# Controlled Growth of Poly(*N*-vinylcarbazole) Films on Pt by Scan Technique Electropolymerization of *N*-Vinylcarbazole

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The growth of poly(*N*-vinylcarbazole) films during the electrochemical oxidation of *N*-vinylcarbazole at a Pt electrode in MeCN by repeated potential scans is controlled by the number of redox cycles and the choice of anion in the supporting electrolyte; for various anions studied ($ClO_4^-$, $BF_4^-$, $PF_6^-$, $AsF_6^-$, and $SbF_6^-$) polymer film thickening is proportional to the number of cycles, and increases as the radius of the anion associated with the doped form of the polymer decreases.

We recently demonstrated that it is possible to obtain homogeneous poly(*N*-vinylcarbazole) (PVCz) films by electrochemical oxidation of *N*-vinylcarbazole (VCz) on Pt[1] and reported their electrochromic properties.[2] Shirota *et al.* have determined that the conductivity of PVCz films obtained by electropolymerization[3] is slightly lower than that of electrochemically doped forms of polymer films chemically deposited on Pt.[4] In view of current interest in thin layers of these materials,[5] we show herein that it is possible to control the thickening of PVCz films during the electrochemical oxidation of VCz by choosing the appropriate electrolyte while conducting repeated potential scans between +1 and −0.8 V *vs.* Ag–Ag$^+$.

During the oxidation of VCz at a Pt electrode in MeCN in the presence of $NBu_4ClO_4$, $NBu_4BF_4$, $NBu_4PF_6$, $NaAsF_6$, $NaSbF_6$, $NaClO_4$, or $PhCH_2NMe_3ClO_4$ salts, the growth of the oxidation and reduction waves (Figure 1) is regular, as in the electropolymerization of other vinyl derivatives.[6] The intensity of the cathodic peak D ($i_D$) and the amount of electricity measured in reduction ($Q_{red}$) vary linearly with the number of redox cycles $n$. The variation of $i_D$ with $n$ is represented in Figure 2.† Moreover, $i_D$ is proportional to the interferometrically determined thickness of the reduced layer.‡ The numerical expression of this linear regression, established for cyclic scans between +1 and −0.8 V *vs.* Ag–Ag$^+$ conducted at 100 mV s$^{-1}$, $e$/nm = 125 $i_D$/(mA cm$^{-2}$) with a correlation coefficient of 0.97, refers to all counter-ions studied. The thickening of these films, which begins with the formation of dicarbazolyl radical cations (wave A) and ends with their electrochemical reduction (wave D), is the result of cationic polymerization. Film growth increases as the anions associated with the oxidized form of the polymer decrease in size (Figure 2); it varies from 35 nm/cycle for the $ClO_4^-$ counter-ion to 2.5 nm/cycle for $SbF_6^-$. In contrast, the rate of growth of the films at the electrode surface is unaffected by the nature of the cation present in the supporting electrolyte. Similar results have been noted for $NBu_4ClO_4$, $PhCH_2NMe_3ClO_4$, and $NaClO_4$. Thus, the rate of growth of PVCz films on Pt appears to be limited by the rate of migration of the anions assuring electroneutrality during the modification of charges on the polymer films which are alternately and successively oxidized and reduced.

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† The $i_D$ value was used in correlations because it is more easily and quickly measured than $Q_{red}$ which requires integration. The value of $i_D$ was practically the same before and after film thickness measurements in the solution with the monomer and in the monomer-free solution.

‡ Film thickness was determined with a Leitz Metalloplan microscope equipped with a Tolansky interferential device with a sodium vapour lamp (λ 589 nm) that generates fringes at intervals of 295 nm. These fringes shift when a film is present (only shifts greater than 1/10th of the interval between fringes are visible with the Leitz–Tolansky light device which can be used to measure PVCz films up to 600 nm thick with ±30 nm accuracy).

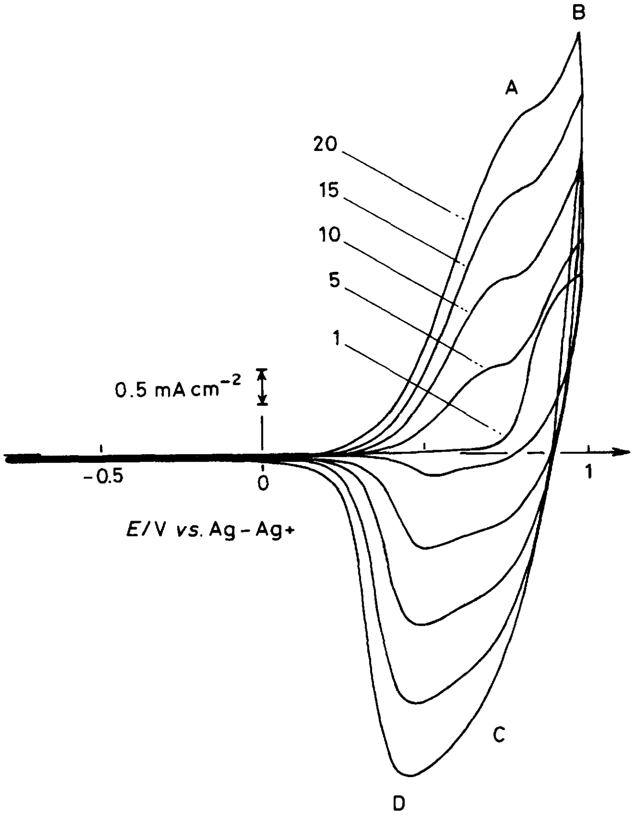

**Figure 1.** Film growth on Pt during repeated potential scans between +1 V and −0.8 V *vs.* Ag–Ag$^+$ (scan rate: 100 mV s$^{-1}$) in MeCN + $NBu_4ClO_4$ ($10^{-1}$ M) + VCz ($6 \times 10^{-3}$ M).

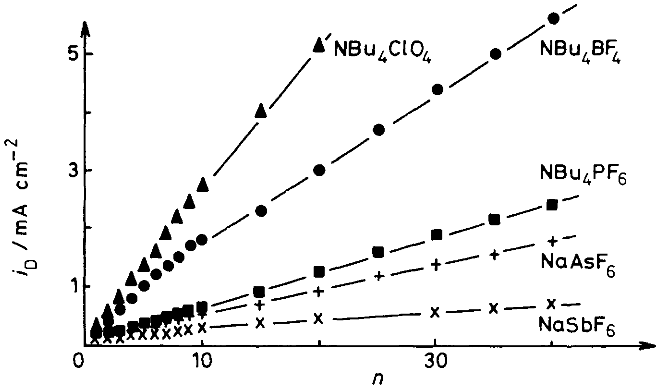

**Figure 2.** Intensity of reduction wave D *vs.* number of redox cycles.

This method is particularly simple for obtaining films with a given thickness. In comparison to electropolymerization conducted at a constant potential,[1,3] scan technique electropolymerization markedly improves the uniformity of deposits (visible with a metallograph microscope) and the adhesiveness of films (confirmable resistance to the Scotch 'yank-test'), thereby extending the range of applicability for PVCz films.

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