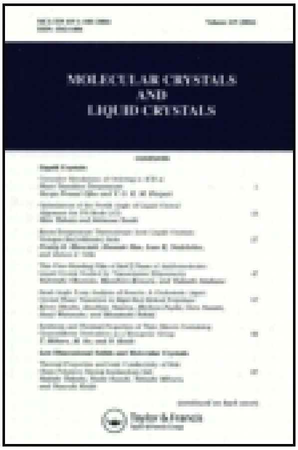

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electropolymerization of Heterocycles on Poly(Vinylch1oride) Coated Electrodes

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To cite this article: Giuseppe Casalbore-Miceli , Giancarlo Beggiato , Alessandro Geri , Anna Berlin , Giorgio Pagani , Gianni Zotti & Marco-Aurelio De Paoli (1992): Electropolymerization of Heterocycles on Poly(Vinylch1oride) Coated Electrodes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 219:1, 173-181

To link to this article: http://dx.doi.org/10.1080/10587259208032132

Mol. Cryst. Liq. Cryst. 1992, Vol. 219, pp. 173–181
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Printed in the United States of America

ELECTROPOLYMERIZATION OF HETEROCYCLES ON POLY(VINYLCHLORIDE) COATED ELECTRODES

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(Received July 12, 1991; in final form December 9, 1991)

Abstract: Processing is one of the most important problems connected with the technological use of the conducting polymers. An interesting method to obtain an utilizable material is the electrochemical polymerization of a suitable monomer on an electrode coated by an easily processable polymer film. This method was applied to several heterocycles with different molecular weights, such as dithienopyrrole (DTPY), N-methyl-10,10-dimethylphenazasiline (SIN) and [1]benzothieno[3,2-b]indole (TNI), polymerized on poly(vinylchloride) (PVC). The results of this research are described and discussed.

Keywords: Dithienopyrrole, N-Methyl-10,10-Dimethylphenazasiline, [1]Benzothieno [3,2-b]indole, Electropolymerization, Poly(vinylchloride)-coated Electrodes

INTRODUCTION

Processing of the conducting polymers is a problem strictly connected with their technological use. Positive results in the production of materials with interesting electrical features and mechanical properties typical for polymers have been obtained by electropolymerizing heterocyclic monomers on electrodes coated by a nonconducting polymer. In this way materials like polypyrrole on poly(vinylchloride)[1], polyaniline on nitrilic rubber[2], poly-thiophene on nitrilic rubber[3] have been produced.

Because many of the previously produced conducting materials are not easily processable, it seemed interesting to extend this useful electrochemical method to as many substances as possible. In this paper we have reported the results obtained by polymerizing on poly(vinylchloride)-coated electrodes some N-heterocyclic compounds: 4H-dithieno[3,2-b;2',3'-d]pyrrole (DTPY), N-methyl-10,10-dimethyl-phenazasiline (SIN), N-vinylcarbazole (VK) and [1]benzothieno[3,2-b]indole (TNI). These N-heterocycles have been choosen because, when polymerized on a platinum anode, they give products with interesting electrical characteristics: films of poly(DTPY)[4] and poly(SIN)[5] show an electrochromic behaviour, while poly(VK)[6] and poly(TNI)[7] can be used in solid state batteries.

EXPERIMENTAL

To obtain a PVC-coated ITO electrode (PVC = poly(vinylchloride), ITO = indium-tin-oxide), a low molecular weight PVC (Sigma product) saturated solution in tetrahydrofuran (THF, Merck p.a.) was evaporated on an ITO plate in a THF saturated atmosphere. The thickness of the electrode films was measured with a Tencor Alfa Step 200 profilometer. 4H-dithieno[3,2-b;2',3'-d]pyrrole (DTPY), N-methyl-10,10-dimethyl-phenazasiline (SIN) and [1]benzothieno[3,2-b]indole (TNI, thionaphthene-indole) were synthesized as described in literature (DTPY[8], SIN[9], TNI[10]). Acetonitrile (ACN, Merck p.a.) was dehydrated with $CaCl_2$, then twice distilled over CaH_2 and stored under nitrogen atmosphere. Tetrahydrofuran was used as supplied. All the electrochemical experiments were performed in 0.1M tetrabutylammonium perchlorate (TBAP, Fluka "purum") by using a multifunction Amel Electrochemolab instrument at ambient temperature in nitrogen atmosphere. The reference was a saturated calomel electrode (SCE).

The spectroelectrochemical experiments were carried out in the cavity of an UV-Vis-NIR Lambda 9 Perkin-Elmer spectrophotometer using a 3x3x1 cm^3 suprasil quartz cell with a 1 cm optical path. The counter electrode was a platinum plate, and for these experiments only a Ag/AgCl electrode was the reference. The working electrodes were polymer films of different thicknesses on ITO plates. The ITO absorbance was always subtracted from the total absorbance of the polymer coated electrode. In these experiments the iR drop was not taken into account.

RESULTS

Poly(dithienopyrrole)

Poly(dithienopyrrole) (poly(DTPY)) was synthesized on Pt and ITO electrodes and characterized as described elsewhere[4] . Cyclic voltammograms of DTPY solutions in ACN on Pt microelectrode (TBAP as the supporting electrolyte) are shown in Fig. 1A.

DTPY was polymerized by potentiodynamic method on PVC-coated ITO electrode (Fig. 1B).

Assuming that the charge to produce the polymer film is 2 electrons per monomer (e/m)[4] , the value of positive charge per monomer unit calculated from the cyclic voltammograms of the oxidized compound (Fig. 1B) is 0.58, in good agreement with the literature (0.6)[4] . Cyclic voltammograms of such a film (Fig. 2A) do not change after many cycles, from -1 V to +1.5 V.

These films show an electrochromic behaviour. Their absorption spectrum, recorded at different voltages, is reported in Fig. 2B. When examined with a profilometer, they do not show any discontinuities, and appear regular and compact. Conducting films of poly(DTPY) in PVC can also be obtained by anodic oxidation of DTPY on ITO electrode coated by PVC at +1.2 V (vs SCE). A 8 um thick film, having an area of 1 cm^2, after the flow of 1 C has a conductivity, measured by a 4 probe test, of 0.65 S cm^{-1}, one magnitude order less than that of DTPY electrolyzed on naked ITO electrode (6 S cm^{-1}).

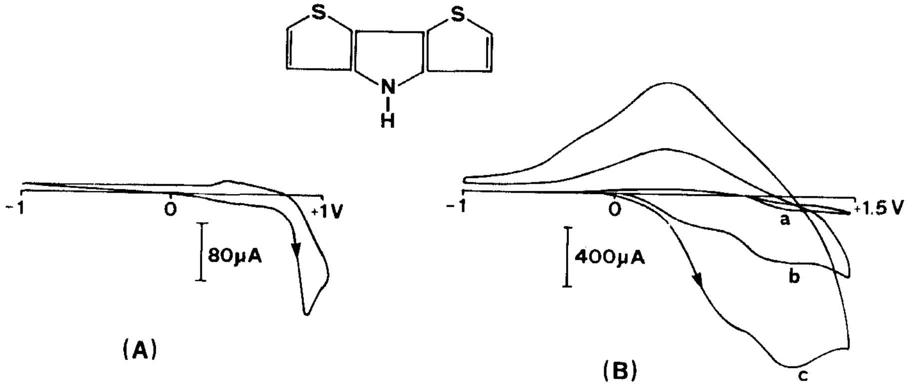


FIGURE 1 A) Cyclic voltammogram of 4.9x10^{-3} M DTPY on Pt microelectrode in ACN (0.1 M TBAP) (sweep rate : 50 mV s^{-1}).
B) Cyclic voltammograms of 4.9x10^{-3} M DTPY in ACN (0.1 M TBAP) on PVC-coated ITO electrode (0.9x0.9 cm^2) : (a) 1st, (b) 5th, (c) 10th cycle (sweep rate : 50 mV s^{-1}).

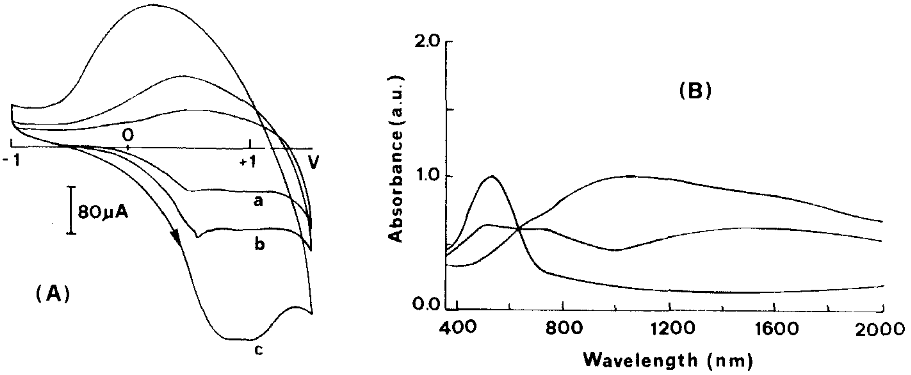


FIGURE 2 A) Cyclic voltammograms of a film of poly(DTPY) in PVC on ITO electrode in ACN (0.1 M TBAP) at (a) 10 mV s^{-1}, (b) 20 mV s^{-1}, (c) 50 mV s^{-1}.
B) Absorption spectra of a film of poly(DTPY) in PVC on ITO electrode in ACN (0.1 M TBAP) at different voltages: (a) +1.2 V, (b) + 0.4 V, (c) -0.2 V.

Poly(N-methyl-10,10-dimethylphenazasiline)

In a previous work[5] the electrochromic behaviour of a conducting film, obtained by anodic oxidation of SIN in methylene chloride, was studied. The same polymer was produced in ACN on PVC-coated ITO electrode, with TBAP as supporting electrolyte. It is worth noting that, while on Pt or ITO poly(SIN) could not be obtained by a potentiodynamic method, but only by electrolysis at +1.2 V, after an electron consumption of about 1 e/m[11]. When a PVC-coated ITO plate is used, an oligomeric film can be produced in ACN by the potentiodynamic technique (Fig. 3A). This films shows electrochromic properties; its optical spectrum, recorded at different voltages (Fig. 4), is similar to that of the polymer electrochemically deposited on naked ITO electrode[11]. The films of poly(SIN) in PVC on ITO show cyclic voltammograms in ACN (0.1 M TBAP) (Fig. 3B) very similar to those shown by films of poly(SIN) on ITO in methylene chloride (0.1 M TBAP), with the same formal redox potential (E = 0.95 V). From potentiodynamic experiments (Fig. 3A) and cyclic voltammograms of Fig. 3B, assuming a value of 2 electrons per monomer for polymer formation on PVC-coated ITO plate, a value of 1 positive charge per monomer unit in the oxidized polymer can be calculated. This is greater than that (0.6 e/m) of the same material deposited on platinum.[5]

Poly(vinylcarbazole)

From vinylcarbazole (VK) electrochromic films can be obtained on metal or ITO electrodes. In some papers[12-14] this polymerization process is described and the spectra of the oligomer, or dimer, produced are shown. Absorption spectra of oxidized, differently substituted dimers[15] show bands in the regions 380-410 nm and 760-800 nm. Preliminary measurements show that in the same experimental conditions utilized for polymerization of the other title monomers, electrochromic films in PVC can be obtained (Fig. 5A). The absorption spectra of these films at several electrode voltages are shown in Fig. 5B.

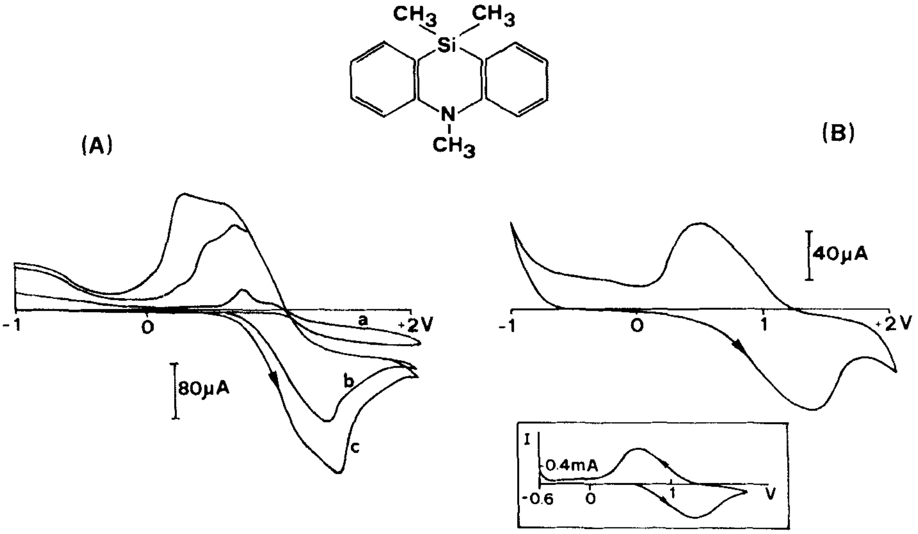


FIGURE 3 A) Cyclic voltammograms of 9.86×10^{-3} M SIN on PVC-coated ITO electrode (0.9×0.9 cm^2) in ACN (0.1 M TBAP) : (a) 1st, (b) 10th, (c) 22nd cycle (sweep rate : 50 mV s^{-1}).
B) Cyclic voltammogram of a film of poly(SIN) in PVC on ITO electrode in ACN (0.1 M TBAP) (sweep rate : 20 mV s^{-1}). B-inset) Cyclic voltammogram[7] of a film of poly(SIN) on ITO electrode in methylene chloride (0.1 M TBAP) (reference electrode : Ag/AgCl; sweep rate : 20 mV s^{-1}).

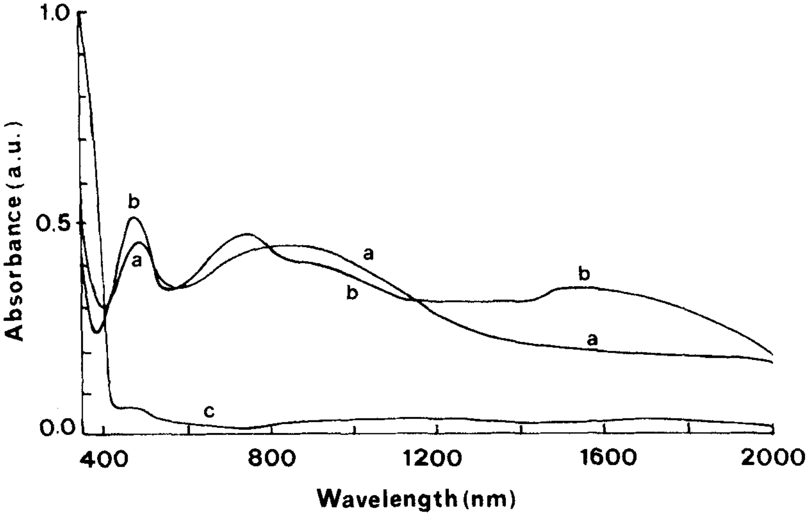
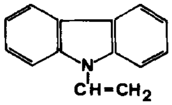


FIGURE 4 Absorption spectra of a film of poly(SIN) in PVC on ITO electrode in ACN (0.1 M TBAP) at different voltages: (a) +1.8 V, (b) +0.6 V, (c) -0.2 V.



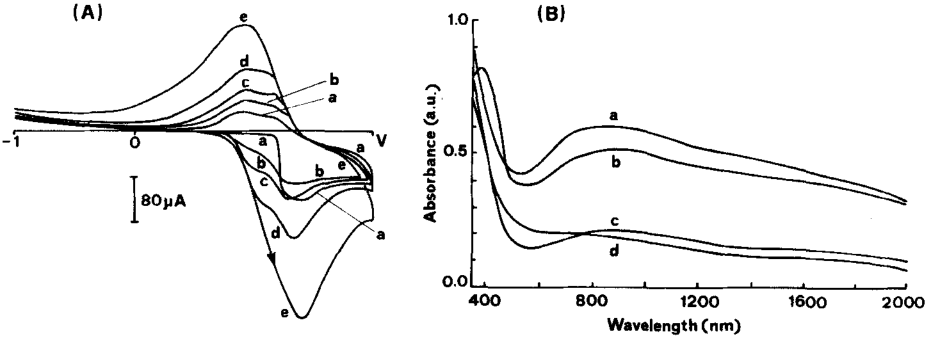


FIGURE 5 A) Cyclic voltammograms of 5.2×10^{-3} M VK on PVC-coated ITO electrode (0.9×0.9 cm^2) in ACN (0.1 M TBAP): (a) 1st, (b) 2nd, (c) 3rd, (d) 5th, (e) 10th cycle (sweep rate: 100 mV s^{-1}). B) Absorption spectra of a film of poly(VK) in PVC on ITO electrode in ACN (0.1 M TBAP) at different voltages: (a) +1.8 V, (b) +0.5 V, (c) -0.5 V, (d) -1.0 V.

Further studies on the properties of poly(VK) films produced by electrochemical technique on these modified electrodes are in progress.

Poly([1]benzothieno[3,2-b]indole)

Poly([1]benzothieno[3,2-b]indole) (poly(TNI)) was synthesized by anodic oxidation of TNI in methylene chloride or ACN at +1.2 V, using TBAP as supporting electrolyte.[16] After the initial formation of the oxidized dimer, which is soluble, the polymer, in the form of a fine black powder, insoluble and non-filmable, begins to deposit. In ACN, with a PVC-coated ITO electrode, we did not obtain by potentiodynamic or potentiostatic oxidation any poly(TNI)-PVC film. Most of the polymerization process occurred directly on the ITO surface, and caused partial detachment of the PVC coating.

Further investigations are in progress in order to improve the process conditions. These take into consideration both the morphology of the resulting polymer and experimental parameters, like density of PVC and monomer concentration.

CONCLUSIONS

Poly(DTPY), poly(SIN), poly(VK) and poly(TNI), produced by anodic oxidation, are electrochemically doped materials characterized by interesting technological features. A promising method to overcome the poor processability of these materials is their inclusion into an easily processable host polymer. In this paper we have shown that all the title polymers, with the exception of poly(TNI), can be included into PVC layers without losing characteristics like electrical conductivity and redox properties. Studies are in progress with the aim of overcoming the polymerization failure of TNI into PVC films.

ACKNOWLEDGEMENTS

Mr. L. Ventura is acknowledged for drawing the figures. This work was carried out with the financial support of Progetto Finalizzato "Materiali Speciali per Tecnologie Avanzate" of Consiglio Nazionale delle Ricerche.

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