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Influence of the electrochemical conditions on the properties of polymerized carbazole

H. TAOUDI, J. C. BERNÈDE
LPSE - FSTN 2 rue de la Houssinière 44322 Nantes
E-mail: jean-christian.bernede@physique.univ-nantes.fr

M. A. DEL VALLE
Laboratorio de Polymeros - Facultad de Quimica - PUCC - Santiago Chile

A. BONNET, M. MORSLI
LPSE - FSTN 2 rue de la Houssinière 44322 Nantes

Polycarbazole (PCZ) was obtained by electrochemical oxidation of carbazole monomers. Two potentials were used: the oxidation potential of the monomer 1700 mV and an over oxidation potential 2500 mV. The carbazole monomers were supplied either in solution in the electrolyte or in the form of pre-deposited thin film evaporated on a working electrode. It is shown that if PCZ is systematically obtained its electrical and morphological properties are strongly dependent on the experimental conditions. The stability of over-oxidized PCZ films corresponds to chain reticulation beyond the first oxidation potential value, with the loss of flexibility of the chains and steric hindrance, which decreases the carrier mobility and, therefore, its conductivity. The polymers obtained at the oxidation of carbazole have conductivity corresponding to higher carrier mobility. These polymers are conjugated. Moreover, in the case of preevaporated carbazole thin film the coverage of the SnO_2 is very high and the films are homogenous.

1. Introduction

Polyvinylcarbazole is an electroluminescent polymer which emits blue light and it can be used in organic light emitting diodes [1]. Works has also be done on polycarbazole [2]. The device performances depend strongly on the polymer thin film properties: stability, homogeneity, etc.

Polymers usually were chemically synthesized. Another way to produce polymers is electrochemistry [3]. This technique allows to synthesize a polymer directly under its conductive doped form. Usually the anodic polymerization is used and “p-doped” polymers are obtained. But post “dedoping process” can be used to obtain neutral films. The properties of the obtained samples depend strongly on the experimental conditions: solvent, electrolyte working electrode, cell atmosphere, etc.

Also the source supplying of monomer is determinant. Usually the polymerization consists in an electrochemical oxidation of the solution of a monomer leading to the coating of the anode with the synthesized polymer using a three-electrode cell. However, we [4, 5] and other authors [6] have shown that electrochemical synthesis is possible by the oxidation of a vacuum deposited film on the anode electrode.

Another very important parameter is the potential at which the polymerization is performed.

In the present paper we discuss the influence of the source supplying of monomer and of the working potential on the properties of the polycarbazole (PCZ).

2. Experimental

A classical three electrode cell (working anode, auxiliary and reference electrodes) was used. The electrochemical experiments were monitored by a potentiostat PG P 20.

The reference electrode was a saturated calomel electrode. The auxiliary electrode was a platinum counter electrode. The working electrode was a SnO_2 coated glass substrate.

As discussed before, the source supplying of monomer was either carbazole in the electrolytic solution (0.1 M) or carbazole thin films evaporated on the working electrode. PCZ samples obtained from the former monomer source were called PCZ_s and those obtained from the latter source-PCZ_{tf}. The carbazole monomer was provided by Aldrich with the purity of 99%.

The area of the working electrode was about 4.8 cm^2. The thin films of carbazole monomer were obtained by thermal evaporation under vacuum [4]. The solvent used had to be optimized in order to avoid the dissolution of thin monomer films before the initiation of polymerization.

As the thin films of carbazole are soluble in pure acetonitrile, a mixing with water was used. The optimum concentration was estimated to be 1/2 in volume ratio. 0.1 M tetraethylammonium perchlorate was used as the electrolyte. A preliminary study, by the cyclic voltammetry, showed that the working potential corresponding to the first oxidation state of the monomer was 1700 mV.

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Therefore, in order to put in evidence, the strong influence of the working potential on the polymer properties, two working potentials were used during this work: the first oxidation potential-1700 mV and an over oxidizing potential-2.5 V.

A SETARAM TGDTA 92 was used for the gravimetric thermal analysis (GTA) at the heating rate of 1 K min^{-1}. The pyrolysis head was used as the heat source for the thermal degradation. 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).

X-Ray photoelectron spectroscopy (XPS) measurements were carried out with a Leybold LHS 12 apparatus (University of Nantes – CNRS) using magnesium as the source of radiation (1253.6 eV) at 10 KV and 10 mA and the pass energy was set at 50 eV. High-resolution scans with good signal ratio were obtained in the C1s, N1s, O1s and C12p regions of the spectrum. The quantitative analysis was based on the determination of the C1s, N1s, O1s and C12p peak areas with 0.2, 0.36, 0.61 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 subtraction of the background using the Shirley method [7]. 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 were carried out without any etching of the surface because etching destroys C-N bonds and results in graphitization of the polymer surface.

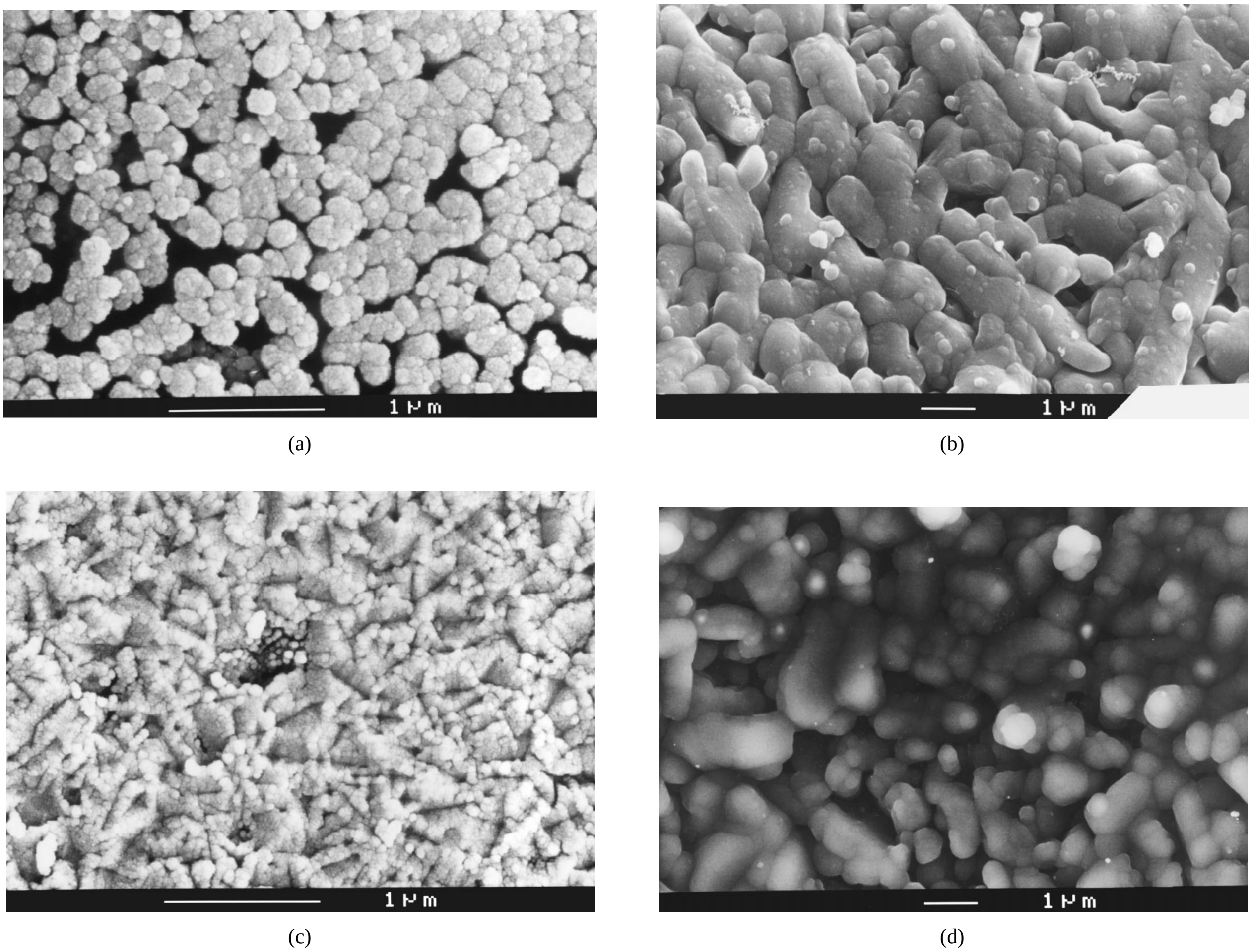
Electron spin resonance (ESR) experiments were performed at ambient temperature on a Bruker ER 200D spectrometer operating at the X band. Spin density Ns was estimated using the ESR comparison technique. The minimal sensitivity of the detector was about 10^{15} spins cm^{-3} mol^{-1}.

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

3. Experimental results and discussion

Whatever the process used after electrochemical polymerization the samples were washed with distilled water and dried for 24 h at a room temperature.

First of all, SEM microphotographs obtained in different samples are visualized (Fig. 1). It can be seen that samples obtained at 2500 mV, whatever the carbazole source supplying was, look inhomogeneous with a more or less fibrilar structure. The results are different in the case of oxidation at a working potential maximum of 1700 mV. PCZ_s thin films contain the high density of holes. The films consist in juxtaposed heaps, which look



(a) (b)

(c) (d)

Figure 1 Scanning electron microphotographs of different PVK samples. (a) PCZ_s. 1700 mV (b) PCZ_bf. 2500 mV (c) PCZ_s. 1700 mV (d) PCZ_tf. 2500 mV.

like a cauliflower. PCZ$_{tf}$ 1700 mV thin films are more homogeneous. They keep in memory the pyramid similar to the shape of the SnO_2 crystallites. It should be noted that the visible structures of the films obtained at 1700 mV are systematically far smaller than those visible in the PCZ 2500 mV films samples.

The thermogravimetric curves (not shown) exhibit a fast decrease in weight of about 3% at the beginning of the heating cycle, then a slow and continuous decrease is systematically measured. It should be noted that the small weight loss at the beginning is probably due to the loss of adsorbed water during the preparation process and it is not necessary associated with any change in the polymers structure.

The significative results are summarized in Table I. It can be seen that polymers stabilities are more or less similar, even if those obtained at 2500 mV are a little more stable.

Quantitative XPS surface analysis are given in Table II. Chlorine is systematically present mainly in the chemical state of the ClO^4 counterion, what justifies the presence of the quite high oxygen atomic concentration. Typical XPS qualitative analysis of the polycarbazoles is proposed in Table III.

The carbon peak of C1s contains three main components. The first one is situated at 285 eV can be assigned to the C-C bond [8] and it was taken as a reference. The second contribution at 286.3 ± 0.2 eV can be attributed to C-N bond in the carbazole molecule [8] but also possibly to some C^+ radicals. The third component should correspond to some surface oxygen contamination.

The decomposition of the N1s peak shows the contribution of two different chemical states. The first one corresponds to the component situated at 400 eV and it corresponds to the well known binding energy of the C-N bond [8, 9]. The second situated at about 401.5 ± 0.5 eV can be attributed to positive nitrogen $N^{\delta+}$ [10].

TABLE I Thermal gravimetric analysis

Measurement temperature	Weight loss PCZ$_{tf}$	Weight loss PCZ$_s$	Oxydation Potential
573 K	15%	20%	2500 mV
543 K	17%	15%	1700 mV

TABLE II XPS quantitative analysis

Sample	Oxidation Potential	Atomic percentage C	N	Cl	O
PCZ$_s$	2.5 v	85	5	2	8
PCZ$_{tf}$	2.5 v	85	5	4	6
PCZ$_s$	1700 mV	84	4.5	1.5	10
PCZ$_{tf}$	1700 mV	84	5.5	2.5	8

TABLE III XPS qualitative analysis

Sample		C-C	C-N	C-O$_x$	N^{s+}	C-N
PCZ$_s$	Binding Energy (eV)	285*	286.5	288.2	402	400.3
	Relative at %	80	13	7	15	85
PCZ$_{tf}$	Binding Energy (eV)	285	286.3	281.3	401.2	400
	Relative at %	85	12	3	20	80

TABLE IV Room temperature ESR and σ measurements

	Oxidation potential	g	Δ Hpp (G)	Ns (Spins mole^{-1} g^{-1})	σ (Ω^{-1} cm^{-1})
PCZ$_s$	2.5 v	1.9998	3	2-7 10^{20}	2.5 10^{-12}
		2.000	8	2-9 10^{29}	
	1700 mV	2.0017	3.1	1.36 10^{20}	5 10^{-7}
PCZ$_{tf}$	2.5	1.9998	2.8	7.2 10^{20}	2 10^{-11}
	1700 mV	2.0029	2.6	2.91 10^{22}	1.5 10^{-5}

The electron spin resonance (ESR) and the conductivity (σ) measurements are summarized in Table IV.

It can be seen that, while the values deduced from the ESR measurements do not differ much, the conductivity of the sample synthesized at 1700 mV is at least 6 order of magnitude higher than the one for those obtained at 2500 mV. A more careful look allows to see that the electron spin density and the conductivity measured in PCZ$_{tf}$ are higher than those of PCZ$_s$.

Usually in semiconductor polymers, such as those studied in the present work, the conductivity increases with the polaron density, this density corresponding to the spin density, since for such low conductivity bipolarons are improbable. However, this is not the case here. Moreover, XPS decomposition does not give significant differences between the two polymer families (1500 mV, 2500 mV). The $N^{\delta+}$ and the possible $C^{\delta+}$ contribution are not very different.

The conductivity is not only related to the carrier density, which appears to vary far less than the conductivity (Table IV), but also to the mobility of these carriers. The longer the polymer chain length is the higher the carrier mobility.

One way to estimate the chain length is the weight loss measured by thermogravimetry. Usually the stability of the polymers increases with their chain length and, therefore, the weight loss increases as the chain length decreases.

It can be seen (Table I and Table II) that the less the polymers are conductive the more they are stable. Therefore, the conductivity variation cannot be explained in this simple way. The stability (weight loss when the temperature increases) of the polymers is not directly related to its chain length but to its molecular weight. Therefore, reticulated polymers can be more stable but less conductive than a really conjugated polymer.

The difference between the two polymer families studied is their working potential:

– 1700 mV, which corresponds to the first oxidation potential of the monomer.
– 2500 mV, which corresponds to an over oxidation potential of the monomer.

For an anode with an over oxidizing potential, electrolysis could lead to a polymer with a higher oxidation level, possibly irreversibly with a low conductivity [3].

The obtaining of a non conductive material could be due to a chain reticulation beyond the first oxidation potential value with the loss of the flexibility of the chain and the steric hindrance to the mobility of the carrier. The overpotential could lead to further irreversible oxidation of the matrices giving rise to less conjugated systems. Such rigid reticulated but poorly conjugated polymer, if stable, will be poorly conductive. This is the case of the polymers synthesized at the working potential of 2500 mV, they are stable and poorly conductive because they are reticulated and their carriers are strongly localized.

Polymers synthesized at 1700 mV are not over oxidized, they are conjugated even if they are not more stable. Their carriers, even if not more numerous have higher mobility and the conductivity of these polymer is far higher. These hypothesis are conforted by SEM microphotographies, where it can be seen that, if larger structures are visible in the films obtained at 2500 mV they are disordered and intertwined.

However, these polymers are only semiconductive and not conductive polymers.

During oxidation the cation radicals will be formed on the carbons possessing the highest impaired electronic density. This allows to predict the polymerization at the most probable sites. However, when there are many carbons in the monomer with small differences of their impaired electronic density, which is the case of carbazole monomer, the probability of non linear polymerization is greater, limiting the conductivity, as discussed before.

Therefore, it appears difficult to overpass some limits of the conductivity of electrochemically synthesized polycarbazole.

As for the different monomer source, it can be seen that the conductivity of PCZ_{tf} is slightly better, what could be related to a better polymerization efficiency caused by some geometrical reasons. The thin carbazole films are in a direct contact with the SnO_2 surface rugosities, what induces a high density of nucleation centers what consequently allows better polymerization homogeneity in comparison with the classical process, where the initiating center density is smaller. The main advantage of the thin film source is, therefore, the high homogeneity of the film after synthesis (Fig. 1), which is promising for the device application, such as DEL. Probably the electrochemical reaction in thin films takes place at the defects, such as pinholes, grain boundaries, which facilitates some diffusion of the electrolyte at the "working electrode/monomer layer" interface.

4. Conclusion

Polycarbazole, when electropolymerized in over oxidation conditions, is nearly insulating even if a high spin density is measured by ESR. The polymer is reticulated and the carriers are localized when obtained at the oxidation potential of the monomers, the PCZ is conjugated, the mobility of the carriers is better and the conductivity is far higher.

Very homogenous films can be obtained when carbazole is pre-evaporated on the working electrode, which is very promising for the OLED application.

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