Polycarbazole Obtained by Electrochemical Polymerization of Monomers Either in Solution or in Thin Film Form

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ABSTRACT: Polycarbazole has been synthesized by electrochemistry. The carbazole monomer source consists either in carbazole in solution in the electrolyte or in carbazole deposited in thin film form onto the working electrode. The two families of polymers have been studied by infrared absorption, X-ray diffraction, thermal gravimetric analysis, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy, electron spin resonance, and electrical conductivity measurements. It is shown that the polycarbazole films obtained with carbazole deposited in the thin film form exhibit a better polymerization efficiency and an electrical conductivity one order of magnitude higher. This result is in good accordance with a higher spin density and homogeneity. It is proposed that not only are some monomers activated during the evaporation but also that the physical contact between the working electrode and the continuous carbazole films induces the growth of homogenous highly polymerized polycarbazole films. In agreement with this suggestion, the SEM study shows that this type of polycarbazole thin films keep in memory the morphology of the SnO_2 under layer. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1561–1568, 2000

Key words: polycarbazole; electrochemistry; electron spin resonance; photoelectron spectroscopy

INTRODUCTION

Conducting polymers are obtainable both by chemical and electrochemical methods. Their properties can be improved by modifying experimental conditions, in particular, in the case of electrochemical polymerization.[1–3]

We have recently reported a comparison of polycarbazole polymers obtained by oxidation of carbazole either in solution or in thin film form.[4] It had been shown that polymerization efficiency was higher when the oligomer source consisted of thin films deposited under vacuum on conducting SnO_2-coated glass substrate. The small electrical conductivity that was measured could be attributed to the electrochemical oxidation conditions with high and constant potential ($V = 2.5$ V). Such extreme conditions had been chosen in order to compare the properties of polycarbazole samples obtained in the same constant experimental conditions.

In this article, results are relative to the electrooxidation of carbazole, using optimum conditions, which have been deduced from the cyclic voltammogram of carbazole in the electrolyte solution.

EXPERIMENTAL

The electrochemical experiments were monitored with a potentiostat PGP 20. The classical one-compartment cell used includes three electrodes. The reference electrode was a saturated calomel electrode. The working electrode was a SnO_2-coated glass substrate, and the third one was a platinum counter electrode.

The carbazole monomer was provided by Aldrich with a purity of 99%. As described earlier,[4] the polymer samples have been obtained from the following two different sources: $0.1M$ carbazole monomer in the electrolytic solution leading to polymer samples later on called PCZ_{sol}; carbazole monomers deposited by thermal evaporation on the SnO2 electrode leading to polymer samples later on called $PCZ_{thin\ film}$.

In both cases, the SnO_2 electrode was about 4.8 cm^2. The thin films of carbazole monomers were obtained by classical evaporation of powder under a vacuum better than 10^{-4} Pa. The evaporation rate (3 nm s^{-1}) and the film thickness were measured *in situ* by the vibrating quartz method.

A SETARAM TGDTA 92 was used for the gravimetric thermal analysis (GTA) at a heating rate of 2 K min^{-1}. Approximately 0.5 g of fine powder was placed in a Pyrex tube. The morphology of the films was visualized by scanning electron microscopy (SEM). Infrared (IR) spectra were obtained using a Fourier transform infrared (FTIR) spectrometer.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Leybold LHS.12 apparatus (University of Nantes, CNRS) using magnesium source radiation (1253.6 eV) at 10 KV and 10 mA, and the pass energy was set at 50 eV. High-resolution scans with a good signal ratio were obtained in the Cls, Nls, Ols, and Cl2p regions of the spectrum. The quantitative analysis was based on the determination of the Cls, Nls, and Cl2p peak areas with 0.2, 0.36, and 0.58 as sensitivity factors. The vacuum in the analysis chamber was about 10^{-6} Pa. All the spectra were recorded under identical conditions.

The decomposition of the XPS peaks into different components and the quantitative interpretation were performed after substraction of the background using the Shirley method.[5] The developed curve-fitting programs allow the variation of parameters, such as the Gaussian–Lorentzian ratio, the full width at half maximum (FWHM), the position, and the intensity of the contribution. These parameters were optimized by the curve-fitting program.

XPS study has been carried out without any etching of the surface because etching destroys C—N bonds and results in graphitization of the polymer surface. The structure of the films was examined with a diffract AT V.3.1. Siemens analytical X-Ray system (wavelength, 1.5406 A°).

Electron spin resonance (ESR) experiments were performed at ambient temperature on a Bruker ER 200D spectrometer operating at the X band. Spin density N_s was estimated using an ESR comparison technique. The minimal sensitivity of the detector is about 10^{15} spins cm^{-3} mol^{-1}.

Electrical conductivity measurements were performed on pressed polymer pellets with the help of an electrometer.

RESULTS AND DISCUSSION

Film Formation

First polycarbazole (PCZ) films were formed progressively by scanning the potential between -2.5 and 2.5 V. The solution used was acetonitrile and water in the volume ratio of 1 to 2 containing $0.1M$ tetraethylammonium perchlorate as electrolyte. It can be seen on the cyclic voltammograms (Fig. 1) that a maximum potential of 1.7 V is sufficient to obtain complete oxidation. Therefore, the oxidation was carried out by scanning the potential between 0 to 1700 mV.

The cyclic voltammetric curves were the same whatever the carbazole source (Fig. 2). During the first cycle of potential cycling, the polycarbazole exhibits a color change from green to translucent on going from high positive potentials (1.7 V) to zero potential. However, the reaction becomes quickly irreversible without the reduction peak being visible. Then, the general features of the curve are marked by a broad anodic irreversible peak at about Epa = +1 V corresponding to oxidation and the doping charge. With repetitive cycling, the anodic peak shifts to a positive value. At the end of the 30 cycles, the anodic peak was situated at Epa = +1.4 V. The formation of green
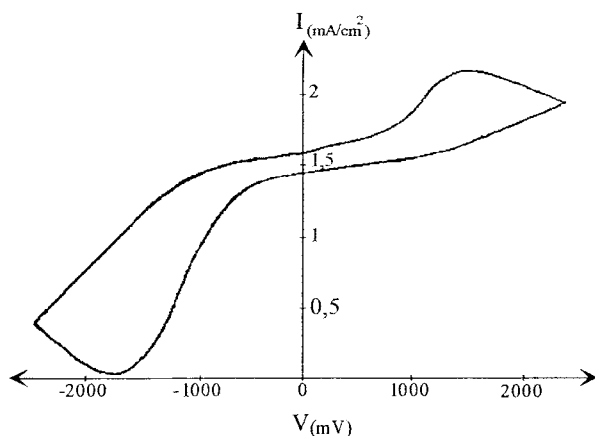
Figure 1 Cyclic voltomogram of polycarbazole electrochemically deposited on SnO_2 in acetonitrile and water (volume ratio: 1 to 2) containing $0.1M$ tetraethylammonium perchlorate: working electrode, Pt; reference electrode, saturated calomel electrode; sweep rate, 500 mV/mn; scanning from -2.5 to 2.5 V.

black film on the SnO_2 electrode was observed upon cycling the potential, with a continuous decrease in the peak current, as expected due to the growth of the diffusion layer at the electrode.[6] The origin of the irreversibility of the oxidation probably is due to a partial degradation of the polymer. It has been already reported that the redox response of the polycarbazole electrode is poor.[3]

Polycarbazole Characterization

After polymerization, the films were washed with distilled water and dried for 24 h at room temper-
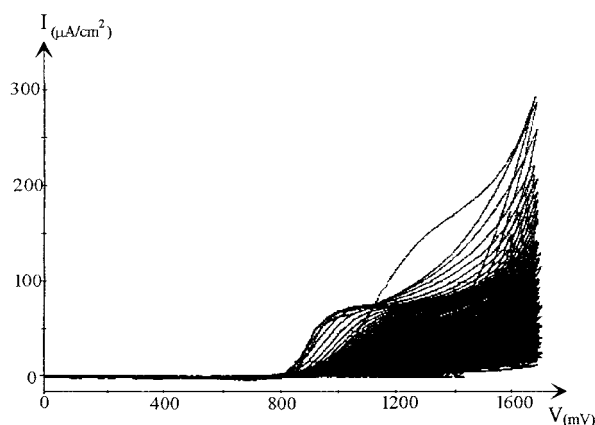

Figure 2 Cyclic voltomogram of polycarbazole electrochemically deposited on SnO_2 in acetonitrile and water (volume ratio: 1 to 2) containing $0.1M$ tetraethylammonium perchlorate: working electrode, Pt; reference electrode, saturated calomel electrode; sweep rate, 500 mV/mn; scanning potential, 0–1700 mV.
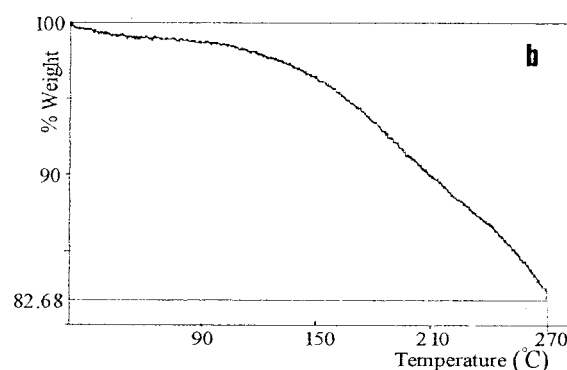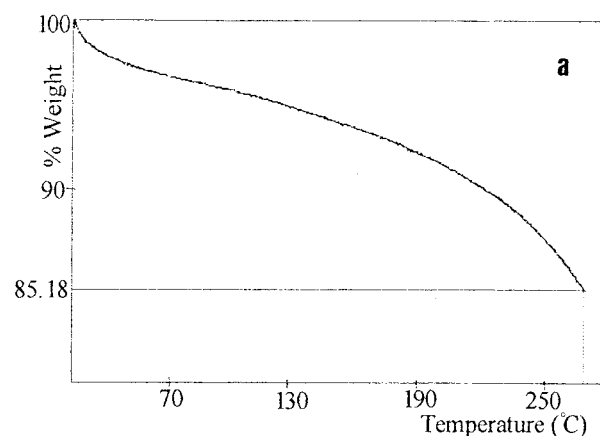

Figure 3 Gravimetric thermal analysis. (a) PCZ_{sol} from 30.6 to 269.6°C; weight percentage change, 5 to about 15%. (b) $PCZ_{thin\ film}$, from 30.6 to 269.6°C; weight percentage change, 5 to about 15%.

ature. For specific experiments, the films were sometimes scratched from the substrate and grinded.

The thermogravimetric curves are given in Figure 3. Polymers first exhibit a fast decrease in weight of 2 to 3% at the beginning of the heating cycle and then a slow but continuous decrease when the temperature increases. While up to 10% weight loss, the $PCZ_{thin\ films}$ is more stable; for higher weight loss, the PCZ_{sol} samples become more stable.

The small weight loss at the beginning of the heating cycle is due to the loss of absorbed water during preparation process and is not necessarily associated with any change in the structure.

At high temperature, it is well known that the weight loss decreases as the chain length increases, which means that the more stable polymers have the higher weight. The continuous decrease of the weight loss shown in Figure 3 means that the distribution of the chain lengths is very

broad. It appears that the PCZ_{sol} polymer contains the longest chains since it is more stable at high temperature, but it also contains the higher density of short chains since it is less stable at low temperature. Therefore, the PCZ_{thin} films samples are more homogeneous.

The IR spectra are reported in Figure 4. By comparison to the carbazole spectrum [Fig. 4(c)], it can be seen that some new broader peaks appear at 1625, 1485, 1380, 1230, 1090, 810, and 725 cm^{-1}. Moreover, the shape of the typical structure of the N—H bond situated at 3420 cm^{-1} in the carbazole is strongly modified after polymerization (not shown in Fig. 4); it becomes broad, and its intensity decreases.

As it will be discussed below, this modification could be attributed to the complex salt formation with the positive radical being situated in the nitrogen.[3,7] Moreover, the presence of some O—H bonds at the end of the polymerization process is probable, as shown by thermogravimetric analysis (TGA) measurements. Among the new IR bonds, some can be attributed to C=C (1625 cm^{-1}), C—C (1495 cm^{-1}), C—N (1320 cm^{-1}), and C—H (725 cm^{-1}) vibrations[8]; the other ones can be attributed either to the complex salt formation (1090 cm^{-1}, 810 cm^{-1})[4] or to O—H vibrations (1230 cm^{-1}). The above results suggest that there is complex salt formation (PCZ^{+}, ClO4^{-}) and that there are some O—H bonds present in the sample, while the broadening of the peaks can be attributed to some disorder in the polymer. Probably, a broad distribution of the chain length spectrum exists, which is in good agreement with the slow decrease in weight when the temperature increases (TGA curves; Fig. 3).

Smooth X-Ray diffraction (XRD) patterns reveal that the samples are amorphous. However, it can be shown by SEM visualization that the surface of the films exhibits clearly organized domains (Fig. 5).

In the case of $PCZ_{thin\ film}$ samples, the overall surface is quite homogeneous, and the SnO_2 thin film electrode is nearly completely covered by PCZ, even if there are some small pinholes. The domains are more or less triangularly shaped. In the case of PCZ_{sol} samples, the films consist in small heaps deposited onto the electrodes with a lot of bare domains between them.

The shape of these small heaps is more or less circular. It should be noted that the size of the structures obtained in the samples studied in this work is systematically smaller than that obtained
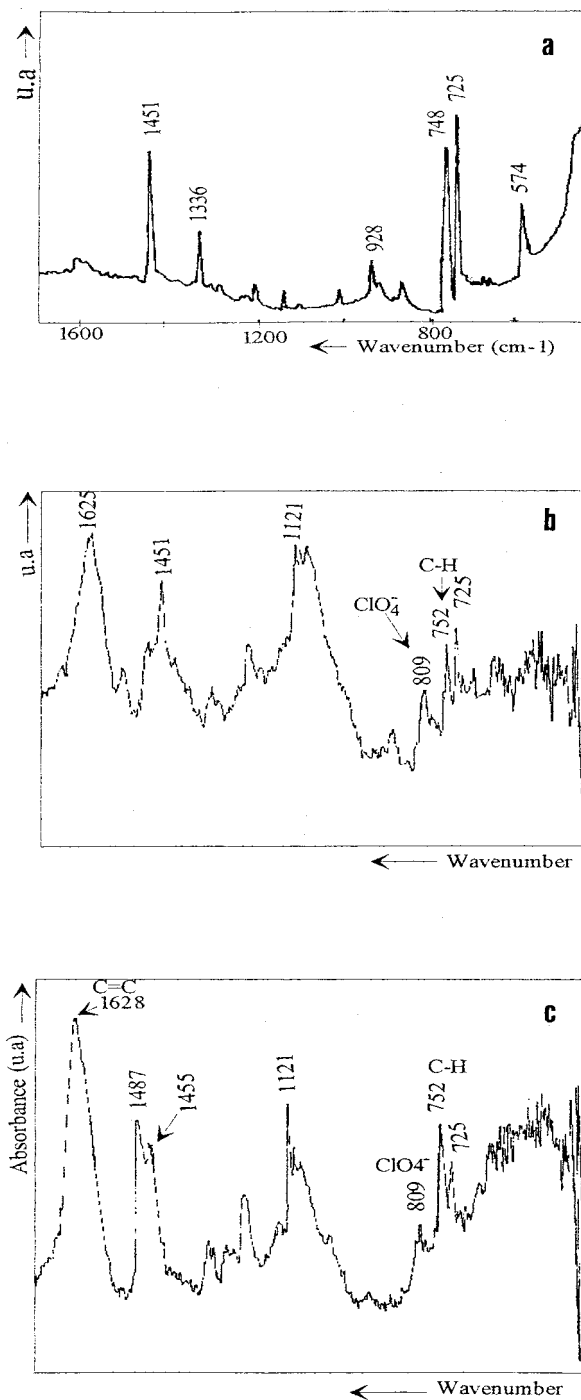

Figure 4 Infrared absorption spectra: (a) carbazole powder; (b) $PCZ_{thin\ film}$; (c) PCZ_{sol}.

when a constant polarization potential of 2.5 V is used.[4]

The higher homogeneity of the $PCZ_{thin\ film}$ samples could be attributed not only to their chain length but also to the carbazole monomer source.
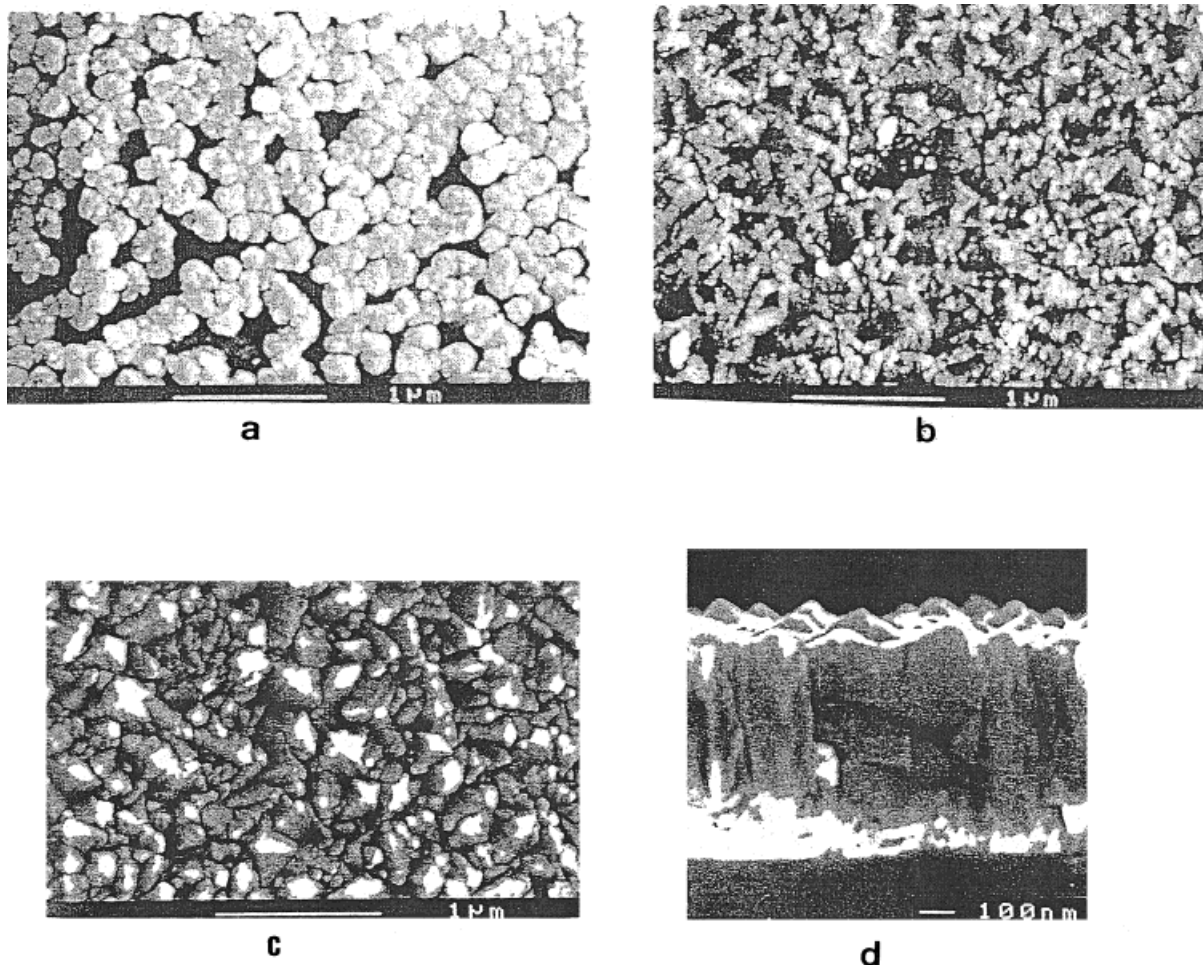
Figure 5 Scanning electron micrographs: (a) PCZ_{sol}; (b) $PCZ_{thin\ film}$; (c) SnO_2 thin film; (d) cross section of SnO_2 thin film.

In the case of PCZ_{sol}, the monomers are diluted in the solution, and the polymerization is initialized on heterogeneities of the SnO_2 electrodes. The electrodes are quite rough [Fig. 5(d)]; and after nucleation, the polymer develops all around these initialization sites, which induces the nearly circular shape of the growing heaps and the empty domains between these heaps. In the case of the $PCZ_{thin\ film}$ layers, there is a striking similarity between their texture and that of SnO_2 films [Fig. 5(c)]. Therefore, even after polymerization, the films keep in memory the structure of the SnO_2 under layer, which means that the electrochemical oxidation process does not lead a large migration of the predeposited carbazole monomers. Therefore, the evaporated monomer films being continuous, the polymerized layer is homogeneously distributed on the SnO_2 electrode.

In the case of evaporated carbazole samples, the small pinholes facilitate some diffusion of the electrolyte at the interface working electrode–monomer layer. The direct physical contact between the working electrode and the material that has to be electrochemically polymerized induces the presence of a very high density of nucleation sites. This induces rapid interaction between the growing polymerized domains, which allows the formation of polymer chain with more homogeneous length distribution than in the case of PCZ_{sol} samples, where the nucleation centers are limited to the broader irregularity features of the SnO_2 films.

The XPS study of the samples is summarized in Table I. It can be seen that the spectra are qualitatively similar, even if there is some more chlorine in the $PCZ_{thin\ film}$.

Table I XPS Results

Sample	C—C[a]	C—N	C—O—H	C=O	N⁻	N	N⁺	C=O	C—O—H
			Cls			Nls			Ols
PCZ$_{thin film}$[a]	284.5	285.5	286.5	288.6		400.1	400.7		532.2
PCZ$_{thin film}$[b]	50	37	11	2		88	12		100
PCZ$_{thin film}$	1.5	1.5	1.5	1.5		1.34	1.34		2.75
PCZ$_{sol}$	284.5	285.3	286.7	288.8	399.2	400	400.7	529.7	532
PCZ$_{sol}$	61	32	5	2	15	57	26	14	86
PCZ$_{sol}$[c]	1.7	1.7	1.7	1.7				2.23	2.23

[a] The first line is the binding energy.
[b] The second line is the relative intensity.
[c] The third line is the full width at half maximum.

The quantitative analysis shows that if the atomic ratio N/C is nearly equal to the theoretical value, and the surface of the samples is contaminated by oxygen (at least 15 at. %); moreover, the Nls and Cls peaks are broad and should be decomposed in different contributions.

After decomposition, the carbon peak Cls can be attributed to three main contributions. The first one situated at 284.5 eV should be assigned to the C—C bonds. This value has been taken as reference. The second component situated at 285.5 eV can be attributed to C—N bonds.[9] However, this relative contribution is higher than the one expected, which means that some C—O—H bonds are present, but also possibly some C⁺ radicals. The third component situated at about 287.2 eV can be attributed to some C=O bonds.[9]

The Nls peak of PCZ$_{thin films}$ should be decomposed in the following two components: the first one situated at about 400 eV corresponds to the well-known amine bond of the carbazole group,[9] while the second one, situated at about 401 eV, could be assigned to positive nitrogen.[10] This positive nitrogen corresponds to charge transfer salt complex formation between carbazole and ClO_4^- ions. In the case of PCZ$_{sol}$, there is a third peak on the low-energy side, which can be attributed to imine bonds. It has been shown that amine bonds can appear irreversibly in the polycarbazole during voltammetric cycling (Fig. 6; Verghese et al.[3]). The absence of such bonds in PCZ$_{thin films}$ corroborates the better homogeneity of these samples.

The ESR study has shown that the carbazole powder does not present any ESR signal before polymerization. After electrochemical oxidation, a well-resolved ESR signal is systematically observed (Fig. 6; Table II). In Figure 6, the spectra were normalized to constant height for comparison of the g factors. Using the pole method integration with a Gaussian or a Lorentzian line shape (or a mixture of two), the theoretical ESR can be fitted.[11]

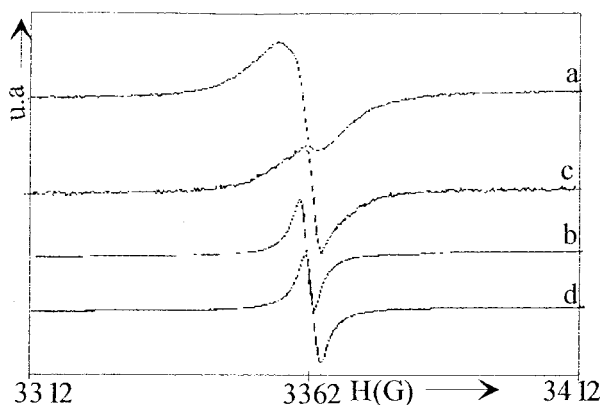All the signals have a Lorentzian shape. The different g, FWHM, and spin density values are

Figure 6 Normalized ESR spectra of PCZ samples: (a) PCZ$_{sol}$ at room atmosphere; (b) PCZ$_{thin film}$ at room atmosphere; (c) PCZ$_{sol}$ at 60°C; (d) PCZ$_{thin film}$ at 60°C.

Table II ESR Results

Sample	g	FWHM	Ns (spin · mol⁻¹ · g⁻¹)
PCZ$_{sol}$	2.0017	3.1	1.36 10^{20}
PCZ$_{thin films}$	2.0019	2.6	2.91 10^{22}
PCZ$_{sol}$			
$T = 60°C$	2.0023	7.1	8.32 10^{21}
PCZ$_{thin films}$			
$T = 60°C$	2.0022	2.4	3.4 10^{22}

reported in Table II. The measurements have been performed at room temperature and at 60°C. It can be seen that the g values can correspond to a polaron signal and also the FWHM value. However, it should be noted that the FWHM is smaller in the case of PCZ$_{thin films}$, while the spin density is two orders of magnitude higher. After heating, both families exhibit an increase of the spin density. This increase corresponds to the improvement of the charge exchange in the complex salt when the temperature increases. Here, also, in the case of the PCZ$_{sol}$ samples, the broadening of the signal can be attributed to a very broad distribution of the chain lengths, as put in evidence by the presence of radicals, which become active when the temperature increases.

This presence of radicals is in good agreement with the XPS study, which has shown that N^+ and C^+ radicals are present in the samples after oxidation.

The room temperature electrical conductivity of the PCZ$_{thin film}$ samples is $\sigma = 1.5 \ 10^{-5} \ \Omega^{-1}$ cm^{-1} and $\sigma = 5 \ 10^{-7} \ \Omega^{-1}$ cm^{-1} in the case of PCZ$_{sol}$ samples. This higher conductivity of the PCZ thin film is in good agreement with the higher spin density and smaller FWHM value of the ESR signal of these samples. The smaller conductivity of the PCZ$_{sol}$ can be attributed to higher disorder related to a broad distribution of chain length. Therefore, as shown earlier in the case of electrochemical oxidation under a dc voltage of 2.5 V,[4] the polymer obtained from predeposited carbazole thin films has a more homogeneous chain length distribution.

As discussed elsewhere,[12] carbazole monomers are activated during the heating needed for evaporation. This activation process facilitates polymer formation. Moreover, as deduced from the SEM visualization of the layers, geometrical considerations should also be taken into account to explain the higher polymerization homogeneity of the evaporated carbazole films.

It should also be noted that when a maximum oxidation potential of 1700 mV is used, the room temperature conductivity obtained is four orders of magnitude higher than that obtained when a dc potential of 2.5 V is used. This confirms that, in the latter case, the process was under overoxidation conditions. Moreover, it has been shown earlier by UPS (ultraviolet photoelectron spectroscopy) measurements[13] that there is still a gap (0.5 eV) between the Fermi energy and the spectral edge of the doped polycarbazole. This gap suggests that even after doping, conductivity as high

as that observed in polypyrrole or polyaniline cannot be expected. However, recent studies have put in evidence that PCZ and related oligomers are very attracting in electroluminescent diodes.[14] It is therefore interesting to understand the properties of electropolymerized polycarbazole in order to improve them. However, the conductivity remains quite small because, as shown by XRD, the films are amorphous. This conformational disorder would probably limit π orbital delocalization to only a few adjacent monomer units. The intermolecular interchain hopping contribution to the conductivity should be quite large, owing to these structural constraints.

CONCLUSION

All the experimental results discussed above have shown not only that polycarbazole thin films obtained by electrochemical oxidation of vacuum predeposited carbazole monomers films can be obtained but that their polymerization efficiency is better than that obtained by polymerization of carbazole monomers in solution in the electrolyte.

This result confirms an earlier study carried out on similar samples but with very different oxidation conditions. Moreover, a careful study of surface features of the polycarbazole layers allows one to conclude that the better polymerization efficiency is not only related to some activation of the monomer during the heating needed for the evaporation of the monomer but also to geometrical reasons. The thin carbazole films is in direct contact with the SnO$_2$ surface rugosities, which induces a high density of nucleation centers, which allows better polymerization homogeneity compared to classical process in which the initiating center density is smaller. Therefore, the quality of the polymerization process depends strongly on the homogeneity and quality of the monomer films.

Although the conductivity of these films is higher than that of the samples obtained by electrochemistry using a 2.5 V polarization voltage, which shows that oxidation conditions have been optimized, the disorder present in the samples limits the conductivity.

Moreover, there is high oxygen contamination of the films. This can be related to the solution used for electrochemistry, and, now, a work using dry solution is starting in the laboratory.

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