Spectrofluorimetric study of electrosynthesized and chemically prepared poly(*N*-vinylcarbazole) films

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(*Received 2 September 1987; revised 29 October 1987; accepted 6 November 1987*)

A spectrofluorimetric method is proposed for the study of chemically prepared and electrosynthesized poly(*N*-vinylcarbazole) (PVCA) films on Pt thin layers. Solid-state fluorescence excitation and emission spectra of PVCA are obtained at room temperature. The effects of electrochemical doping and polymer film growth on fluorescence spectral properties are investigated. ClO_4^- electrochemical doping of PVCA films causes fluorescence quenching. *In situ* measurements of the changes in fluorescence intensity of PVCA films during electrochemical cycles are described. The sensitivity of the spectrofluorimetric method is very high for the quantitative determination of polymer films, with a detectable minimal mass of about 2.5×10^{-10} mol cm^{-2} of PVCA, corresponding approximately to the equivalent of a monolayer.

(Keywords: spectrofluorimetry; fluorescence; electropolymerization; poly(*N*-vinylcarbazole); thin film)

INTRODUCTION

During the last 10 years, electrogenerated polymer films have attracted a growing interest because of their electrical conductivity properties and of the wide range of possible applications (electrochromism, electrocatalysis, etc). The electrosynthesis of poly(*N*-vinylcarbazole) (PVCA) films has recently been performed, in both oxidized and neutral forms, by electropolymerizing the monomer species in organic solution[1,2]. Several spectroscopic methods such as i.r., e.s.c.a., e.p.r. (*ex situ*), or u.v.-visible absorption (*in situ*) have already been used for studying the structure of PVCA films formed on Pt surfaces[1]. Recently, luminescence spectroscopy has appeared as a method for the investigation of polymer thin films, because of its high sensitivity, and its potential usefulness for the determination of polymer microstructure[3]. However, it has practically not been applied to electrosynthesized polymers, with the exception of a recent report concerning the photoluminescence quenching in poly(thiophene) films by electrochemical doping[4].

The luminescence properties of PVCA chemically prepared by various film-forming procedures (cationic or free-radical polymerization) have been extensively investigated[5-14]. Several authors have shown that polymerization conditions such as temperature, mode of preparation, and thermal treatment of sample films resulted in important changes of the fluorescence and phosphorescence spectral characteristics of PVCA films, due to modifications of their structure[6,12-14]. The goal of the present work is to compare the room-temperature fluorescence properties of electrosynthesized and chemically prepared PVCA, and to study the effect of electrochemical doping and growing thickness of these films on fluorescence. We will also report *in situ* measurements of fluorescence in PVCA films during electrochemical cycles.

EXPERIMENTAL

Chemicals

N-vinylcarbazole (Fluka, pure) and poly-(*N*-vinylcarbazole) (Aldrich, secondary standard), were used as received. Tetrabutylammonium perchlorate (Fluka, pure) was dried under vacuum at room temperature. Acetonitrile (Aldrich, spectrophotometric grade) and dichloromethane (Aldrich, h.p.l.c. grade) were utilized as solvents.

Instrumentation

Electrochemical and spectrofluoroelectrochemical measurements were performed with a Princeton Applied Research (PAR) Model 173 potentiostat driven by a PAR model 175 pilot, using a SEFRAM Model TGM 164 X-Y recorder. For the electropolymerization of films, an electrochemical cell with a classical three-electrode mounting was used. The working electrode was made of a rectangular glass slide (10 × 70 mm). One of its faces was coated with a platinum thin layer (about 300 nm) deposited by cathodic sputtering, using a Balzers-Sputron II with a platinum target (Balzers, purity 99.9%). The counter electrode was a platinum grid. The reference electrode was Ag/Ag^+ (10^{-2} M) in acetonitrile. For spectrofluoroelectrochemical *in situ* measurements, a laboratory-built Teflon top holding a three-electrode assembly was inserted into a quartz 10 × 10 mm rectangular cuvette. The electrode assembly included a deposited platinum thin layer rectangular glass slide as

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working electrode, a Pt wire as counter electrode, and an Ag wire as a pseudo-reference electrode. The excitation beam was at 45° to the platinum electrode.

Spectrofluorimetric measurements were carried out with a Perkin–Elmer Model LS-5 luminescence spectrophotometer equipped with a Perkin–Elmer model R100A recorder, using the front-surface accessory for *ex situ* studies, and the standard four-position turret cell holder for *in situ* measurements.

Procedure

The chemically deposited films were prepared by spotting a dichloromethane solution of PVCA (1–5 μl) on platinum-coated glass slides. The slides were placed in a desiccator under an argon stream at room temperature in order to achieve slow evaporation of the solvent. Concentrations of PVCA solutions used were between 10^{-1} M and 10^{-5} M.

The electropolymerized films were obtained by cyclic potential scans in acetonitrile solution of $6 \cdot 10^{-3}$ M *N*-vinylcarbazole with 10^{-1} M $(Bu)_4NClO_4$. The polarization of the platinum-coated electrode was performed at a speed of 100 mV s^{-1}, between +1.0 V and −0.8 V *vs.* Ag/Ag$^+$. For *in situ* studies, the scan speed was reduced to 20 mV s^{-1}, in order to assure simultaneous electrochemical and spectrofluorimetric measurements.

RESULTS AND DISCUSSION

Fluorescence excitation and emission characteristics

The fluorescence excitation and emission spectra of chemically deposited and electropolymerized PVCA films on thin-layer Pt plates are shown in *Figures 1* and *2*. The electrosynthesized PVCA films were prepared in a monomer solution by submitting the Pt electrode to two successive cyclic potential scans which were stopped at a reducing potential value of −0.8 V (corresponding to the neutral form). It can be seen that the excitation spectra of both types of PVCA films occur in the same region, between about 250 nm and 360 nm, and present a fine vibrational structure, which is better resolved in the case of the chemically prepared polymer. Indeed, the latter compound has well-defined excitation maxima at 240, 255, 280, 306, and 350 nm. The excitation spectrum of PVCA recorded in dichloromethane solution is distinctly different from the film excitation spectrum, since it presents a broad band with only two maxima at 280 and 335 nm. This important difference in the spectral behaviour could be due to the existence in the solid state of several intermolecular excited-state associations, of varying configurations, between the PVCA chains themselves and also between the PVCA chains and Pt thin layers.

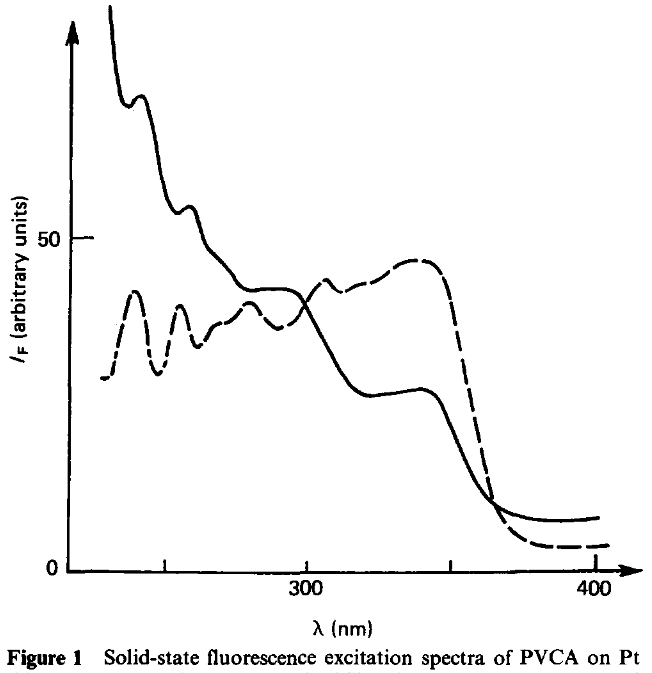

Figure 1 Solid-state fluorescence excitation spectra of PVCA on Pt thin-layers. ——, Electropolymerized film obtained after two scans and polarization at $E = -0.8$ V ($\lambda_{em} = 430$ nm); ----, chemically deposited film obtained with 200 ng of PVCA ($\lambda_{em} = 412$ nm)

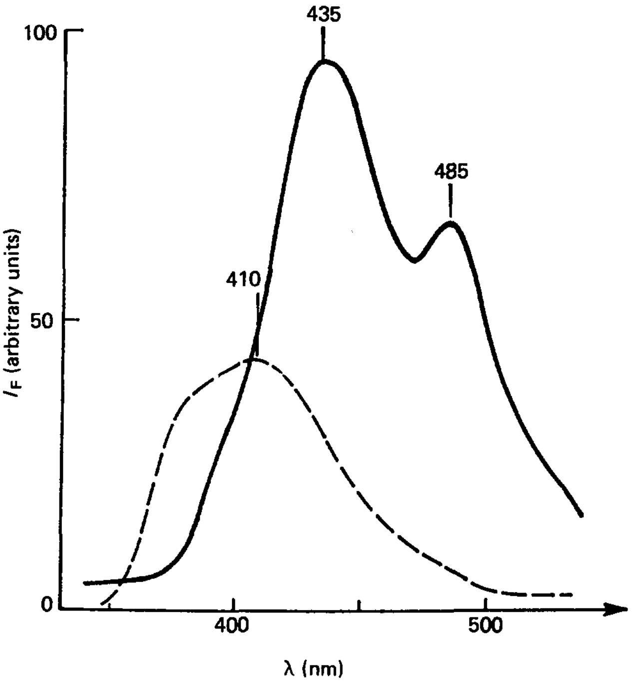

Figure 2 Solid-state fluorescence emission spectra of PVCA on Pt thin-layers. ——, Electropolymerized film obtained as in *Figure 1* ($\lambda_{ex} = 280$ nm); ----, chemically deposited film with 200 ng of PVCA ($\lambda_{ex} = 280$ nm)

In the case of the fluorescence emission spectra, the electropolymerized PVCA film has two maxima at around 435 and 485 nm, while the chemical polymer exhibits only one broad emission band at about 410 nm. The latter value is close to those found for PVCA on a Cu surface (*ca.* 420 nm)[9] or on quartz discs (*ca.* 375 and 420 nm)[12]. Therefore, in our case, a significant 25 nm red shift for the fluorescence emission maximum of the electrosynthesized PVCA film is observed relative to the chemically deposited polymer. This shift of the emission wavelength may be due to a shorter relaxation time in the singlet excited state prior to emission, in the case of the crosslinked and more rigid electropolymerized PVCA films. This observation is in agreement with the hypothesis of a cationic polymerization process which has been recently postulated by Desbene-Monvernay *et al.*[2] for the electropolymerization of *N*-vinylcarbazole.

Quenching of fluorescence by electrochemical doping

The influence of electrochemical doping of PVCA films on their emission fluorescence spectra is presented in *Figure 3*. The cyclic voltammograms observed under

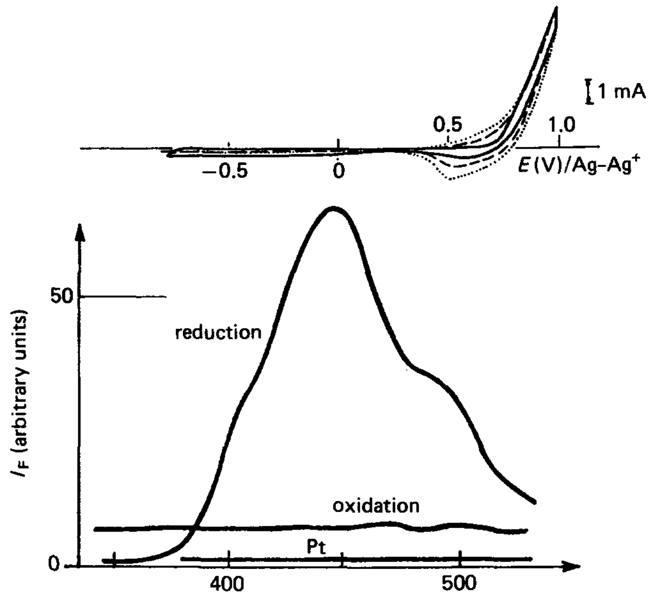

Figure 3 Effect of electrochemical ClO_4^- doping on the fluorescence emission spectra of PVCA. Reduction: spectrum obtained after stopping the potential scanning at −0.8 V; oxidation: spectrum after stopping the potential scanning at +1.0 V; Pt: fluorescence background spectrum of the naked platinum thin-layer. The voltammograms corresponding to the emission spectra are given in the upper part of the figure (see text for explanation)

anodic and cathodic scans, and leading to the formation of a polymer film at the Pt electrode surface are given in *Figure 3*. The emission fluorescence spectrum with a maximum at around 440 nm was recorded *ex situ*, in the solid state, after submitting the Pt electrode to three successive scans which were stopped at −0.8 V (corresponding to the neutral form). By stopping the scan at a potential value of +1.0 V (oxidized form), we found that fluorescence was completely quenched (see oxidation-labelled emission spectrum in *Figure 3*). This fluorescence quenching is apparently due to the electrochemical doping of PVCA films by ClO_4^- anions. However, the precise origin of this quenching phenomenon is not quite clear. The presence of mobile carriers, resulting from the formation of polarons and bipolarons in the oxidized state, providing non-radiative decay processes, may partly explain this quenching of fluorescence. Specific interactions could also occur between the oxidized PVCA films singlet excited state and diffused perchlorate counterions, producing non-radiative bimolecular deactivation processes. Very recently, a similar phenomenon was described by Hayashi *et al.*[4], who observed the quenching of photoluminescence in poly(thiophene) and poly(3-methyl thiophene) films by electrochemical doping. The fluorescence quenching effect allows differentiation between reduced (undoped) and oxidized (doped) PVCA films.

Effect of the film growth on fluorescence

We studied the effect of the number of cyclic potential scans on fluorescence properties of PVCA films. It was shown earlier[2] that PVCA film thickening occurs progressively on bulk Pt electrodes during electrochemical potential scans. The effect of the film growth on fluorescence was investigated in two ways. First, we found slight changes in the shape of the fluorescence emission spectra according to the number of redox scans and, therefore, to the thickness of the PVCA films. In particular, the second emission component at 485 nm was more or less well resolved according to the film sample considered, as can be seen by comparing emission spectra of undoped films in *Figures 2* and *3*, obtained after two and three successive scans, respectively. Until now, no precise correlation could be found between the number of scans and the relative heights of the two emission band components, which varied irregularly from experiment to experiment. Second, the change of fluorescence intensity (I_f) with the number (n) of electrochemical scans was investigated (*Figure 4*). The curve I_F vs. n is characterized by a sharp increase of fluorescence intensity, reaching a maximum value for two to three scans, followed by a decrease for four to five scans. Then, for a number of scans larger than five, the curve levels off, and I_F remains practically constant at a relatively weak value. The decrease of fluorescence intensity with the number of electrochemical scans may be due to the decreasing complete reduction of radical cation sites, and to increasing heterogeneity of PVCA films with thickening. That a significant number of oxidized (doped) sites does remain at the surface of the polymer after reduction, is supported by *ex situ* measurements performed after four to six scans. Indeed, upon applying a constant reduction potential of −0.8 V over 30 min, the I_F of PVCA films increases by about 35%. On the other hand, electron microscope analysis of PVCA samples shows that the polymer layers are less and less homogeneous when the number of electrochemical scans increases[15]. This increasing heterogeneity of films, which occurred after four to five scans, results probably from weaker interactions between PVCA layers. When the reduction of the film is performed the inner layer becomes neutral and insulating, and therefore, the reduction of the outer layer is stopped. This effect would produce a considerable decrease in the fluorescence signal.

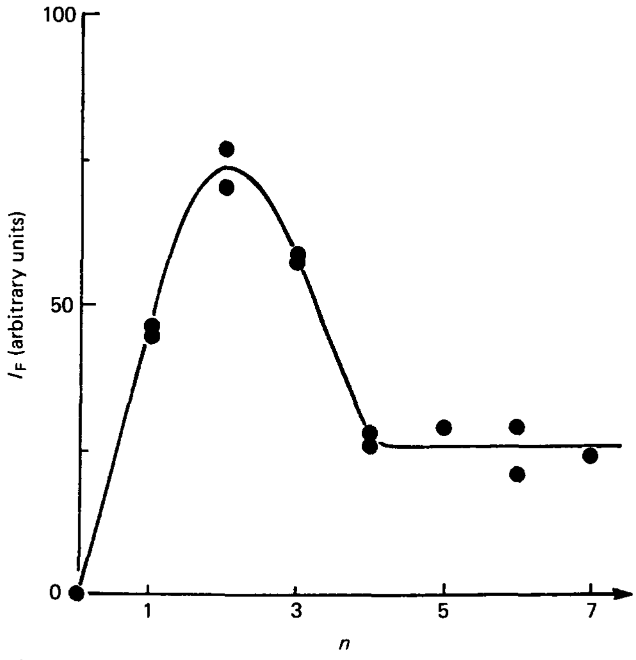

Figure 4 Effect of PVCA film growth on *ex situ* fluorescence intensity: I_F (obtained at the fluorescence maximum wavelength of 440 nm) *versus* the number of redox cycles at 100 mV s^{-1}

In situ fluorescence measurements during electrochemical cycles

A Pt thin-layered electrode, coated by a PVCA film, was submitted to a cyclic linear potential sweep in a 0.1 M $N(Bu)_4ClO_4$ acetonitrile solution. The I_F and the current intensity were simultaneously recorded as a function of the potential. *Figure 5* shows the successive fluorescence emission spectra obtained *in situ*, with an excitation wavelength of 282 nm, after successive electrochemical cycles. There is a slight blue-shift of the emission band, which is located initially at about 440 nm for the unpolarized film. *Figure 6* represents the *in situ* variation of PVCA fluorescence intensity at the emission peak of 440 nm (*Figure 6a*) and the corresponding cyclic voltammogram (*Figure 6b*). The oxidation wave of PVCA is accompanied by a decrease of I_F, when $E > 0.5$ V *versus* Ag pseudo-reference electrode, corresponding to the reaction:

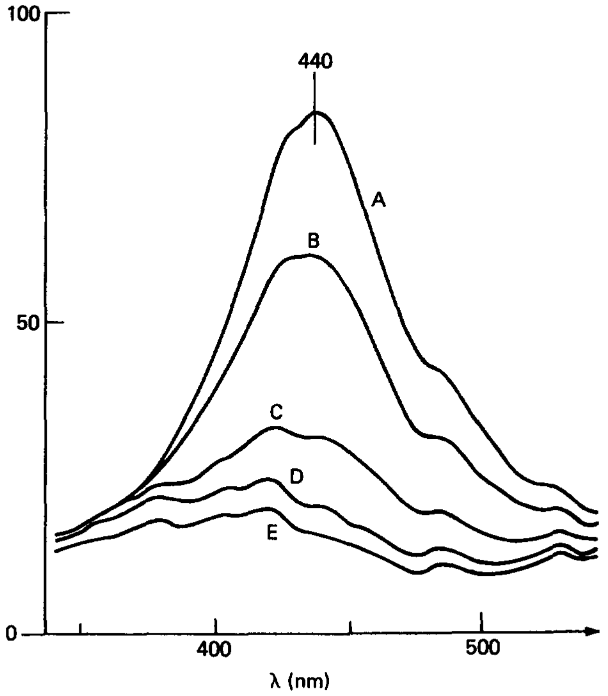

Figure 5 *In situ* fluorescence emission spectra of electropolymerized PVCA films in 10^{-1} M $N(Bu)_4ClO_4$ acetonitrile solution. A, film before polarization; B, after one scan; C, after two scans; D, after three scans; E, after four scans

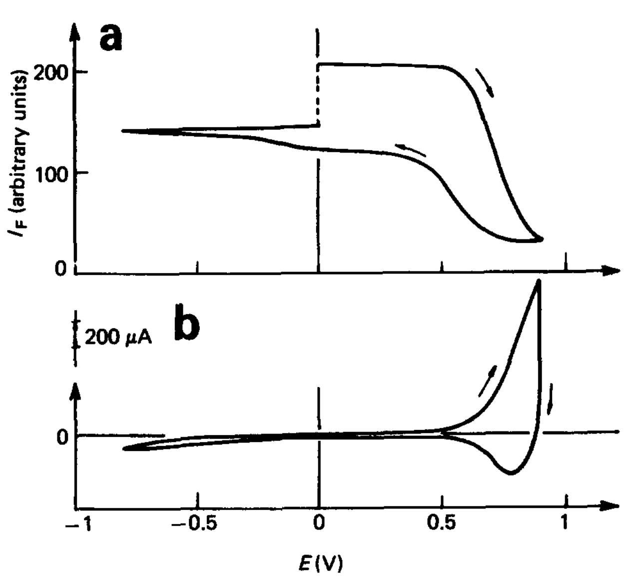

Figure 6 *In situ* spectrofluoroelectrochemical study of a PVCA film obtained after two scans and cathodic polarization ($E = -0.8$ V). (a) Variation of fluorescence intensity ($\lambda_{em} = 440$ nm) during the electrochemical cycle performed at 20 mV s^{-1}, (b) cyclic voltammogram

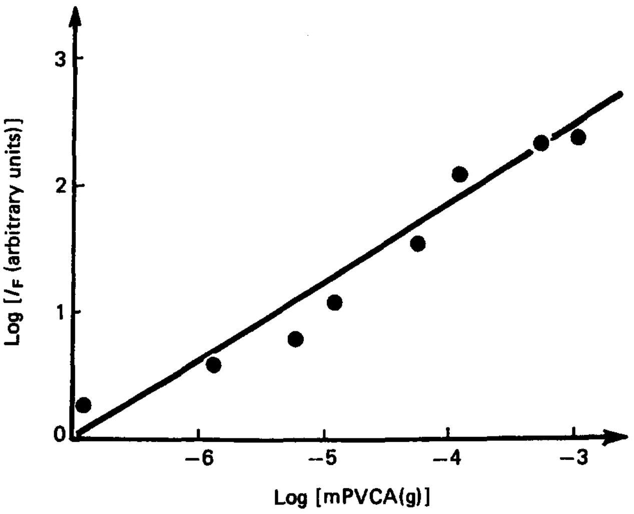

Figure 7 Fluorimetric calibration curve of chemically deposited PVCA

$$PVCA \rightarrow PVCA^{x+} + xe^-$$

Then, an increase of I_F occurs during the reduction part of the voltammogram, when $-0.3 < E < 0.5$ V, corresponding to the reversed reaction:

$$PVCA^{x+} + xe^- \rightarrow PVCA$$

but without reaching the initial I_F value. Since the doped PVCA films are much more conductive than the neutral form, the reduction process should be much slower than the oxidation one. This is in agreement with the very slow increase of I_F during the reduction wave as compared with the fast decrease of I_F occurring during the oxidation wave of the voltammogram. That the initial fluorescence intensity is not restored after completing the electrochemical cycle may be due partially to the fact that the undoping of PVCA film is not complete, and that quenching centres due to the residual presence of doping ClO_4^- anions persist in the film. Therefore, fluorescence emission can be used as a probe for monitoring *in situ* microstructural changes occurring at the surface of electrically conducting organic polymer films during electrochemical cycles. Our remarks illustrate the generality of similar conclusions reached recently in the case of electrosynthesized poly(thiophene) and poly(9-vinyl anthracene) films[4,16].

Quantitative studies

Fluorescence can also be used as an analytical tool for quantitative studies of polymer films. We tested its performance in the case of chemically deposited PVCA. The log–log fluorimetric calibration curve between I_F and PVCA mass is linear (*Figure 7*). The slope is 0.60, and its correlation coefficient ($r = 0.978$) indicates good precision. We evaluated the sensitivity of the technique. The detectable minimal mass by solid-state fluorescence is about 2.5×10^{-10} mol cm^{-2} of PVCA, which corresponds approximately to a monolayer. This detection limit was determined by evaporating a PVCA sample (1 μl) on Pt thin layers. The standard deviation of fluorimetric measurements of PVCA films deposited on

Pt thin layers is between 1.7% and 2.7% (for six measurements), according to the PVCA mass. All these analytical data demonstrate that fluorescence is a sensitive and reproducible technique for quantitating chemically prepared PVCA films. In contrast, in the case of electrochemically polymerized PVCA films, we did not obtain linear fluorimetric calibration curves. This nonlinear behaviour can be attributed to the noted increasing heterogeneity of the film structure with the layer thickness. Therefore, we can conclude that the fluorescence method should also be a valuable criterion for differentiating between homogeneous and heterogeneous polymer film structures.

CONCLUSION

The compared spectrofluorimetric study of chemically deposited and electropolymerized PVCA films demonstrates the existence of important differences in the polymer structure. The red-shift of the emission wavelength results probably from differences in relaxation time in the excited state, prior to emission, associated with the crosslinking of the carbazyl moieties in the electrosynthesized PVCA films. Fluorescence also allows differentiation between doped and undoped conducting polymers such as PVCA, and to monitor *in situ* the microstructural changes of the polymer resulting from polarization effects. Further studies concerning the fluorimetric determination of the degree of heterogeneity of PVCA films, and of the doping of these films by various electrolyte anions, are currently under way.

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