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Electropolymerization of N-vinylcarbazole in the presence of Galvinoxyl

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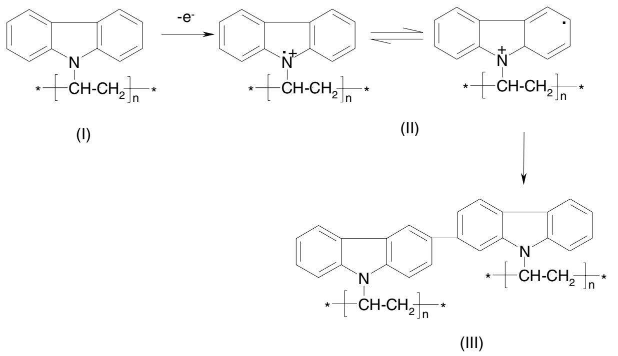
Summary

The electropolymerization process of N-vinylcarbazole in anhydrous medium in the presence of 2,6-tert-butyl-a-(3,5-di-terbutyl-4-oxo-cyclohexadien-1-ylidene)-p-tolyloxy (Galvinoxyl), stable nitroxide radical, was studied. Electrolysis of the monomer at constant potential in the presence of Galvinoxyl, generated an adduct between both species. In order to corroborate the structure of the products, they were separated from the electrolytic medium by chromatography and then characterized using UV-vis, ^{1}H-NMR and ^{13}C-NMR spectroscopy, and elemental analysis. The adduct turned out to be a stable species formed by the union of the nitroxide radical to the vinyl group of the monomer. Blocking of this polymerization site allows, by further electro-oxidation, the selective formation of the green polymer, which corresponds to a polymer obtained by the link through crabons of the aromatic rings of the monomer, i.e., through a site that is not very reactive. Thus, we have a simple and swift aletrnative to produce *in situ* the appropriate precursor to obtain a deposit whose structure and electrochemical response may be useful for the development of sensors. In addition, the possibility that Galvinoxyl being able to "trap" the radical species generated by electro-oxidation of the monomer, affordds a better control upon the electropolymerization process, and, consequently, upon the morphology of the respective deposit. This approach was corroborated by scaning electron microscopy (SEM) which demonstrated that the surface is much more homogeneous when the polymer is obtained from the adduct between N-vinylcarbazole and Galvinoxyl.

Introduction

Recently, many studies have been conducted concerning the application of conductive polymers.The applicability of such polymer depends on their properties, such as catalysis, protection of materials, micro-electronics, photovoltaic cells, diodes, etc.[1-3]. Special interest exists on those polymers bearning groups that may confer them utility as electro-chromic devices, potentiometric or amperometric sensors, and so on [4-6]. Poly(N-vinylcarbazole) (PNVK), usually employed in electro-chromic displays and electroluminescent devices, has been amply investigated because its oxidized form presents a deep-green color, whereas the reduced form is white [7-9]. The deep-green color of the deposit is the result of the oxidation of white PNVK, following the stages depicted in scheme 1:



Scheme 1. Oxidation of polyN-vinylcarbazole mechanism

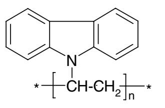
On the other hand, it has been demostrated that the electropolymerization is produced through a radical mechanism that yields a mixture of oligomers in the proximity of the electrode [10], leading to a greater poly-dispersion of the deposits generated in this way. Based upon data related to living radical polymerization [11,12], where the use of stable nitroxide radicals, such as Tempo and Galvinoxyl, allows the polimerization to be controlled originating a great decrease of the polydispersion, the effect of Galvinoxyl on the electropolymerization of N-vinylcarbazole in non-aqueous medium will be dealt with in the present paper.

Experimental

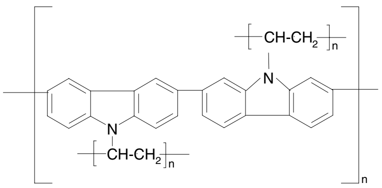
All chemicals were purchased from Aldrich and were used as received. Solutions were deoxygenated by flushing with high purity argon. An argon blanket was kept during all the electrochemical experiments. A conventional three-electrode electrochemical cell was employed for the electropolymerization and electrochemical characterization of the polymers, and the data was collected on a VoltaLab PGZ 50 system. The working electrode was a disc or a sheet made of AISI 316 stainless steel (SS), with a geometric surface area of 0.07 cm^2 and 8 cm^2, respectively. Before use, the working electrode was polished to a mirror finishing on a piece of cloth using alumina slurry of 0.3μm particle size, and finally rinsed with distilled water and acetonitrile. The auxiliary electrode was a platinum wire. All potentials quoted in this paper are referred to Ag/AgCl electrode in tetraethylammonium chloride to match the potential of a SCE at room temperature [13]. The concentration of the monomer, Galvinoxyl, and supporting electrolyte (tetraethylammonium hexafluorophosphate, $TEAPF_6$) used throughout this work were 0.01, 0.01 and 0.05 $mol\cdot dm^{-3}$, respectively. Cyclic voltammetry (CV) was utilized for the electrochemical characterization while the adduct formation and polymerization were performed either by CV or at constant potential under experimental conditions to be specified further on. UV-vis spectra were recorded on an Analytik Jenna, Model Specord 40 spectrophotometer, with 1mm cells. Elemental analysis of C, H, O, N and S and SEM were run on a Leo 1420 VP, Leo Microscopy Ltd. NMR spectra were recorded on a Bruked Model ACP 200 spectrometer.

Results and Discussion

It is noteworthy first of all that the study must be carried out in a strictly anhydrous medium to ensure the stability of Galvinoxyl. Consequently, the electrochemical characterization of all the species was previously performed under water-free solution containing the monomer and supporting electrolyte. Two oxidation peaks are observed, ascribed to polymerization through the vinyl group, peak I at 1100mV:



and peak II at 1200 mV, corresponding to the polymerization due to the link through carbon-3 of the aromatic ring:



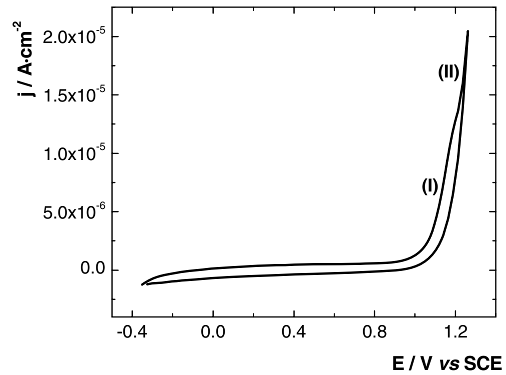


Figure 1. Successive potentiodynamic scans. Interface: SS/0.01mol·dm^{-3} N-vinylcarbazole + 0.05 mol·dm^{-3} TEAPF$_6$ in CH$_3$CN. Scan rate: 10 mV·s^{-1}

These peaks have been described in the literature mentined above [7-9]. A continuous increase in current on successive scans was observed that provokes a progressive increase in the thickness of the polymeric film deposited on the electrodic surface. In addition, the peak potential shifts to more cathodic values attributed to an increase in conjugation as the chains grow, facilitating thus the oxidation.

Transients obtained by applying a potential step perturbation program, Fig. 2, show that a deposit is formed only at potentials above 1100 mV. Below this value, just the exponential drop of the current is observed whereas above 1100 mV an increase of current due to nucleation [14] is obtained. In such a case a continuous growth of the deposit, now as function of the applied potential step duration, is observed too.

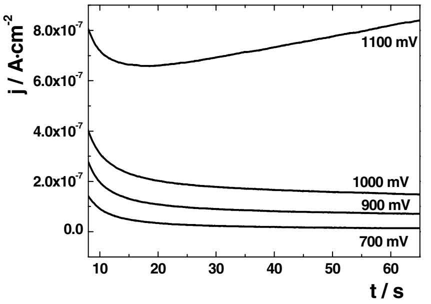


Figure 2. Potentiostatic transients. Conditions as in Fig. 1

On applying the potential step to the SS electrode inmersed in the working solution of Fig. 2, a considerable amount of a white deposit, insoluble in the commonest organic solvents, is formed. Figure 3 shows a SEM micrograph of the surface of the deposit obtained under the above mentioned conditions. The deposit, a little irregular, is mainly made of granules, but filaments that form once the electrode is fully coated with the polymer, are observed as well. In other words, the deposit originates from different types of nuclei [14].

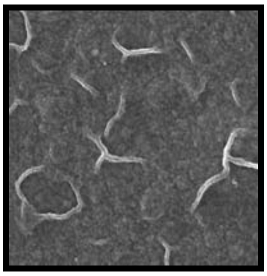


Figure 3. Micrograph of the poly(N-vinylcarbazole) deposit obtained by potentiostatic method at 1100 mV under conditions of Fig. 1

As far as the characterization of Galvinoxyl is concerned, the electro-oxidation of 0.01 mol·dm^{-3} on SS, using 0.05 mol·dm^{-3} TEAPF$_6$ as supporting electrolyte, and CH$_3$CN as solvent, proved that a potential window from -500 to 1200 mV only produces residual current. At potential higher than 1200 mV the current begins to increase due to Galvinoxyl oxidation, which sets the limit of the anodic potential to be used in the presence of this compound. Other conventional materials, such as gold or platinum, utilized as working electrode turned out to catalyze the oxidation of Galvinoxyl, which now takes place at quite lower anodic potentials, making these materials unsuitable for the purpose of the present investigation. On the other hand, working in anhydrous conditions, allows working within this potential range, because in the presence of water the anodic limit diminishes (electrolyte discharge occurs at lower potential).

With these observations in mind, we proceeded to the potentiostatic electrolysis of a solution containing equal molar concentrations of the monomer and nitroxide radical. The largest SS electrode was employed as working electrode, and the constant potential was 1100 mV. The transient obtained in this case, Fig. 4, indicates the lack of the nucleation that would be expected at the same potential in the absence of Galvinoxyl. However, a reaction do exists because a distinctive change in color, from very dark deep-red to pale yellow, occurs when the residual current is achieved after more than three hours of electrolysis, respectively, shows the disappearance of the absorption peak at *ca.* 430 nm, characteristic of free-Galvinoxyl in solution.

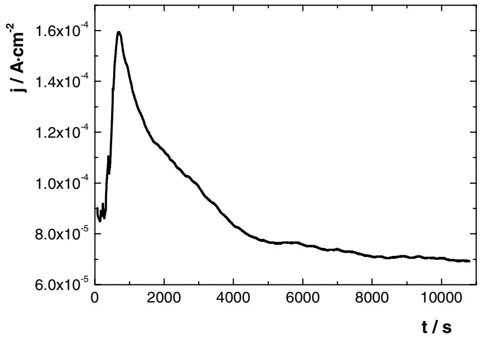


Figure 4. Potentiostatic transient at 1100 mV. Conditions as for Fig. 1, +0.02 mol·dm^{-3} Galvinoxyl

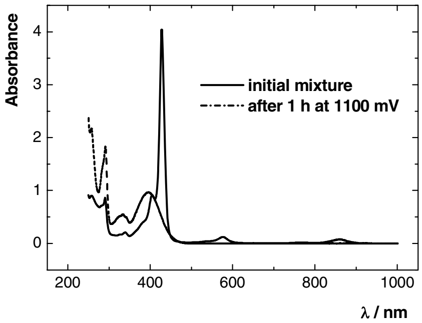


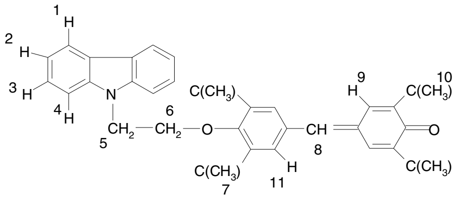
Figure 5. UV-vis spectrum of the electrolyte in Fig. 4, before and after the application of 1100 mV potential step for 1h

Concomitantly, the reaction was followed by thin-layer chromatography using n-hexane/ethyl acetate (6:1) as eluent. The disappearance of the starting materials and the formation of a new product was observed. Once the electrolysis was over, the new substance, that from now on will be called "adduct", was quantitatively isolated utilizing thin-layer preparative chromatography using the same eluent. Table 1 summarizes R_f values for reactants and the adduct. In order to dry the product, soluble in CH_3CN and other common organic solvents, the solvent was evapored in a rotatory evaporator at a temperature below 50° C to avoid decomposition.

Table 1. R_f values of the products studied, using n-hexane: ethyl acetate 6:1 as eluent on silic

Product	N-vinylcarbazole	Galvinoxyl	adduct
R_f	0.7	0.60; 0.85(0xid.)	0.51

Once purified, the adduct was characterized by elemental analysis, Table 2, ^{1}H-NMR and ^{13}C-NMR. From these results the following structure was suggested, Scheme 2.



Scheme 2. Structure of the adduct obtained by reacting NVK and Galvinoxyl and numbering for ^{1}H-NMR

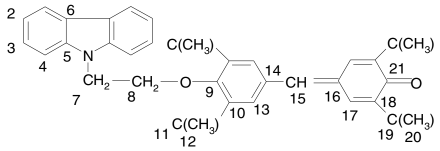
Table 2. Elemental analysis of the adduct formed by reacting NVK and Galvinoxyl

Component	Theorical	Experimental
Nitrogen (%)	2.28	2.32
Carbon (%)	84.18	84.08
Hydrogen (%)	8.32	8.24
Sulphur (%)	-	-
Oxigen (%)	5.22	5.24

Table 3 summarizes the signals of the ^{1}H-NMR spectrum for the adduct based upon the numbering indicated in Scheme 2.

Table 3. ^{1}H-NMR signals of the adduct formed by reacting NVK and Galvinoxyl

Signal	δ (ppm)
1	8.2
2	7.2
3	7.0
4	7.8
5	3.5
6	3.6
7	2.9
8	6.2
9	8.6
10	1.3



Scheme 3. Structure of the adduct labeling for ^{13}C-NMR

Table 4 shows the ^{13} C-NMR signals assigned following the labeling in Scheme 3.

Table 4. ^{13} C-NMR signals of the adduct formed by reacting NVK and Galvinoxyl

Signal	ppm	Signal	ppm
1	112.343	12	30.372
2	112.043	13	124.179
3	120.545	14	121.121
4	111.110	15	126.292
5	131.491	16	125.636
6	119.571	17	124.624
7	35.498	18	136.202
8	63.097	19	35.087
9	141.750	20	29.605
10	126.635	21	153.989
11	29.988		

After purification and characterization of the adduct, that corroborates the proposed structure, electrochemical characterization was performed using cyclic voltammetry. Only one peak was observed at 1200 mV corresponding to the oxidation process. Now we proceed to electrolyze NVK at this potential, whereupon a large amount of the green product was deposited on the working electrode. Figure 6 is a micrograph of the deposit obtained in these conditions and shows the marked morphological difference of the deposit with that depicted in Fig. 3, when the polymer was generated in the absence of Galvinoxyl.

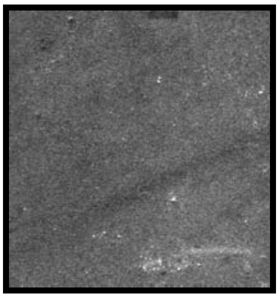


Figure 6. Micrograph of poly(N-vinylcabazol) deposited in the presence of Galvinoxyl

The electrochemical response of this film in a solution containing just the supporting electrolyte presents a wide electrochemical range, in which no redox process at all is observed. This feature makes the material promising for the development of electrochemical sensors. Besides, the substance presents high stability to enviromental conditions, and its morphology may provide more “orderly” deposits when the process of electropolymerization is controlled by the use of these nitroxide radicals. Furthemore, improvement and/or control the macroscopic properties are expected. Presently, we are studying the feasibility of carrying on the polymerization by cleavage of the adduct reported herein.

Conclusions

Oxidation of N-vinylcarbazole in the presence of Galvinoxyl allows the generation of an adduct between both species that blocks further polymerization of the vinyl moiety, this permits the polymerization to be performed through carbon-3 of the rings, yielding a green polymer with a more homogeneous and compact surface that the one obtained by straight polymerization of the monomer, i.e., in the absence of Galvinoxyl. Consequently, it is possible to have a method that, avoiding a previous synthesis, generates *in situ* the appropiate species to be polymerized through rather un- reactive unions. Furthermore, adduct formation predicts the feasibility of "trapping" the radical species generated during the electropolymerization process. This may be a suitable route to decrease polydispersity, which is common when these polymers are prepared by electrochemical means.

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References

[1] X. G. Li, L. Kresse, J. Springer, J. Nissen, Y. L.yang, *Polymer*, 42 (2001) 6859.

[2] A. J. Heeger, *Synthetic Metals,* 125 (2002) 23.

[3] M. Tejos, R. Schrebler, F. R. Díaz, M. A. del Valle, *Thin Solid Films*, 409 (2002) 172.

[4] M. A. del Valle, F. R. Díaz, M. E. Bodini, T. Pizarro, H. Gómez, R. Córdova, R. Schrebler, *Journal of Applied Electrochemistry,* 28 (1998) 943.

[5] M. A. del Valle, G. M. Soto, L. Guerra, J. H. Vélez, F. R. Díaz, *Polymer Bulletin*, 51 (2004) 301.

[6] J. P. Soto, F. R. Díaz, M. A. del Valle, C. M. Núñez, J. C. Bernéde, *Polymer Bulletin,* 54 (2005) 85.

[7] A. Desbene- Monvemay, P. C. Lacazew, J. E. Dubois, *Journal of Electroanalytical Chemistry*, 152 (1983) 87.

[8] F. J. Davis, H. Block, R. G. Compton, *Journal of Chemical Society, Chemical Communications*, (1984) 890.

[9] S. N. Bradani, *Journal of Applied Polymer Science*, 42 (1991) 1271.

[10] M. A. del Valle, F. R. Díaz, M. E. Bodini, G. Alfonso, G. M. Soto, E. Borrego, *Polymer International*, 54 (2005) 526.

[11] H. Fischer, *Chemical Reviews*, 101 (2001) 3581.

[12] C. J. Hawker, A. W. Bosman, E. Harth, *Chemical Review*, 101 (2001) 3661.

[13] G. A. East, M. A. del Valle, *Journal of Chemical Education*, 77 (2000) 97.

[14] M. A. del Valle, L. Ugalde, F. R. Díaz, M. E. Bodini, J.C. Bernéde, A. Chailou, *Polymer Bulletin*, 51 (2003) 55.