Electrochemical Deposition of Polycarbazole Thin Films onto Tin Oxide Coated Glass: Physicochemical and Optoelectronic Characterizations

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ABSTRACT: Polycarbazole (PCz) thin films have been synthesized by electrochemistry. The influence of the deposition technique, potentiostatic or potentiodynamic, on the properties of the PCz films has been studied using the deposition time and the potential maximum as parameters. The PCz films have been characterized by thermal analysis, X-ray photoelectron spectroscopy (XPS), near ultra violet, visible and infra red absorption, photoluminescence (PL) measurements, scanning electron microscopy and microprobe analysis. Whatever the technique used, polymerized carbazole (Cz) films are deposited onto tin oxide coated glass. It is shown that potential maximum of 1400 mV or more induces some Cz nucleus destruction with N—N bonds formation. It is also shown by different techniques such as XPS, visible and IR absorption, microanalysis, PL, that the oxido–reduction reaction is reversible. Moreover, after dedoping treatment, nearly pure PCz film can be obtained, which allows obtaining PCz depoped films with good PL properties. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1568–1575, 2007

Key words: polycarbazole; electrochemistry; thin films; oxido–reduction reversibility

INTRODUCTION

Organic devices could be competitive for low-cost applications requiring large area coverage and low-temperature processing compatible with flexible substrates.

Intense research efforts are focussed currently on more defined polymeric material. Many of the research on this area have been addressed to conjugated thiophene, pyrrole, vinylene, and so on.[1–3] However, others conjugated polymer families are of interest. For example, in the case of organic light emitting diodes (OLED), green and blue light emission can be achieved by using carbazole (Cz) derivatives.[4–11]

Organic devices are based on a transparent conductive oxide (TCO), which is used as a transparent electrode. Usually the organic thin film is deposited onto the TCO by spin coating or vacuum sublimation. In polycarbazole (PCz), π–π*electron system along its backbone imports rigidity to the polymer and, therefore, makes it infusible and poorly processable. PCz is insoluble and cannot be deposited by spin coating. If vacuum deposition allows to prevent Cz molecule decomposition it induces polymer chain breaking and the deposited films are composed of oligomeres only.[12] Recent advances in synthesis methods have revived interest in PCz. The Langmuir Blodgett[13] technique and the electrochemical[8,10,14] techniques are useful for the fabrication of such polymer. The Langmuir Blodgett technique is useful for the fabrication of ultrathin films, while electrochemistry allows to cover easily a broad field of thickness.

Moreover, electrochemical polymerization present interesting advantages such as[15]:

Direct deposition of the polymer onto the TCO substrate.
Formation of a film with good adhesion and mechanical properties.
Possibility to control different parameters during

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the polymerization by varying parameters, such as the concentration of starting material, the solvent, salt combination, as well as electrochemical melt.

All this makes possible to tailor the final polymer film material into a certain structure and morphology.

In this article we report the physicochemical and optical characterization of PCz thin film deposited by electrochemical oxidation of Cz in solution. It is shown that the oxido–reduction reaction is reversible, which allows to achieve dedoped thin films electrochemically polymerized. These films are photoluminescent.

EXPERIMENTAL

The electrochemical depositions were monitored with a potentiostat/galvanostat PGP 201. A classical one compartment cell with three electrodes was used. The reference electrode was Ag/AgCl ([TMACl] $\approx 0.1M$).[16] The working electrode was a SnO_2 coated glass substrate and the third one was a platinum sheet counter electrode. The SnO_2 active area was 1 cm^2.

All solutions were purged with dry argon, which was maintained over the solution during the experiments. Electrochemical depositions were carried out at room temperature (20°C).

Before deposition the SnO_2 coated glass substrates were cleaned using a H_2O_2 treatment. The substrates were treated with a hot (80°C) mixed solution (5 : 1 : 1 volume parts) of fresh distilled water, hydrogen peroxide solution (reagent H_2O_2), and ammonium hydroxide, 25% NH_3 (NH_4OH), for 20 min followed by rinsing with boiling distilled H_2O for 5 min. Then the samples were dried with a dry nitrogen flow.

The Cz monomer was provided by Fluka with a purity of 99%. Acetonitrile (anhydrous 99.98%) was provided by Aldrich. The electrolyte salt used was the lithium perchlorate ($LiClO_4$, purity > 98.0%) purchased at Fluka. We have shown in a preceding article[8] that the best deposition conditions were achieved in an anhydrous acetonitrile solution containing $0.1M$ of Cz and $0.1M$ of $LiClO_4$. The optimum solution composition was as follows: $5.10^{-3}M$ Cz, $0.1M$ $LiClO_4$ in acetonitrile. The potential sweep rate used was 500 mV/min.

We compare the properties of the films deposited by potentiostatic (Ps = 1.1 V) and by the potentiodynamic techniques, for different values of deposition time (t) and of maximum potential (Pd), respectively. For potentiodynamic deposition, PCz films have been obtained by sweeping potential between 0 mV and Pd mV (1300 mV < Pd < 1500 mV), starting at −100 or −200 mV. We have shown[8] that when the films are deposited by potententiodynamic tech-

nique, cyclic voltamogramm exhibits two anodic peaks at V_{a1} = 920 mV and V_{a2} = 1230 mV, while two cathodic peaks are visible at V_{c1} = 830 mV and V_{c2} = 960 mV. V_{a1}, V_{a2} are oxidation peaks while V_{c1} and V_{c1} are reduction peaks. Since V_{a2} = 1230 mV allows to obtain electrochemical deposition of polycarbazole (PCz). In the case of potententiostatic deposition, the used potential potentiostatic was fixed during 30 min or 60 min.

After polymer deposition, the electrochemical technique was also used to optimize the dedoping of the PCz films. In that case the redox activity was studied using $LiClO_4$ ($0.1M$) as electrolyte in acetonitrile, the potentidynamic study has been done with a scanning rate of 500 mV/min.

The sample thickness ℓ versus the surface area A and the number of cycles N is expressed by eqs. (1) and (2) derived from Faraday's law.[17]

$$\frac{q}{A} = \frac{1}{A}\int_0^{t_{final}} I\,dt = \frac{1}{A}\int_O^N I\,\Delta t\,dN = \gamma\,N\Delta t \quad (1)$$

$$\ell = \beta\frac{q}{A} = \beta\gamma N\Delta T \quad \beta = \frac{M_m}{M_v}\frac{1}{n}\frac{1}{F_y} \quad (2)$$

where q represents the total electrical charge corresponding to the flow of current, I, through the cell during the experiment, n is the number of electrons per molecule involved in the oxido–reduction reaction (two electrons in this study), M_m = 167 g mol^{-1}, M_v = 1.1 g cm^{-3} are, respectively, the molar and volumetric weights of Cz; F_y = 96,500 C represents the Faraday constant, Δt is the duration of one cycle, and γ denotes the growth coefficient. $\gamma N\Delta t$ is the whole charge per surface unit. It is estimated from the airs of the voltammogramms. These values are obtained with the help of the "Volta Master 1" software.

The morphology of the surface of the films and their cross-sections have been visualized with a field emission scanning electron microscope, JEOL F-6400.

A calorimeter METLER TGS equipped with a thermo balance was used for the gravimetric thermal analysis at a heating rate of 8 or 20 K min^{-1}. The pyrolysis head was used as the heat source for the thermal degradation. The powder, $\sim$ 0.2–0.4 mg, was heated from 293 to 603 K.

The crystallization state of the films has been checked by X-ray diffraction by a Siemens D 500 diffractometer using Kα radiation. The doping and the dedoping efficiency of the films by cyclic voltammetry was checked by electron probe microprobe analysis (EPMA) using a JEOL 5800F.

The films have also been studied by X-ray photoelectron spectroscopy (XPS).

The spectrometer was a Leybold LHS-12 apparatus. A magnesium X-ray source (E = 1253.6 eV)
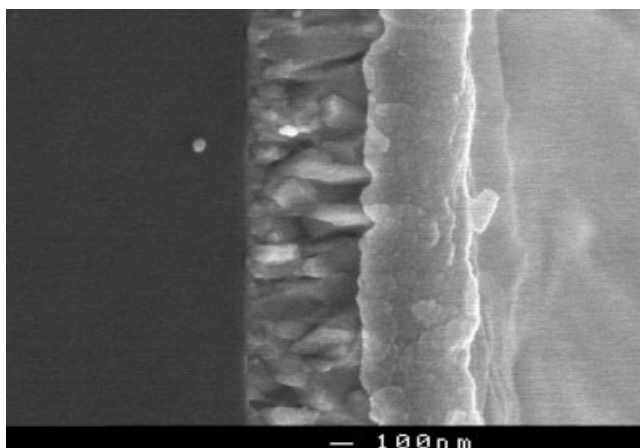
Figure 1 Cross section of a PCz film deposited by the potentiodynamic technique (10 cycles; Pd = 1400 mV stop at 0 mV).

operating at 10 kV and 10 mA was used. The pass energy was set to 50 eV. High resolution scans with a good signal to noise ratio was obtained in the C 1s, N 1s, O 1s, Cl 2p regions of the spectrum. The quantitative studies were based on the determination of the C 1s, N 1s, O 1s, Cl 2p peak areas with 0.1, 0.36, 0.6, and 0.58 as sensitivity factors, respectively. The sensitivity factors of the spectrometer are given by the manufacturer.

The decomposition of XPS peaks into different components and the quantitative interpretation were made after subtraction of the background using the Shirley method.[18] The developed curves fitting programs permit the variation of parameters such as the Gaussian/Lorentzian ratio, the full width at half maximum, the position and the intensity of the contribution. These parameters were optimised by the curve fitting program.

Infra red spectra were recorded with a FTIR Nicolet spectrometer (205XC), absorption band positions are given in wave numbers (cm^{-1}).

Optical transmission spectra of the films are carried out by a Cary spectrophotometer. Photoluminescence (PL) spectra are recorded at room temperature. The PL spectra were recorded using the Jobin Yvon Tg HG2S spectrophotometer with holographic gratings. The signal was detected with a Peltier cooled photomultiplier. The sample was excited with the 337 nm line of a filtered xenon lamp (150 W). The laser power at the sample was held below 2 mW.

RESULTS

As aforementioned, the thickness of the deposited PCz films has been estimated from electrochemical measurements. For example in the case of potentio-

dynamic deposition, for 10 cycles with 1400 mV as maximum potential, the charge density q/s is 70.5 mC cm^{-2} and the thickness of the deposited polymer film is estimated to be 550 nm. In the case of potentiostatic mode, with Ps = 1100 mV the measure of the current $I(t)$ shows, using $t_f = N\Delta t$ and $I(t) = I_0$, that the deposition rate was about 10 nm min^{-1}.

The cross section visualization allows, using simple software, to measure the thickness of the films. In Figure 1 we can see the cross section of a film deposited using the potentiodynamic process, with Pd = 1400 mV, 10 cycles, end of process at 0 mV. It can be seen in Figure 1 that the film thickness varies between 500 and 600 nm, which is in good agreement with the average value of 550 nm deduced from voltammetry measurements.

As said before the oxido–reduction process (doping–dedoping) of the polymer was studied in a solution with 0.1M LiClO$_4$ in acetonitrile, but without any Cz monomer.

The oxido–reduction reaction can be written as:

$$PCz + nClO_4^- \rightleftarrows [PCz^{n+} nClO_4^-] + ne^-$$

To check the doping–dedoping efficiency we have measured the atomic ratio chlorine/nitrogen by EPMA analysis. It can be seen Table I that, after oxidation, whatever the technique used, potentiodynamic or potentiostatic, the Cl/N ratio, is around 0.65. After reduction this ratio decreases to 0.14, which shows that even after reduction some chlorine is still present in the PCz films. Moreover, after dedoping, only some trace of chlorine is present in the film. Some electrolyte ions can be trapped in the PCz during deposition.

Thermal analysis (TGA) indicated a gradual weight loss between 293 and 603 K (Fig. 2). The weight loss between 303 and 333 K can be attributed to the escape of some solvent which have been trapped in the film during electrochemical PCz deposition. Then the progressive weight loss can be attributed to some perchlorate dopant escape[19] and also to some PCz evaporation, the polymer with shorter chain length having higher vapour pressure than the long chain polymer. The total weight loss between 293 and 603 K is 19%. This result can be compared to TGA of Cz monomer. In that case it

TABLE I
The Atomic Ratio Chlorine/Nitrogen by EPMA Analysis In PCz Films

	Oxidized		Reduced	Dedoped
Technique method	Pd	Ps	Pd	Pd
Potential of end process	Pd	Ps	0	0
Cl/N ratio	0.65	0.67	0.14	0.04
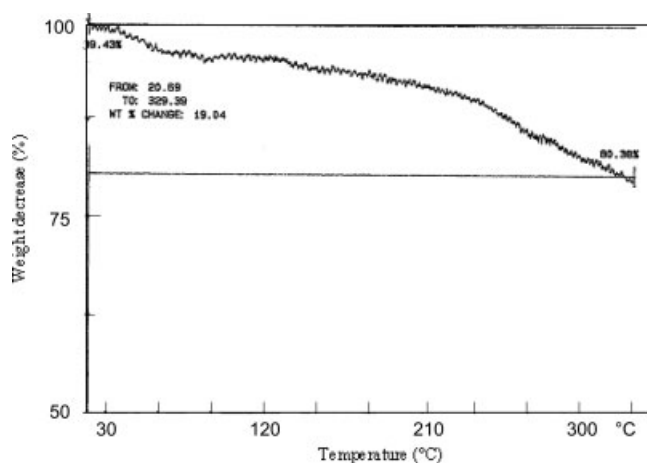
Figure 2 Thermal gravimetric curve of a PCz thin film.

has been shown[20] that there is a weight loss of 40% between 458 and 518 K. This result corroborates the polymerization efficiency of electrochemical synthesis since the thermal stability of polymer increases with its chain length. The polymer had the same behavior whatever the deposition technique—potentiostatic or potentiodynamic—used. Also, in the temperature range investigated, there was no influence of the maximum potential used.

It should be noted that, as shown by XDR study, while the Cz powder is crystallized the PCz thin films are amorphous.

XPS analysis shows that C, N, O, Cl, and Li are present at the surface of the films. The signal corresponding to Li is very faint (less than 1 at %) and should correspond to some contamination of the film during electropolymerization. The atomic ratio Cl/N measured by XPS in oxidized films is around 0.6, i.e. nearly the same value than the one measured by EPMA, which confirms the homogeneity of the doping from the surface (XPS) to the bulk (EPMA).

About oxygen, it should noted first that, after etching, the O1s peak decreases strongly, which means that the main part of the oxygen present at the surface of the film corresponds to surface contamination by room air (Fig. 3).

The decomposition of the different contributions is visualized in Figure 4. In the case of carbon [Fig. 4(a)], the contributions situated at 285, 286.7, and 287.3 eV can be attributed to C—C, C—N, and surface contamination (C=O...), respectively.[21]

The nitrogen N1s peak [Fig. 4(b)] can be decomposed in two contributions, the main is at 399.3 eV corresponds to the C—N bond of Cz, while the one at 402 eV can be attributed to N$^+$, the intensity of this contribution depends on the oxidation state of the films.[22]

Also, in the case of oxidized films, the binding energy of the Cl2p doublet [Fig. 4(c)], 207.6 eV, corresponds to chlorine in the ion ClO_4^-,[23] contribution which decreases strongly in reduced films.

The decomposition of the O1s peak shows that [Fig. 4(d)], as shown earlier, two contributions are present. The O1s at 532.9 eV corresponds to some surface contamination, while the one at 532.9 eV is related to the ClO_4^- dopant, in good agreement with the discussion of the Cl peak. In the case of reduced films, the contribution related to the ClO_4^- ion decreases strongly, while the atomic ratio Cl/N is 0.2, which shows the reversibility of the oxidation of the PCz films even at the surface. If, as discussed earlier, the XPS spectra are sensitive to the oxidation state of the PCz films, there is no difference between the XPS spectra of films grown by potentiostatic and potentiodynamic techniques.

To study by IR absorption the polymers, some PCz films were scratched off and powdered. Then infra red spectra were obtained by the KBr disk method using the FITR spectrometer from 400 to 4000 cm^{-1}. Large spectra of reduced and oxidized PCz are shown in Figure 5. The main absorption bands and their attributions are reported in Table II. Also, some typical absorption bands are magnified in Figure 6. The attribution of the main absorption bands has been done following the literature.[23–25] More precisely, [Fig. 6(a)], the bending vibrations situated at 725 and 748 cm^{-1} can be attributed to the disubstitution 1.2, which testifies that Cz nucleus are not destroyed during the electrochemical process. Also bands situated at 796 and 889 cm^{-1} correspond to C—H bending vibrations attributed to trisubstitutions on the phenyl nucleus. The stretching vibration C—N situated at 1237 cm^{-1} is also visible [Fig. 6(b)]. In the case of high maximum potential (potentiody-
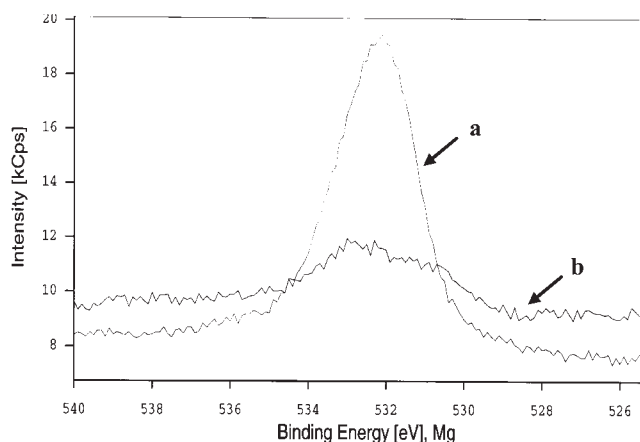
Figure 3 O1s peak before (a) and after (b) 1 min of etching.
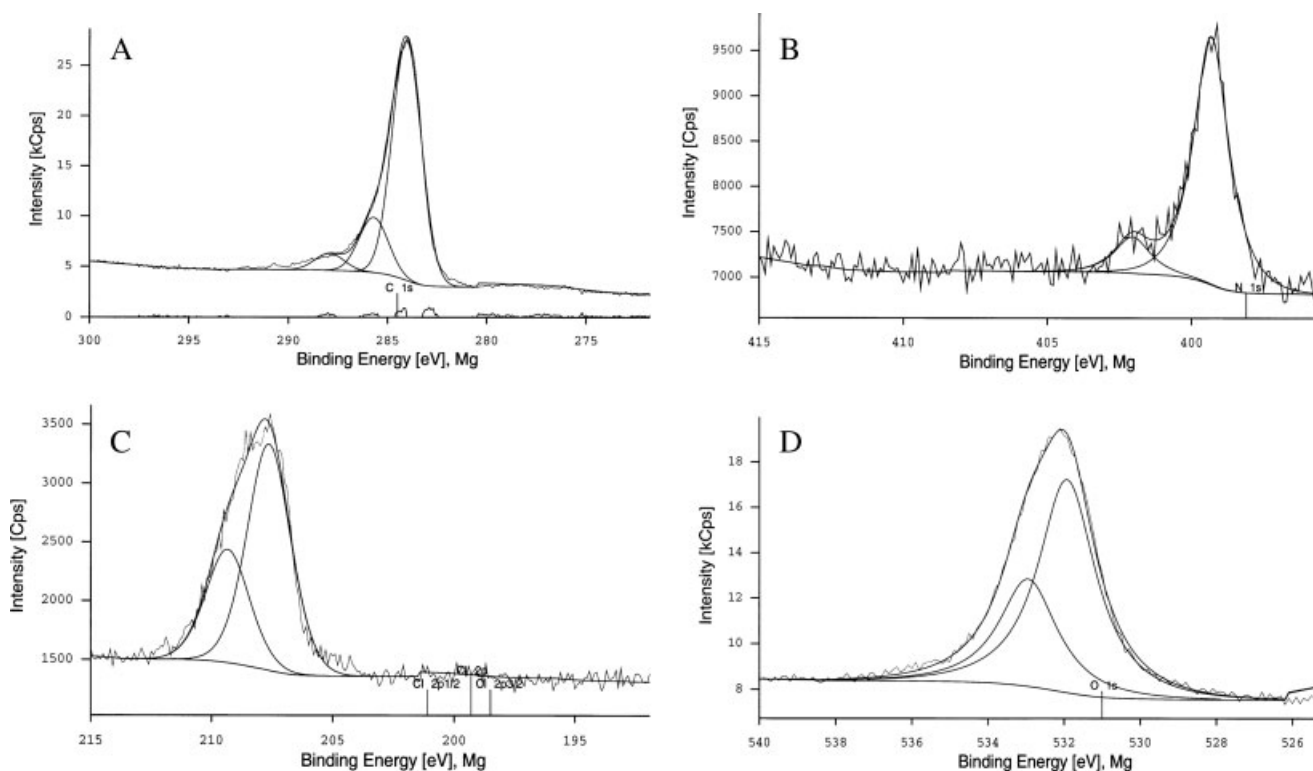
Figure 4 XPS spectra of the (a) C1s, (b) N1s, (c) Cl2p, (d) O1s, peaks: /\\/\\ experimental data ——— theoretical curve and different components.

namic deposition: Pd > 1400 mV) or high deposition time (potentiostatic deposition, $t \geq 60$ mn) a faint absorption band situated at 1575 cm^{-1} is visible (Table II). It can be attributed N—N binding vibration.[24,26]

Oxidized films exhibits absorption bands situated at 626 and 1098 cm^{-1} (Table II), which can be attributed to chlorine perchlorate incorporated during the electro-oxidation. These bands nearly disappear in the reduced films. As in the case of XPS, the IR spectra are modified following the oxidation state of the PCz films, moreover the presence of the N—N binding vibration testifies that, in the case of high maximum potential there is some Cz nucleus degradation, which allows defining more accurately the optimum electrochemical deposition conditions.

The optical absorption spectra of PCz films are reported in Figure 7. The spectrum of Cz monomers is also visible. It can be seen that, as expected, the polymerization induces a red shift of the absorption threshold. The band gap, corresponding to the transition $\pi \to \pi^*$ can be roughly estimated from the absorption threshold. The band gap of Cz is 3.6 eV, the values estimated for the PCz thin films vary between 2.9 and 3.3 eV. Uchiyama[27] has shown that the band gap decreases when the chain length increases. Here the band value is broader in the case

of dedoped films, which means that the dedoping process induces some band breaking. The smoothness of the absorption threshold means that there is a broad chain length distribution in the electopolymerized PCz films.

A broad absorption band is visible around 770 nm, mainly in doped films, such feature can be attributed to the presence of dopant in the films.[25] Also the small hump at 350–400 nm can be associated with the dopant present in the films.[13] Effectively these absorption bands are clearly visible in curves b and d, i.e. in the case of oxidized PCz, while they are not visible in the case of curve c, i.e. in the case of reduced PCz films.

The PL spectra of Cz and PCz film are visible in Figure 8(a,b). Here also there is a red shift effect of the PL emission band after polymerization. It can be seen in Figure 8(b) that, as expected, the PL intensity increases when the doping of the films decreases. Moreover the PL signal does not depend significantly on the deposition technique used.

A visualization of the surface morphology of the films is presented in Figure 9. It can be seen that the PCz films have a high covering efficiency, they are continuous and homogeneous.

Such covering efficiency is necessary for the use of polymer thin films in organic devices.
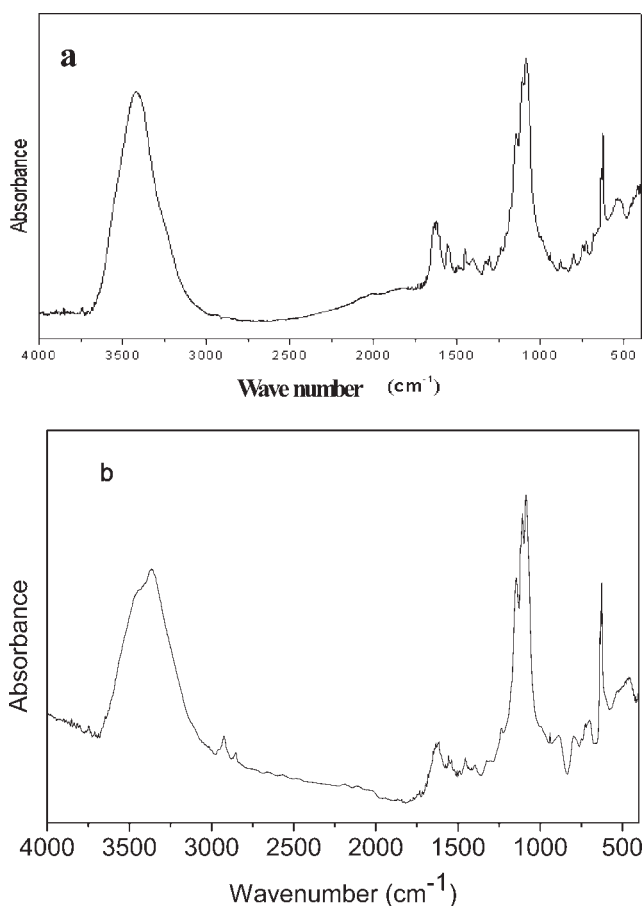
Figure 5 Infra red absorption spectra of a PCz film deposited by the potentiostatic (a) and the potentiodynamic (b) technique.

DISCUSSION

The high thermal stability of the PCz synthesized by electrochemistry, the red shift of the absorption threshold and PL emission band, the preservation of the Cz units shown by IR absorption testifies that electrochemistry allows synthesizing PCz polymer thin films, with expected properties, when optimized maximum potential is used.

The reversibility of the oxido–reduction reaction is proven by different experimental techniques. The variation of the atomic ratio Cl/N put clearly in evidence this reversibility, whatever the sample domain studied (volume or surface). The dedoping is effective in the potentiodynamic mode when $V_d = 0$ mV, even if some dopant is still present in the film. To achieve nearly completely the dedoping a special electrochemical treatment is necessary.

In that case the dedoping of the thin film can be achieved nearly completely as shown by XPS, EL emission, visible, and IR absorption measurements. This dedoping possibility is promising for OLED applications. The reversibility of the oxido–reduction reaction is clearly visible in the XPS, EPMA quantitative analyses (Table I) but also in the qualitative IR and XPS analyses. In the case of infra red absorption, the bands at 626 and 1098 cm^{-1} correspond to ClO_4^- ions. In the case of XPS, if the N$^+$ contribution corresponding to oxidized N is clearly visible, it decreases strongly after dedoping. Also the broad absorption band situated at 770 nm and the small hump at 350–400 nm in the absorbance spectrum of oxidized PCz clearly indicate the presence of polarons i.e. of the doping of the films, these absorption bands disappear after dedoping.

It is known that the luminescence properties of polymers depend strongly on its purity. Here the influence of the electrolyte ions trapped in the PCz films can be discussed from experimental results. If the PL signal of an oxidized PCz film is used as reference, the signal obtained with reduced PCz film is 1.4 higher, while that with dedoped films is 3.2

TABLE II
The Main Absorption Bands of PCz Films

Wave number (cm^{-1})	Intensity	Absorption bands
3440	High, $\pm$ wide	N—H
3364	High, $\pm$ wide	N—H
1600	Middle	C—C
1576	Very low	N—N (in the case of high maximum potential or high waiting time deposition)
1491	Low	C=C
1456	Middle	C=C
1237	Very low	C—N
1098	$\pm$ High	ClO_4^-
889	Middle	C—H
796	Middle	C—H
748	Low	C—H
725	Low	C—H
626	Middle	ClO_4^-
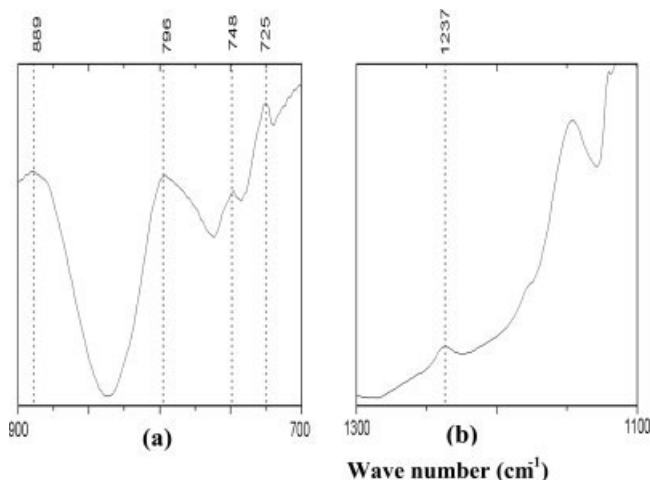
Figure 6 High resolution, infra red spectra between 700 and 900 cm^{-1} (a), 1100 and 1300 cm^{-1} (b).
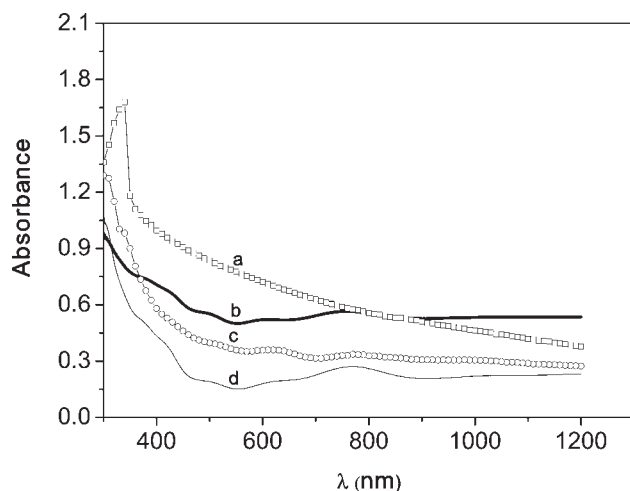
Figure 7 UV, visible spectrum of (a) carbazole and PCz films deposited by: the potentiodynamic technique (1300 mV, 10 cycles, oxidation) (b), the potentiodynamic technique (1300 mV, 10 cycles, reduced) (c), the potentiodynamic technique (Ps = 1100 mV, t = 30 mn) (d).

better. Therefore, since as discussed earlier the presence of electrolyte ions in the PCz films is clearly put in evidence by XPS, EPMA, optical absorption
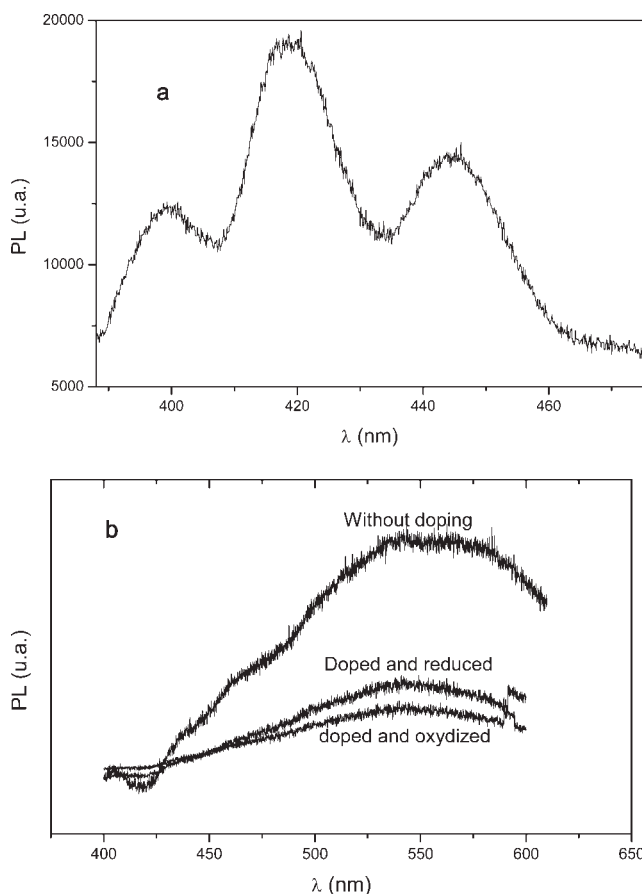
Figure 8 Photoluminescence spectra of (a) carbazole monomer and (b) PCz thin films (b1 dedoped; b2 reduced; b3 oxidized).
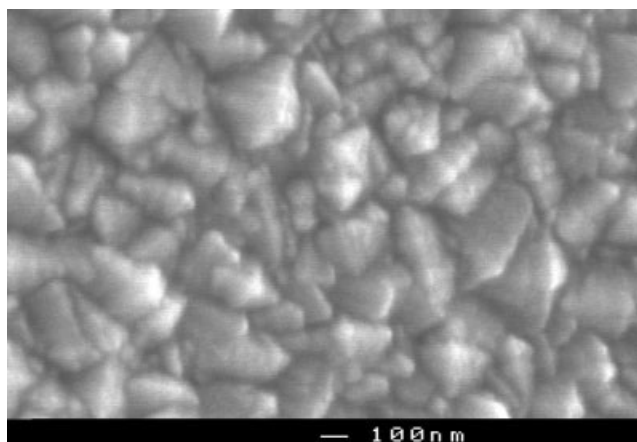
Figure 9 Scanning electron micrograph of a PCz film deposited onto SnO_2.

(visible and infra red absorption) measurements it can be concluded that there is a clear relationship with the photoluminescent properties and these experimental characterizations.

The study of the influence of polarization potential on the films properties shows that in the case of high maximum potential there is irreversible over oxidation, which induces some polymers degradation such as destruction of the Cz nucleus and N—N band formation.

The PCZ films emit light in the green domain. As expected the PL intensity increases when the doping concentration decreases. This effect allows to use the electrochemical PCz synthesized films in OLED's.

CONCLUSION

PCz films can be synthesized electrochemically by potentiodynamic and potentiastatic electrochemical deposition process.

The maximum potential used during electrochemical polymerization should be smaller than 1500 mV to avoid destruction of the Cz nucleus and formation of N—N bonds. The oxido–reduction process is reversible. In the case of potentiodynamic process, it is shown that when the deposition cycle is stopped at the maximum potential value, the films are oxidized while they are reduced when the cycle is stopped at V_d = 0 mV. Moreover it is shown that, whatever the deposition technique, potentiodynamic or potentiastatic, used it is possible to dedope the polymer by voltametry process using $0.1M$ $LiClO_4$ in acetonitrile solution. Such dedoped thin films exhibit PL in the green domain.

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