro-conducting polymer on the anode surface and the precipitation of a photo-conducting polymer in the bulk of the solution. The former is a dark green cross-linked polymer obtained mainly by polymerization through the carbazole units and the latter is a white, comb-like polymer in which the polymerization takes place through the vinyl group [18–21].

The electrochemical polymerization of NVK proceeds through an ECE mechanism [22–25], as shown in Scheme 1, which starts with the oxidation of the monomer to the corresponding cation-radical (**1** → **2**) followed by a fast dimerization at position 3 of the carbazole unit (**2** → **3**). The two-electron oxidation **3** → **4**, which occurs at less positive potential than that required for the oxidation of the monomer, leads to the formation of a dimer bond between the carbazole units (**4**). When dimerization occurs, H^+ ions split-off and provoke the polymerization of NVK through its vinyl group. The

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* Corresponding author. Tel.: +52 55 5622 5363; fax: +52 55 5550 1572.
E-mail address: roquero@servidor.unam.mx (P. Roquero).

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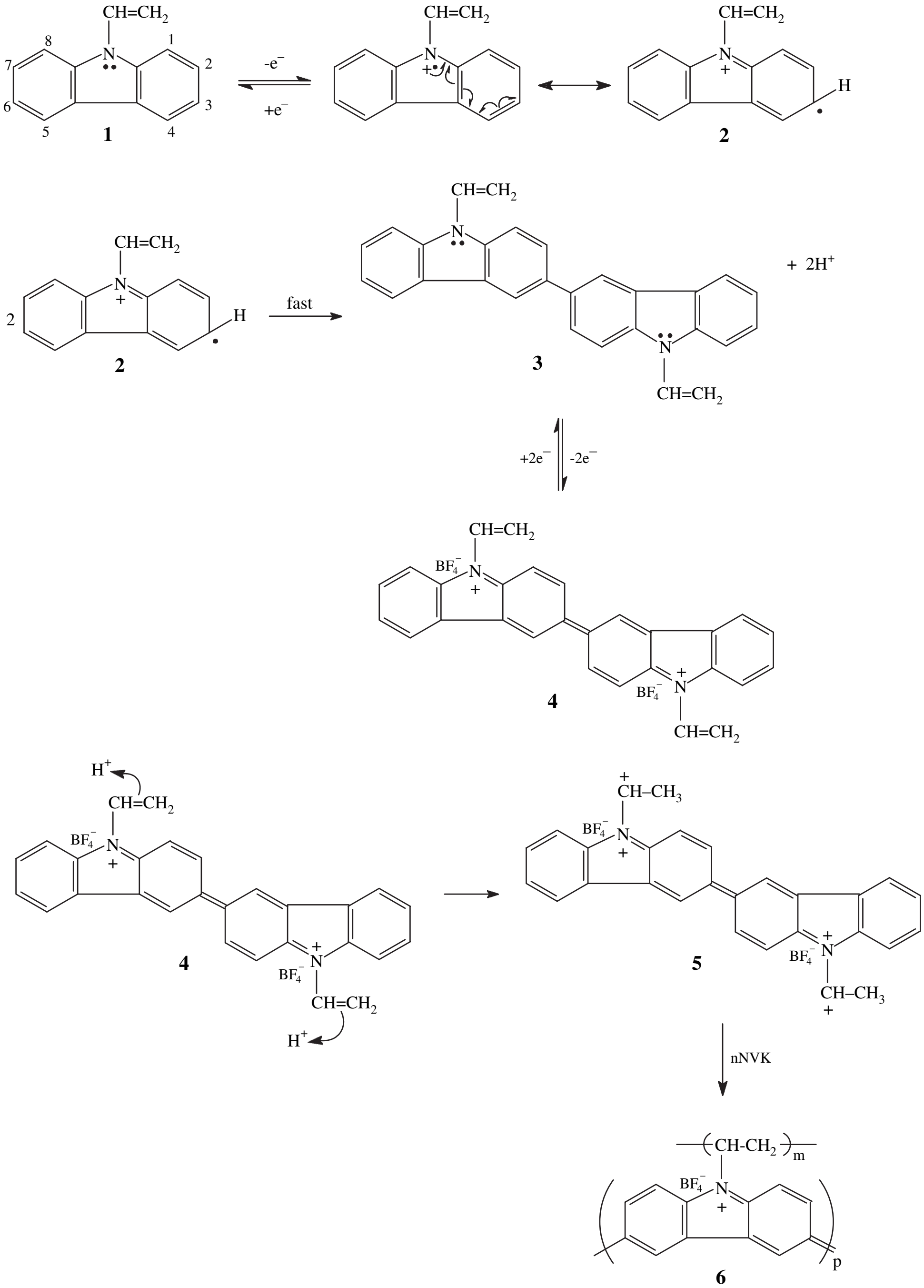
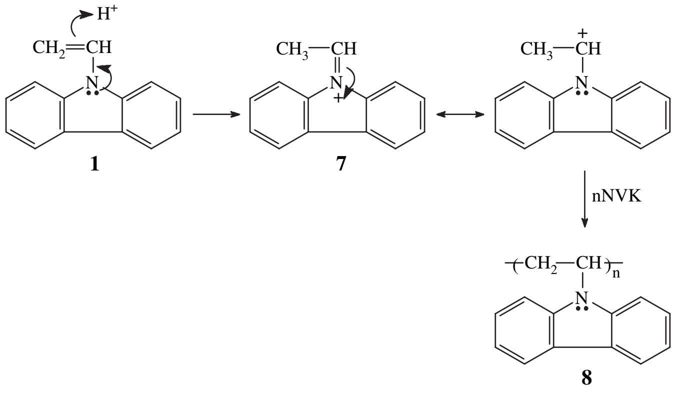


Scheme 1. Polymerization reactions in the synthesis of poly(3,6-*N*-vinylcarbazole). BF_4^- is the doping anion.

attack of these protons (H^+) on the vinyl group of the growing electro-conducting polymer (**4** → **5**) causes cross-linking (**5** → **6**), whereas the activation of the vinyl group of the monomer in solution leads to the formation of the photoconducting polymer (structure **8**, Scheme 2) [22–25]. The deposit formed on the anode surface, poly(3,6-*N*-vinylcarbazole) named here as P3,6NVK, can exhibit different cross-linking degrees (*m* in structure **6**, Scheme 1) depending on the synthesis conditions.

Previous works have reported the influence of the anode substrate [26], electro-deposition conditions [27], deposition potential [28], type of supporting electrolyte [29–34] and amount of water in the solvent [35–37] on the electrochemical polymerization of *N*-vinylcarbazole. However, the influence of the acidity level on the electrolyte has been scarcely considered.

The above-mentioned conditions implicate that NVK polymerization may depend in a big measure on the acid–base properties of the electrolytic media. Although control of the acidity level of the electrolytic media has not been widely studied in the polymerization processes, in non-aqueous media it has been employed in the control of the electro-reduction of



Scheme 2. Polymerization of *N*-vinylcarbazole through the vinyl group.

some organic compounds [38], where it has been possible to control the proton availability involved in the electron transfer reactions. Therefore, in this study, it was considered the possibility to use this strategy to control the polymerization pathways of this monomer in order to synthesize P3,6NVK selectively.

The main goal of the present work is to investigate the effect of two different basic additives on the anodic polymerization of *N*-vinylcarbazole in order to avoid, as far as possible, the acid-catalyzed polymerization through the vinyl group (**4** → **5**, Scheme 1) and to obtain P3,6NVK (structure **6**, Scheme 1), with a polymerization degree ratio m/p lower than that of the polymer obtained with no additive, where p is the polymerization degree through the carbazole units. Tetraethylammonium benzoate ($pK_a = 20.7$ in acetonitrile) and tetraethylammonium monohydrogen phthalate ($pK_{a1} = 14.3$ in acetonitrile) were used as scavengers for the protons released during the polymerization reaction through the carbazole units.

2. Experimental part

2.1. Cell, electrodes and apparatus

All experiments were carried out in a three-electrode undivided cell, using acetonitrile (ACN) as solvent, tetraethylammonium tetrafluoroborate (Et_4NBF_4) as supporting electrolyte and a Ag–AgCl as reference electrode, which was immersed in dry acetonitrile for 20 min before each experiment. All potentials in this work are referred to the ferrocinium/ferrocene (Fc^+/Fc) redox system. Platinum was used as working and auxiliary electrode in disc, wire and foil shape. In cyclic voltammetry experiments the working electrode was a platinum disc with a surface area of $0.0314\ cm^2$ and the auxiliary electrode was a platinum wire. For the synthesis of the polymer in an amount enough to enable polymer characterization, a Pt foil of $2\ cm^2$ surface area was used as working electrode as well as a $4\ cm^2$ foil was used as an auxiliary electrode. An Autolab PGSTAT100 potentiostat was employed for cyclic voltammetry and a PAR 173 potentiostat/galvanostat for exhaustive electrolysis.

All polymers obtained were prepared in the same way and further characterized. Polymer samples were washed with pure acetonitrile in order to remove the unreacted monomer and then dried at room temperature. Scanning electron microscopy (SEM) images were obtained in a JEOL 5290 SEMLV microscope. FTIR spectra of the polymers were obtained in KBr pressed pellet using a Nicolet 510 spectrometer with a Michelson Interferometer with a $2\ cm^{-1}$ resolution.

Thermal properties of the polymers were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). T_{10} (10% weight loss temperature), T_g (glass transition temperature), and T_m (melting point) were determined. TGA was conducted on a Hi-Res TGA 2950 instrument (from 20 to 800 °C) and DSC was carried out on a DSC 2910 TA instrument (from 20 to 300 °C), in both cases with a heating rate of 10 °C/min.

Absorption spectra of the polymers in pressed pellet (KBr) were recorded on a Varian Cary 1 Bio UV/vis spectrophotometer model 8452A. Electrical conductivity of the polymers was measured in pressed pellet at 100 °C, using a Dielectric Analyzer DEA 2970 following the four-probe method.

2.2. Chemicals

Phthalic acid, benzoic acid, tetraethylammonium hydroxide, and *N*-vinylcarbazole (NVK) were purchased from Aldrich and used as received. Tetraethylammonium tetrafluoroborate (Et_4NBF_4) was crystallized from a methanol–hexane solution and dried under vacuum for 72 h at 70 °C. Acetonitrile (ACN) was distilled over phosphorus pentoxide (P_2O_5) in order to remove traces of water.

Tetraethylammonium benzoate (Et_4NBz) and phthalate (Et_4NPh) were synthesized by the reaction of tetraethylammonium hydroxide (TEAOH) with the corresponding carboxylic acid at 40 °C at a reduced pressure of 9 mmHg [38].

2.3. Procedure

Electrolytic solutions were prepared with 0.1 M Et_4NBF_4 in the following concentration ranges: 0.001–0.02 M NVK; 0.0005–0.05 M Et_4NBz or Et_4NPh. A 15 mL electrochemical cell was placed inside a Faraday cage and the electrolyte was purged with nitrogen for 40 min, prior to each experiment. Potential sweeps were performed from low to high potentials, up to a potential (E_λ) in which the direction of the scan was inversed. In all the experiments reported here, the potential scan rate was $50\ mV\ s^{-1}$. To prepare samples to be used for the whole characterization, potential sweeps were stopped at E_λ.

3. Results and discussion

3.1. Electropolymerization without acidity control

Fig. 1A shows the voltammograms corresponding to P3,6NVK synthesized in the presence of 0.1 M Et_4NBF_4 by the successive application of 35 potential cycles. When the potential scan is switched at $E_\lambda = 0.923$ V, current increases with

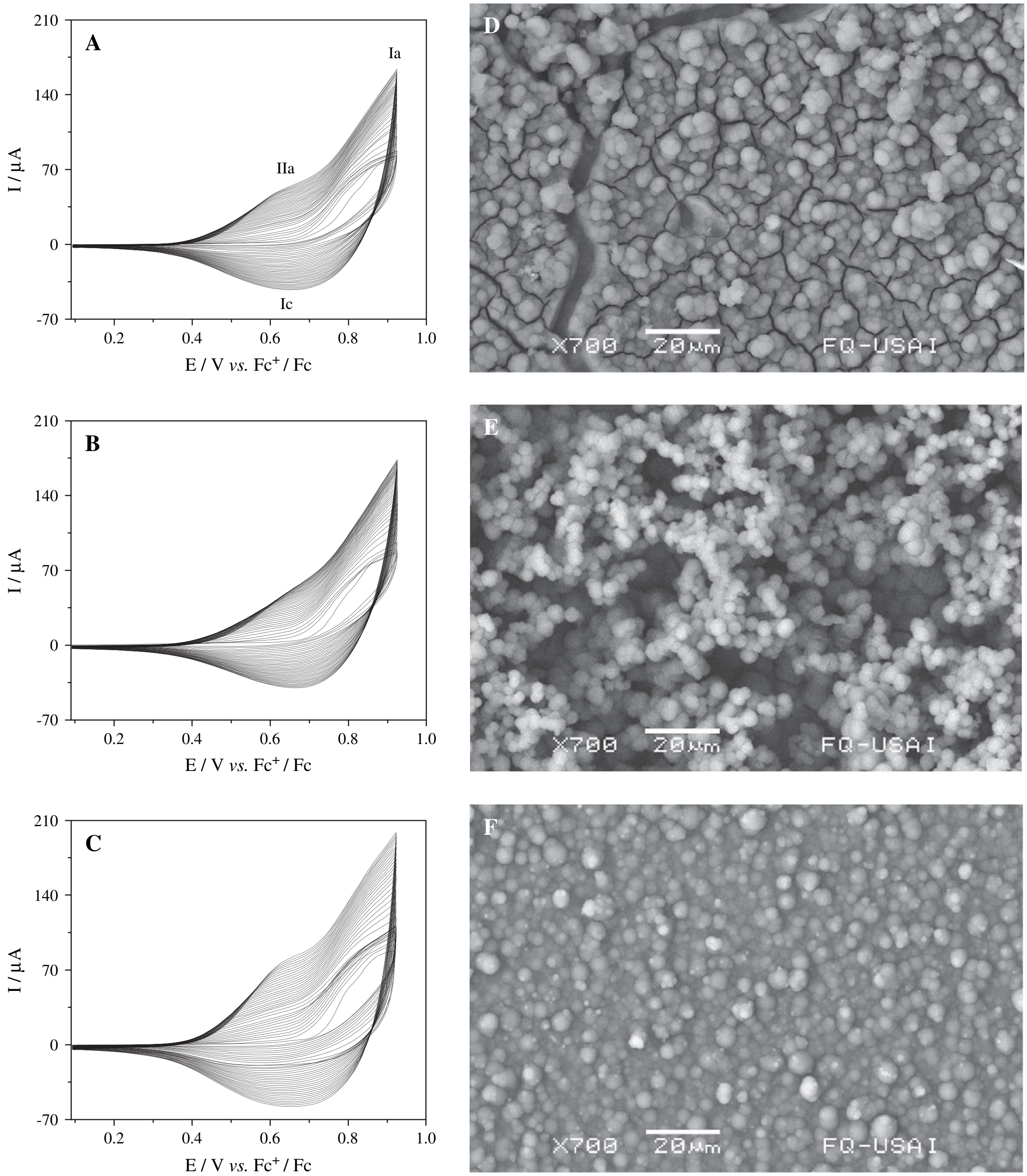


Fig. 1. Cyclic voltammograms (A–C) and SEM images (D–F) obtained from 5 mM NVK in 0.1 M Et_4NBF_4/acetonitrile, $E_\lambda = 0.923$ V. The potential was successively scanned during 35 cycles: (A, D) without acidity control, (B, E) 0.5 mM Et_4NBz, and (C, F) 0.5 mM Et_4NPh.

each cycle due to the growth of the P3,6NVK chain. During this process two peaks Ic and IIa appear at 0.718 V and 0.728 V; which correspond to the reduction and oxidation of the formed polymer, respectively. This polymer was doped by the incorporation of the supporting electrolyte anions into its framework.

3.2. Electro-polymerization with acidity control

As it has been already mentioned, the electrochemical electropolymerization of NVK releases protons in the medium, which favor the polymerization through the vinyl group besides the polymerization through the aromatic rings, leading to the formation of cross-linked polymers. In order to carry out a selective polymerization through the aromatic rings of NVK, avoiding the possibility of polymerization through the vinyl group, two different basic additives, Et_4NBz and Et_4NPh, were added to the electrolytic medium. This was done in separate experiments to control the presence of $H^+(CH_3CN)_n$ ions (protons solvated by acetonitrile) in the electrode–solution interface. Due to the fact that Et_4NBz and Et_4NPh are strong electrolytes in acetonitrile, in this work these species will be identified as the corresponding benzoate (Bz^-) and monohydrogen phthalate (Ph^-) ions. Cyclic voltammetries of Et_4NBz and Et_4NPh in 0.1 M Et_4NBF_4/acetonitrile show that Bz^- and Ph^- are not electroactive in the potential range where NVK polymerization occurs.

Voltammograms of the electropolymerization of NVK carried out in the presence of the basic additives, Bz^- and Ph^-, are shown in Fig. 1B and C, respectively. Cathodic and anodic currents are higher in the electrolytic medium containing Ph^- (Fig. 1C), than those measured in other media (Fig. 1A and B).

Fig. 2 shows the variation of the accumulated electrical charge and charge per cycle during the voltammetric electropolymerization using different acidity levels. The accumulated charge curves (Fig. 2A) reveal that the presence of the basic additives (Fig. 2A, ii and iii) provokes higher charges than in the case of electrolysis without base (Fig. 2A, i). In the first 18 cycles, the accumulated charge (Fig. 2A, ii and iii) observed in the presence of any basic additive is practically equal. In cycle 20 and further cycles, the charges obtained with Ph^- (Fig. 2A, iii) are higher than in the other two cases.

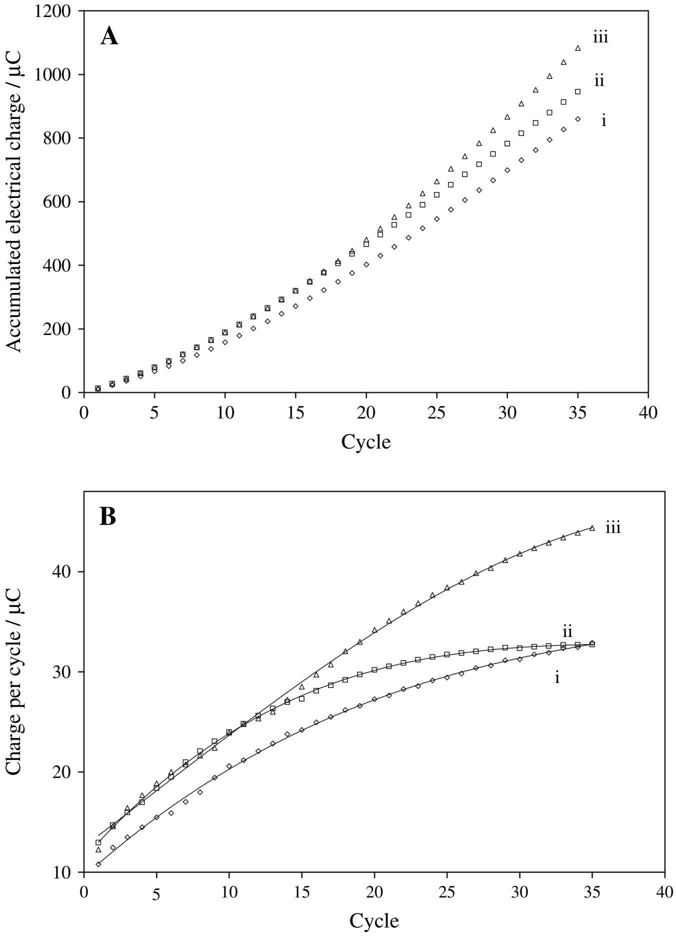


Fig. 2. Variation of (A) the accumulated electrical charge and (B) charge per cycle during the voltammetric electropolymerization of 5 mM NVK in 0.1 M Et_4NBF_4/acetonitrile under different conditions of acidity level: (i) without acidity control, (ii) 0.5 mM Et_4NBz, and (iii) 0.5 mM Et_4NPh. Evaluated from Fig. 1A−C.

The charge per cycle curves (Fig. 2B) show important details about the polymerization evolution. In the absence of basic additives and in the presence of Bz^-, the charge per cycle grows asymptotically (until 32 μC, Fig. 2B, i and ii), and the presence of Ph^- provokes the continuous increase of the charge per cycle (Fig. 2B, iii). Fig. 2 suggests that in the first polymerization steps, Bz^- and Ph^- can improve the polymerization of NVK by trapping the protons released during the step **2** → **3** (Scheme 1). The Ph^- and Bz^- ions act as proton scavengers, decreasing the polymerization through the vinyl group, enabling a more efficient incorporation of the doping anion and favoring the growth of the conjugated polymer. Nevertheless, the influence of Bz^- is only effective until the 13th cycle. When Ph^- is used as base, once the first polymer layers are formed, Ph^- acts as an effective proton scavenger, leading to increased currents with successive cycling, whereas the Bz^- base seems to promote the polymerization through the vinyl group. This dissimilarity in the behavior of Bz^- and Ph^- could be due to their different acid−base properties or due to the hygroscopic behavior of Et_4NBz. There could be a smaller amount of Bz^- in the solution because of the presence of traces of HBz in the added salt. This fact may explain the behavior of the curve shown in Fig. 2B, ii since probably there is no more free Bz^- to control the acidity level after the 13th cycle.

It is worth to point out that the monomer/basic additive concentration ratio, $C_{\mathrm{mon}}/C_{\mathrm{base}}$, also determines the polymer formation. When the $C_{\mathrm{mon}}/C_{\mathrm{base}}$ ratio was equal or lower than 1 the electropolymerization failed. In these cases, the current decreased with successive cycling, indicating that the electrode became passivated (not shown). This is due to the fact that at higher concentrations, basic additives may also behave as nucleophilic agents, trapping the radical-cations formed during the oxidation of NVK, thereby inhibiting the polymer formation. When the monomer concentration is at least two times that of the basic additive the P3,6NVK was obtained. In this work, $C_{\mathrm{mon}}/C_{\mathrm{base}}$ ratios of 10 and 20 were used. The obtained polymer films were rinsed with CH_3CN and further characterized by cyclic voltammetry and *ex situ* spectroscopic techniques.

3.3. Cyclic voltammetry

Cyclic voltammetry characterization of the obtained polymers was performed in acetonitrile solutions containing only supporting electrolyte. Potential scans were performed up to $E_\lambda = 0.688$ V. Fig. 3 shows the typical voltammograms obtained for the different polymers. In all cases, a shoulder at 0.598 V is observed. The highest current corresponds to the polymer synthesized in the presence of Ph^- (Fig. 3C), and the current begins to increase at lower potentials than in the other films. The lowest current is attributed to the polymer obtained without basic additive (Fig. 3A). This indicates that the polymer obtained in the presence of Ph^- exhibits the highest electrical conductivity. All the films show a current density decrease with the successive scans (not shown) until a typical reproducible voltammetric behavior is established, which is in

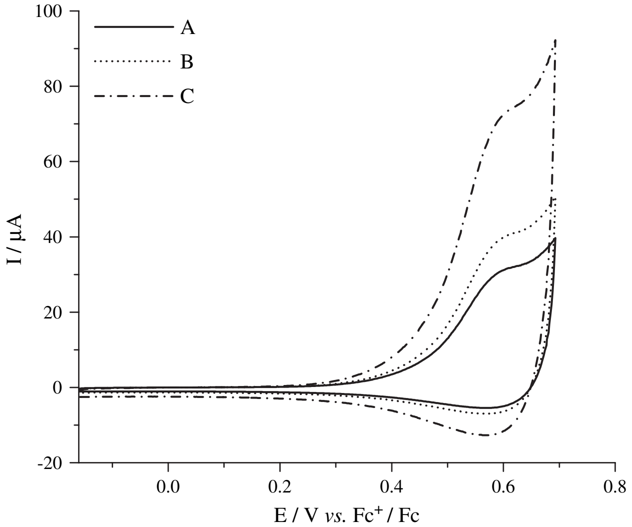


Fig. 3. Cyclic voltammetry characterization of the polymers previously obtained from 20 mM NVK in 0.1 M Et_4NBF_4/acetonitrile under different acidity level conditions and after being washed with acetonitrile (A) without acidity control, (B) 1 mM Et_4NBz, and (C) 1 mM Et_4NPh.

agreement with similar results previously reported in the literature [27,28]. In this work, the currents are reproducible after five scans.

3.4. Scanning electron microscopy

SEM images of the polymers, presented in Fig. 1D–F, show that the morphology of P3,6NVK films depends strongly on the electrolyte composition. The presence of Bz^- or Ph^- induces important differences in the polymer morphology (Fig. 1E and F), with respect to the polymer formed in absence of basic additives (Fig. 1D). The film obtained in the presence of Bz^- (Fig. 1E) is more porous than that obtained in the absence of basic additives. In the cavities of the P3,6NVK (Fig. 1E) a layer of a very compact film can be observed, where a globular structure grows. These globular aggregates are characteristic of the propagation reaction through the vinyl group [39]. These two polymerization stages are in agreement with the charge per cycle curve results (Fig. 2B, ii). The polymer obtained in the presence of Ph^- (Fig. 1F) shows a more regular morphology than the polymer obtained without basic additives (Fig. 1D).

3.5. FTIR spectroscopy

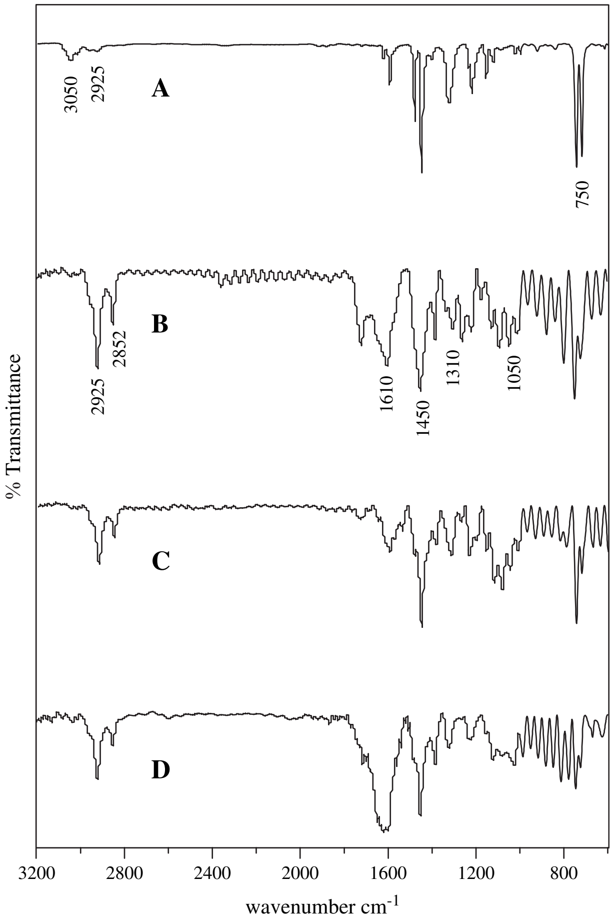


Fig. 4. FTIR spectra of (A) PVK; and P3,6NVK previously electropolymerized from 20 mM NVK in 0.1 M Et_4NBF_4/acetonitrile under different acidity level conditions and after being washed with acetonitrile (B) without acidity control, (C) 1 mM Et_4NBz, and (D) 1 mM Et_4NPh.

FTIR spectra of the electrosynthesized polymers were recorded in pressed pellet (KBr). Fig. 4 shows the FTIR spectra of typical PVK precipitated in the bulk of the solution and P3,6NVK polymers obtained under different acidity level conditions. For typical PVK (Fig. 4A), a band at 3050 cm^{-1}, ascribed to the =C–H stretching vibrations of the aromatic ring followed by a second band at 2925 cm^{-1} due to the aliphatic –C–H, was observed [40,41]. In addition, a series of bands at 1610 and 1450 cm^{-1} attributed to the C=C bond (stretching) of the carbazyl ring, at 1310 cm^{-1} due to C–N bonds [42,43], and at 750 cm^{-1} (out-of-plane) due to the H–C= bonds present in the carbazole unit [20] were also observed. The absence of vinyl bands at 860 and 960 cm^{-1} confirms that the polymerization takes place selectively through the vinyl groups. By contrast, these bands can be seen in the FTIR spectra of the P3,6NVK series (Fig. 4B–D). Therefore, in these polymers some vinyl groups remained intact.

On the other hand, in the FTIR spectra of P3,6NVK (Fig. 4B–D), the decrease in intensity of the band at 3050 cm^{-1}, the new bands at 800 and 880 cm^{-1} due to 1,2,4-substituted benzene rings [42,43] as well as the band at 1050 cm^{-1} related to the incorporation of BF_4^- counterions [44] prove that in these polymers the polymerization takes place mainly through the carbazole units. The bands at 2925 and 2852 cm^{-1} due to the aliphatic –C–H bonds [40,41] indicate that some side polymerization through the vinyl group in P3,6NVK polymers can also occur. The different ratios of intensities (B1/B2) of the 750 cm^{-1} band (B1) with respect to the bands at 2925 and 2852 cm^{-1} (B2) suggest that the extent of polymerization through the carbazole units varies significantly depending on the base.

From the FTIR spectra (Fig. 4B–D), the intensity ratios (B1/B2) for the P3,6NVK obtained with no base, Bz^- and Ph^- are 1.3, 1.7 and 1.1, respectively. As we can see, the B1/B2 value is the lowest for the polymer obtained with Ph^- (1.1, Fig. 4D), compared to those obtained without acidity control and with Bz^- (Fig. 4B and C). These spectroscopic features suggest that the cross-linking degree in P3,6NVK is lower in the presence of Ph^- than in the presence of Bz^- or absence of base. In addition, when Bz^- is used, the extent of polymerization through the vinyl group is the highest. From these results, we can affirm that Ph^- could be considered as an efficient proton scavenger in this reacting system capable of decreasing considerably the polymerization through the vinyl group (pathway showed in Scheme 1).

3.6. Thermal properties

Thermal properties of the electro-conducting polymers were determined by TGA from 20 to 800 °C (Fig. 5) and DSC from 20 to 300 °C. Fig. 5A shows that the poly(3,6-*N*-vinylcarbazole) obtained without acidity control exhibits a T_{10} (10% weight loss temperature) value of about 260 °C. This polymer showed fast degradation, reaching a 50% weight loss at 425 °C and almost total degradation at 500 °C. By contrast, P3,6NVK obtained in the presence of Bz^- (Fig. 5B) exhibited a T_{10} value of 361 °C. This polymer degraded in two steps showing fast degradation between 320 and 470 °C and beyond 600 °C reaching total degradation at 751 °C. Finally, P3,6NVK obtained in the presence of Ph^- (Fig. 5C) showed higher thermal stability than their homologues. This polymer possesses a T_{10} value of 408 °C and showed a first degradation step around 210 °C reaching a 7% weight loss. Furthermore, a second degradation step was observed beyond 570 °C and 18% of the sample remains at 800 °C.

According to these results, the strongly higher thermal stability of P3,6NVK obtained in the presence of Ph^- is due to linear polymer backbone. It seems that this polymer possesses a higher molecular weight as well as an extended conjugation length. P3,6NVK FTIR spectra (Fig. 4D) of this polymer confirmed that the polymerization takes place mainly through the carbazole rings of the monomer.

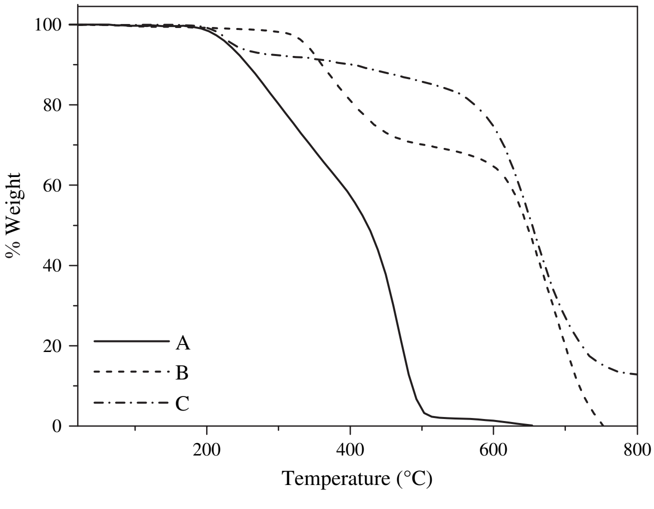


Fig. 5. TGA curves of obtained P3,6NVK (A) without acidity control, (B) with 1 mM Et_4NBz, and (C) with 1 mM Et_4NPh. Heating rate is 20 °C/min.

On the other hand, the fact that the P3,6NVK obtained in the presence of Bz^- exhibited lower thermal stability than that obtained with Ph^-, but higher than that obtained in the absence of base can be explained in terms of the structure. According to the FTIR spectrum of P3,6NVK obtained in the presence of Bz^- (Fig. 4C), this polymer showed a high cross-linking degree, which confers thermal stability to the molecule. This cross-linking changes significantly the morphology of the polymer, which can be observed by SEM. This polymer presents cavities in its structure, which has not been observed in the case of P3,6NVK obtained with Ph^- and that obtained with no base.

DSC of the different obtained polymers (Fig. 6) showed that these materials showed no glass transition temperature in the range between 20 and 300 °C. However, the DSC curves of P3,6NVK obtained with no base (Fig. 6A), Bz^- (Fig. 6B) and Ph^- (Fig. 6C) exhibit endotherms at 103, 104 and 90 °C, respectively, which reveal the presence of a softening point for these polymers. This indicates that the obtained P3,6NVKs partially melt due to the presence of crystalline domains. P3,6NVK obtained in the presence of Ph^- exhibits a lower softening point than its homologues. We believe that this polymer is the most crystalline and linear and possesses the most ordered structure, since the polymerization takes place in more extent through the carbazole units. These results fit well with those obtained from FTIR spectroscopy, SEM and TGA. On the other hand, for P3,6NVK obtained with Bz^- (Fig. 6B) and P3,6NVK obtained with Ph^- (Fig. 6C), we can observe a drastic exothermic behavior beyond 250 °C, due to the degradation of the polymer during heating.

3.7. Optical properties and electrical conductivity

Because of the poor solubility of the polymers, their absorption spectra were recorded in pressed pellet (KBr). All the absorption spectra exhibit a broad absorption band between 200 and 400 nm, followed by an absorption tail, which indicates how extended the conjugation length in the polymer is. The absorption spectrum of P3,6NVK obtained in the presence of Ph^- (Fig. 7) shows the broad absorption band in the range mentioned above, showing discrete peaks at 234, 254, 275, 296, 338 and 383 nm, which can be attributed to the carbazole unit. These bands barely correspond to those reported for carbazole ($\lambda = 250$, 263, 295, 330 and 343 nm in $CHCl_3$ solution). The absorption spectrum of this polymer shows also a long tail with a shoulder at 700 nm, which indicates that the polymer is highly conjugated. The polymers obtained in the presence of Bz^- or in the absence of base, exhibit similar absorption bands but with shorter absorption tails, thus showing a minor conjugation length.

On the other hand, conductivity (σ) of the polymers in the non-doped state was measured in pressed pellet at 100 °C giving values of $\sigma = 2.1 \times 10^{-9}$, 7.3×10^{-8} and 1.6×10^{-7} S cm^{-1} for P3,6NVK obtained with no base, Bz^- and

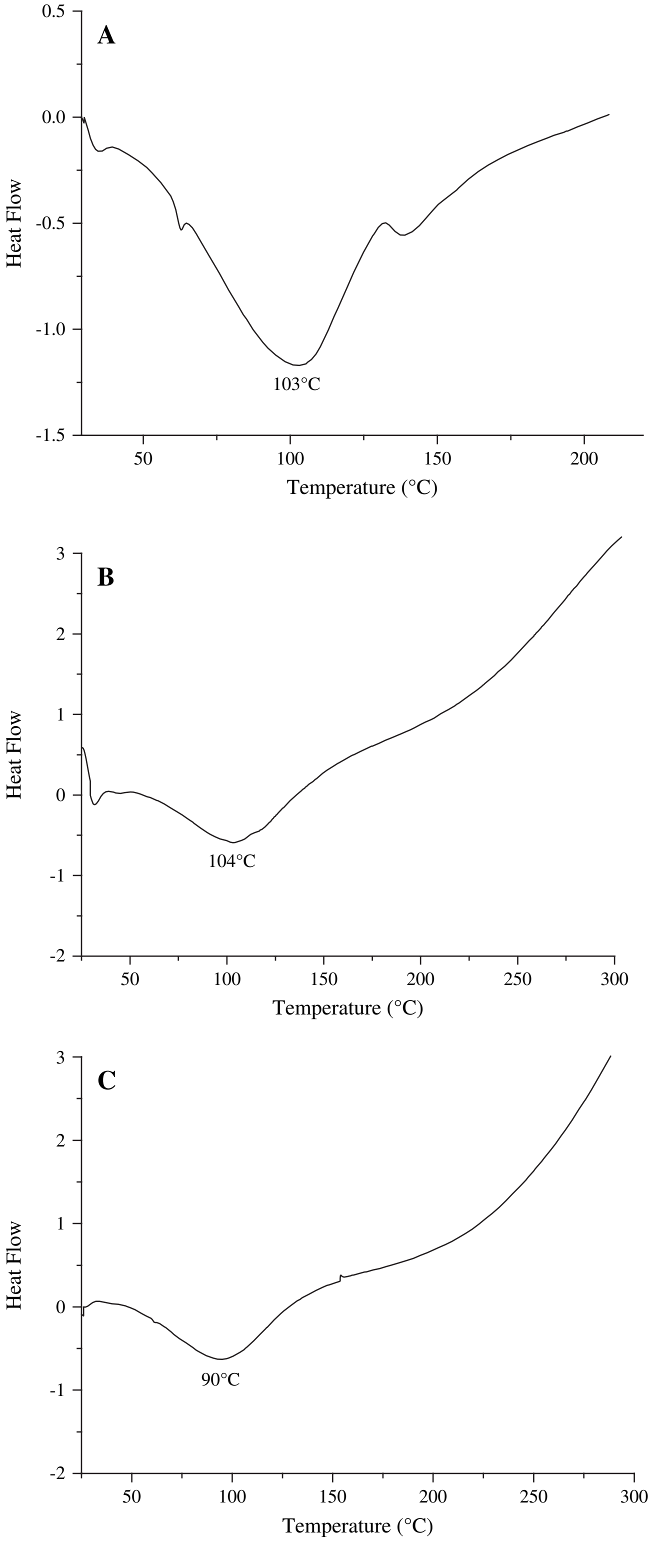


Fig. 6. DSC curves of obtained P3,6NVK (A) without acidity control, (B) with 1 mM Et_4NBz, and (C) with 1 mM Et_4NPh. Heating rate is 20 °C/min.

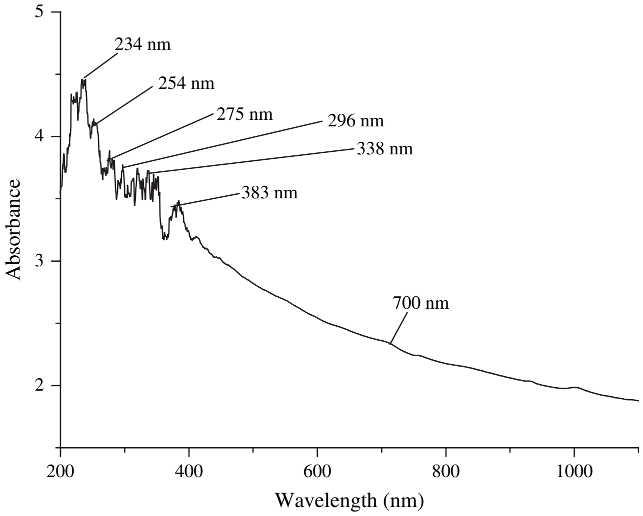


Fig. 7. Absorption spectrum (KBr pressed pellet) of obtained P3,6NVK with 1 mM Et_4NPh.

Ph^-, respectively. These results suggest that the electron-conductive polymer obtained in the presence of Ph^- has a more linear structure, which was confirmed by FTIR spectroscopy and SEM. This allows a higher incorporation of doping anions into the polymer chains, thus favoring an increase of the electrical conductivity. By contrast, the polymer obtained in the presence of Bz^- might have longer chains than that obtained without acidity control, so that this polymer could incorporate more doping anions into its framework, thereby exhibiting a higher conductivity than its homologue obtained with no base. These results agree with those obtained by cyclic voltammetry characterization, SEM, thermal analysis, and FTIR and absorption spectroscopies.

4. Conclusion

The electrochemical polymerization of *N*-vinylcarbazole has been investigated in the presence of two basic additives, which modify the reaction conditions in the electrolyte. The potential cycling synthesis can be applied to form a poly(3,6-*N*-vinylcarbazole) deposit when the potential is switched at the beginning of the carbazole oxidation peak. The electrode passivates and the polymerization is inhibited when a high basic additive concentration is employed. Optimum electrochemical synthesis is achieved by using a monomer/basic additive concentration ratio about 2 or higher.

The addition of small amounts of Et_4NBz and Et_4NPh to the electrolyte leads to the formation of polymer films with quite different morphology, chemical structure, thermal, optical properties and electrical conductivity. The presence of Bz^- during the electropolymerization process yields globular non-uniform films with high cross-linking degree. Therefore this additive cannot be considered as an effective proton scavenger in the studied medium. The presence of Ph^- during the electropolymerization process decreases the extent of polymer cross-linking through the vinyl group, as confirmed by FTIR spectroscopy. Besides, the SEM images showed a more homogenous morphology of this polymer. These facts are associated with the higher electrical currents and charges obtained during the electropolymerization of NVK in the presence of Ph^-. The highest electrical conductivity of P3,6NVK obtained in the presence of Ph^- was expected according to cyclic voltammetry results, SEM, TGA, FTIR and absorption spectroscopies.

The presence of Ph^- during the electropolymerization process can be considered as an interesting modifier of the polymer structure, because it prevents the cross-linking. The presence of unreacted vinyl groups in the polymer formed under these conditions could be useful for further polymerization reactions with other monomers, and provide improved polymer films for different applications, such as LEDs and sensing devices.

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References

[1] Papež V, Josowicz M. J Electroanal Chem 1994;365:139–50.
[2] Kakuta T, Shirota Y, Mikawa H. J Chem Soc Chem Commun 1985;553–4.
[3] Huang ZE, Chen Y, Cai RF, Rui CG, Zhang FP. J Appl Polym Sci 1996;60:573–7.
[4] Desbène-Monvernay A, Lacaze P, Dubois J. J Electroanal Chem 1983;152:87–96.
[5] Kido J, Shionoya H, Nagai K. Appl Phys Lett 1995;67:2281–3.
[6] Jiang X, Liu Y, Song X, Zhu D. Synth Met 1997;87:175–8.
[7] Jiang X, Liu Y, Song X, Zhu D. Synth Met 1997;91:311–3.
[8] Ma D, Wang D, Hong Z, Zhao X, Jing X, Wang F. Synth Met 1997;91:331–2.
[9] Kusano H, Hosaka S, Shiraishi S, Kawakami S, Sugioka K, Kitagawa M, et al. Synth Met 1997;91:337–9.
[10] Sanetra J, Armatys P, Chrząszcz R, Pielichowski J, Barta P, Nizioł S. Synth Met 1999;102:1115.
[11] Hong H, Sfez R, Yitzchaik S, Davidov D. Synth Met 1999;102:1217.
[12] Li BZ, Tamada M, Koshikawa H, Kimura Y, Suwa T, Seguchi T. Polymer 2000;41:7043.
[13] Ouro S, Bernède J, Marsillac S. Synth Met 2001;122:131–3.
[14] Liang Y, Lin Q, Zhang H, Zheng Y. Synth Met 2001;123:377–9.
[15] Ha HO, Lim H, Cho WJ, Ha CS. Opt Mater 2002;21:165–8.
[16] Tao D, Xu Y, Zhou F, Huang B, Duan N, Zhang T, et al. Thin Solid Films 2003;436:281–5.
[17] Li T, Fukuyama H, Yamagata Y, Lan H, Kido J. Polym Adv Technol 2004;15:302–5.
[18] Desbène-Monvernay A, Dubois JE, Lacaze PC. J Electroanal Chem 1985;189:51–63.
[19] Sezai A, Sezer E, Ustamehmetoğlu B. Polym Adv Technol 1997;8:556–62.
[20] Sezai A, Sezer E. Polym Adv Technol 1999;10:135–40.
[21] Ustamehmetoğlu B, Sezer E, Sezai A. Polym Int 2001;50:728–33.
[22] Desbène-Monvernay A, Lacaze PC, Dubois JE. J Electroanal Chem 1981;129:229–41.
[23] Davis F, Block H, Compton R. J Chem Soc Chem Commun 1984;890–2.
[24] Compton R, Davis F, Grant S. J Appl Electrochem 1986;16:239–49.
[25] Desbène-Monvernay A, Lacaze P, Delamar M. J Electroanal Chem 1992;334:241–6.
[26] Cattarin S, Mengoli G, Musiani M, Schreck B. J Electroanal Chem 1988;246:87–100.
[27] Skompska M, Peter L. J Electroanal Chem 1995;383:43–52.
[28] Skompska M, Hillman A. J Electroanal Chem 15 August 1997;433(1–2):127–34.
[29] Mano E, Calafate B. J Polym Sci Polym Chem 1983;21:829–35.
[30] Desbène-Monvernay A, Dubois J, Lacaze P. J Chem Soc Chem Commun 1985;370–1.
[31] Bhadani S. J Appl Polym Sci 1991;42:1271–3.
[32] Balaei S, Aaron J, Desbène-Monvernay A, Lacaze P. Synth Met 1992;53:95–107.
[33] Carlier V, Skompska M, Buess-Herman C. J Electroanal Chem 1998;456:139–52.
[34] Vico S, Carlier V, Buess-Herman C. J Electroanal Chem 1999;475:1–8.
[35] Topart A, Josowicz M. Talanta 1994;41:909–16.
[36] Skompska M, Peter L. J Electroanal Chem 1995;398:57–66.
[37] Skompska M, Kudelski A. J Electroanal Chem 1996;403:125–32.
[38] Bautista-Martínez J, González I, Aguilar-Martínez M. Electrochim Acta 2004;49:3403–11.
[39] Papež V, Inganäs O, Cimrová V, Nešpůrek S. J Electroanal Chem 1990;282:123–39.
[40] Sezer E, Ustamehmetoğlu B, Sezai A. Synth Met 1999;107:7–17.
[41] Safoula G, Touihri S, Bernède, Jamali M, Rabiller C, Molinie P, et al. Polymer 1999;40:531–9.
[42] Li Y, Yang J, Xu J. J Electroanal Chem 1995;399:79–82.
[43] Li Y, Yang J, Xu J. J Appl Polym Sci 1996;61:2085–9.
[44] Saçak M, Akbulut U, Cheng Ch, Batchelder D. Polymer 1994;35:2495–500.