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Electropolymerization of poly(2-vinylpyridine) films on zinc

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The electroreductive polymerization on a zinc substrate of 2-vinylpyridine in aqueous solution produces thin films. Various electropolymerization conditions have been studied. The deposits have been characterized structurally and compositionally. The best films were obtained at 50° C by potentiostatic polymerization at −1.26 V vs NHE for 15 min.

1. Introduction

In a previous paper [1], electropolymerization of organic monomers and properties of polyaniline and polypyrrole films obtained by anodic oxidation were described. In that paper the aim was to coat metals with a thin continuous electronically conducting film in order to protect the metal against corrosion. Attempts to obtain films by cathodic reduction of vinylpyridine complexes of iron were not successful.

Research on electropolymerization is still very active around the world. Oxidation and reduction reactions of various monomer types (benzenic substituted derivatives, organometallic complexes and heteroaromatic compounds) [2–8] have been studied recently.

The advantage of electropolymerization, in comparison to the procedure of evaporating a polymer solution at the surface of the metal, is mainly a better thickness and structure control (if the mechanism is known) and the possibility of covering metallic parts of any shape.

In the case of electroreduction, the oxidation of the substrate does not occur simultaneously with the organic film deposition but few systems have been studied by electroreduction. Fauvarque *et al.* [9, 10] and Shiavon *et al.* [11, 12] have studied the synthesis of poly(1,4-phenylene) and poly(2,5-thienylene). Cathodic electropolymerization of polythiophene on platinum and semiconductor electrodes has been studied by Xu *et al.* [13]. Poly(*N*-ethyl-3,6-carbazolediyl) [14] and polymers obtained from vinylpyridine or vinylbipyridine complexes of osmium, ruthenium and iron [15, 16] have been synthesized recently.

Sekine *et al.* [17] have produced various polymer films on mild steel by electrooxidation and electroreduction. They have shown that the film having the best corrosion resistance in their study was poly(2-vinylpyridine) after polymerization by electroreduction followed by thermal curing at 120° C for 30 min.

According to their results, the best way to obtain such a corrosion resistant film was to work at constant potential in a two-electrode cell. The current density decreased rapidly after a few minutes, then gradually, with electropolymerization, to reach an almost constant value at which the formation and growth of poly(2-vinylpyridine) continued.

The corrosion resistance of the coated steel sheets was measured by means of polarization curves and electrochemical impedance spectroscopy in a test solution (3 wt % NaCl + 0.5 M Na_2SO_4 in water). The u.v.-visible spectra of the monomer and the polymer were compared before and after curing. The structural formula of poly(2-vinylpyridine) formed by electropolymerization was $(C_7H_7N)_n$. Polymerization continued during curing.

The 2-vinylypyridine monomer (2-(CH_2=CH)-C_5H_4N or C_7H_7N possesses an electronic structure similar to styrene. Vinylpyridine polymer applications are particularly important as polyelectrolytes, polymer reagents and in electrical applications. It is possible to polymerize this monomer by radical or anionic mechanisms [18]. For the radical polymerization benzoyl peroxide may be used as initiator and the reaction occurs at 70° C [19]. Anionic initiators for vinylpyridine monomers include *n*-butyllithium, 2-ethyl pyridyllithium and dibenzylmagnesium. The variety of anionic initiators allows control of both the rate of overall polymerization and the microstructure of the polymeric product [18].

It is also possible to dope poly(2-vinylpyridine) with iodine or organic electron acceptors. Semiconductors with conductivities ranging from 1 to $10^2\,S\,m^{-1}$ were obtained [18, 19]. But this iodine doped polymer would probably be inefficient in protecting metals against corrosion, the iodine compound being soluble in water. Owing to the great industrial potential interest of poly(2-vinylpyridine) films, and despite the previous negative results obtained in the laboratory [1], it was decided to start a new research programme based on experiments by Sekine *et al.* [17]. The present paper summarizes the results of this research.

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2. Experimental details

Early measurements made in the laboratory at 25 ° C showed that is was possible to obtain very irregular films on mild steel substrates while intense hydrogen evolution occurred on stainless steel cathodes with little film formation. It was therefore decided to perform all experiments on zinc: many steel structures are protected by a sacrificial zinc layer.

The chosen electrolytic cell was a 400 ml three-electrode cell with a double wall in order to maintain a constant temperature. The reference electrode was a saturated calomel electrode and the counter electrode a platinum grid. The working electrode was either a rotating electrode or a plate. The electrolyte contained 0.25 M 2-vinylpyridine, 0.05 M ammonium perchlorate as supporting electrolyte and a 9 to 1 ratio volume of water and methanol as solvent. The zinc substrates were polished up to 1200 SiC paper grade and washed ultrasonically in water before plating.

Polarization curves with the rotating electrode (1000 and 1500 rpm) were recorded with a potentiostat (Tacussel PRT 40-1X and 20-2, pilot type Servovit Tacussel) at 50° C in the range between +1.24 V and −4.76 V vs NHE at a scan rate of 0.2 V min^{-1}.

Potentiostatic experiments with magnetic stirring were performed on plates at potentials in the range −1.16 to −1.76 V vs NHE and at temperatures ranging from 40 to 60° C, for 0.5 to 180 min. Galvanostatic depositions were also studied with the current density ranging from 0.2 to 0.5 A dm^{-2} and duration ranging from 10 to 67 min.

The film morphologies were studied using an optical microscope (Reichert–Jung MeF3) and a scanning electron microscope (Jeol JSM-820 SEM). To detect the presence of thin deposits, Auger electron spectroscopy (Φ Physical Electronics 590) was used.

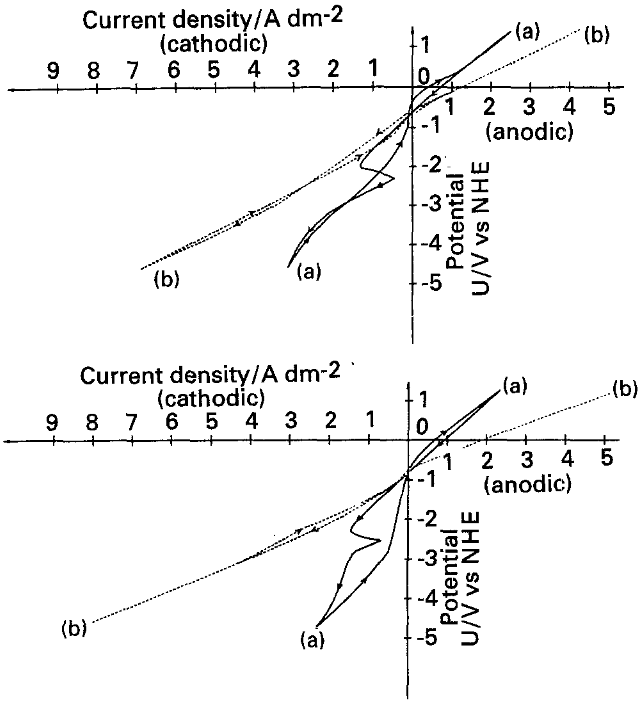

Fig. 1. Polarization curves on zinc with (a) and without (b) monomer. Zinc cathode area: 10^{-4} m^2; temperature: 50 ° C; scan rate = 0.2 V min^{-1}. Upper: 1000 rpm; lower: 1500 rpm.

Porosity tests were made by cementation of copper from a 0.1 M $CuSO_4$ solution for 30 s. Image analysis was used to quantitatively evaluate the surface ratio of copper to deposit.

Fourier transform infrared spectroscopy (Bruker IFS 25 FTIR), u.v.–visible spectroscopy (HP Vectra

Table 1. Influence of potential and temperature on the current density (J), charge density (Q) and mean charge density by time unit (Q′) during formation of films on zinc cathodes by electropolymerization (magnetic stirring, zinc plate electrode)

Influence of potential

Duration /min	*Temperature* /°C	*Potential* /V vs NHE	*J* /A dm^{-2}	*Q* /C dm^{-2}	*Q′* /C dm^{-2} min^{-1}
180	50	−1.16	0.098 after 3/4 h	965	5.4
180	50	−1.26	0.263 after 3/4 h	270	15
90	50	−1.36	0.083 after 3/4 h	650	7.2
95	50	−1.56	0.108 after 3/4 h	710	7.5
22	50	−1.76	0.185 after 1/3 h	390	17.7

Influence of temperature at −1.358 V vs NHE

Duration /min	*Temperature* /°C	*Potential* /V vs NHE	*J* /A dm^{-2}	*Q* /C dm^{-2}	*Q′* /C dm^{-2} min^{-1}
90	40	−1.36	0.051 after 3/4 h	290	3.2
90	50	−1.36	0.083 after 3/4 h	650	7.2
90	60	−1.36	0.102 after 3/4 h	560	6.2

Influence of temperature at −1.158 V vs NHE

Duration /min	*Temperature* /°C	*Potential* /V vs NHE	*J* /A dm^{-2}	*Q* /C dm^{-2}	*Q′* /C dm^{-2} min^{-1}
30	40	−1.16	0.045 after 1/2 h	145	4.8
90	40	−1.16	0.060 after 3/4 h	350	3.9
180	50	−1.16	0.098 after 3/4 h	965	5.4

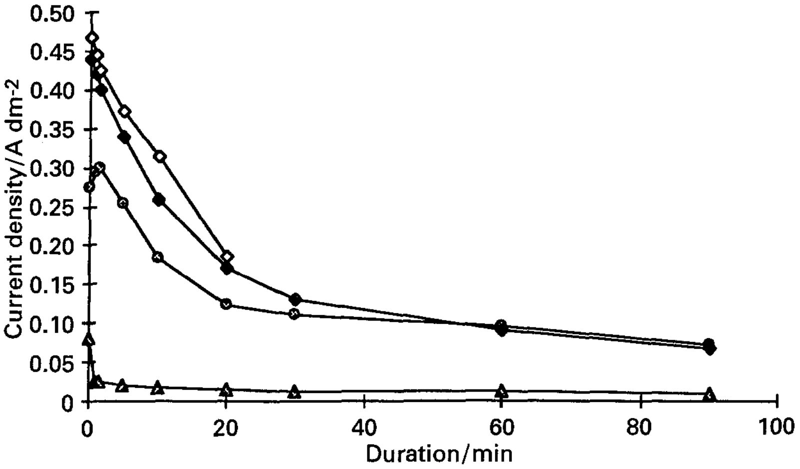

Fig. 2. Dependence of current density on time for different zinc cathode potentials during potentiostatic polarization. Temperature: 50 ° C; magnetic stirring; zinc plate cathode. Key: (△) −1.16, (○)−1.36, (◆) −1.56 and (◇) −1.76 V vs NHE.

QS/165) in the range 190 to 350 nm and X-ray photoelectron spectroscopy (ISS–XPS with an analysing spot diameter equal to 10^{-3} m) were also used to characterize the composition of the layer.

Some films were cured in an oven at a temperature of 120° C under air for 30 min [17].

It was also possible to determine the distribution of molecular weights for the formed poly(2-vinylpyridine) by Gel Permeation Chromatography (GPC) [20]. This type of measurement was performed in a trichlorobenzene solution.

3. Results

The polarization curves on zinc at 50° C with and without monomer are represented at 1000 and 1500 rpm in Fig. 1. With monomer in the solution, a current peak with a maximum at about −2.15 V vs NHE appeared. This peak was not affected by an increase in electrolyte stirring. The current density at potentials more negative than the peak potential was smaller in the presence of monomer than in a monomer-free electrolyte.

The results of the potentiostatic polarizations at various potentials are summarized in Table 1 and Figs 2 and 3. Figure 4(a) shows a deposit obtained after 90 min electropolymerization at −1.16 V vs NHE at 40° C. At −0.96 V vs NHE the current density was very low (10^{-3} A dm^{-2}). For identical electrolysis durations, the current density and the charge density increased when the potential was more negative, in the range −1.36 to −1.76 V vs NHE (see Fig. 2). At a constant potential of −1.36 V vs NHE, the charge density reached a maximum at 50° C (see Table 1) and the current density increased with increasing temperature (see Fig. 3).

For potentials lower or equal to −1.36 V, very irregular deposits were obtained (see Fig. 4(b)). These films coated the substrates and a minimum of 50 min erosion (4 kV – Ar$^+$ – 25 mA) was needed to reach the zinc signal by AES (Auger electron spectroscopy). The films were however brittle. Thinner films were then considered, to avoid internal stresses and rupture of the coating. For less than 3 min of polarization at −1.36 V vs NHE no carbon was detected by AES. For 5 min of electropolymerization at the same potential carbon and zinc were detected by AES. However the film did not cover the substrate completely (see Table 2).

The films obtained for durations equal to or longer than 20 min contained cracks. A potential of −1.26 V vs NHE was also studied (see Table 3) and the best result was obtained for a potentiostatic deposition of 15.6 min at this potential. The current densities (J) observed for these samples were in the vicinity of 0.2 A dm^{-2}.

Other films were also obtained by the galvanostatic method or with a fixed potential between a zinc cathode and a platinum counter electrode (without reference electrode). These films were neither more regular nor more covering than the potentiostatic films.

The results of porosity tests are summarized in Table 3. For electropolymerization durations longer than 20 min, the deposits were already cracked (see Fig. 5). For shorter durations only little black copper dots were observed. Their concentration decreased as the deposition duration increased from 3 to 10 min.

The XPS analysis made on a 5 min electropolymerized sample at −1.36 V vs NHE and 50° C showed that the electrode was completely covered by the polymer because the zinc signal was not detected in the general spectrum. The C/N atomic ratio in the polymer was

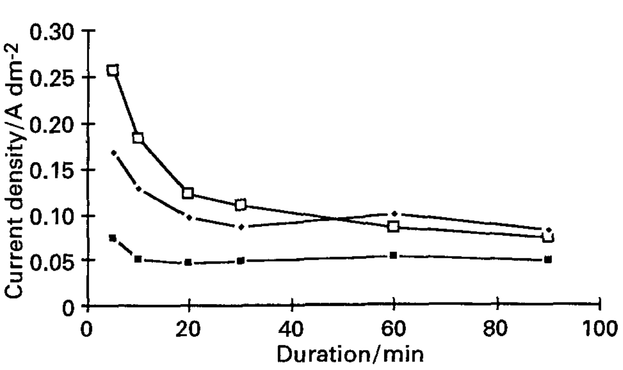

Fig. 3. Influence of temperature on current density as a function of time. Zinc cathode potential: −1.36 V vs NHE; magnetic stirring; zinc plate cathode. Key: (■) 40, (□) 50 and (◆) 60 ° C.

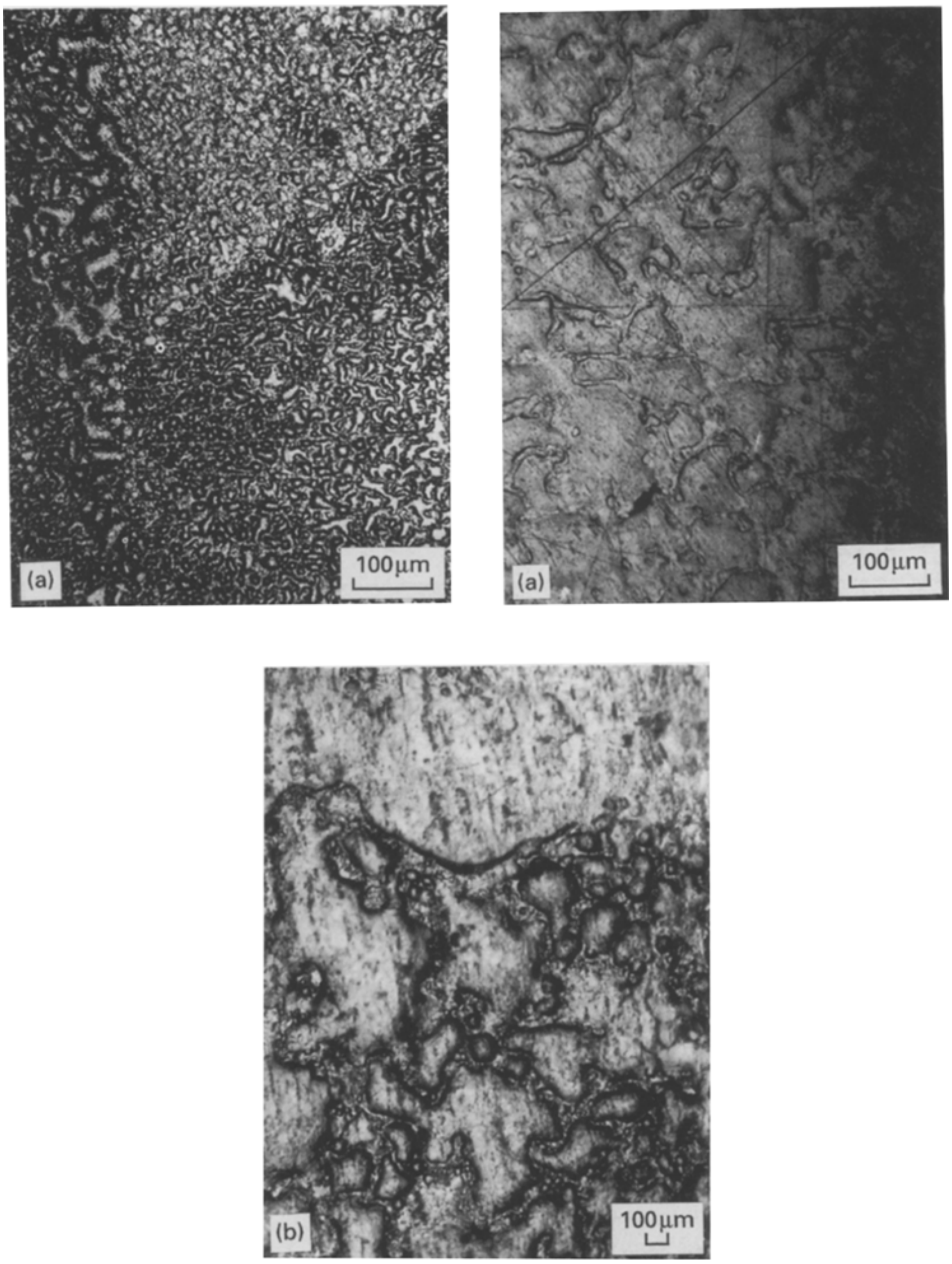

Fig. 4. Optical microscopy. (a) Deposit obtained at −1.16 V vs NHE and 40 ° C for 90 min. (b) Irregular deposit obtained at −1.76 V vs NHE and 50 ° C for 22 min.

Table 2. Results for the thin deposits: current density (J), charge density (Q) and Auger electron spectroscopy results (AES) (zinc plate cathode)

Duration /min	*Potential* /V vs NHE	*Temperature* /°C	*J* /A dm^{-2}	*Q* /C dm^{-2}	*AES*
0.5	−1.36	50	0.23 after 0.5 min	8	no C
3	−1.36	50	0.20 after 3 min	37	no C
5	−1.36	50	0.20 after 5 min	73	C, Zn
10	−1.36	50	0.21 after 10 min	147	C
20	−1.36	50	0.22 after 10 min	271	C

Duration /min	*Potential* /V vs NHE	*Temperature* /°C	*J* /A dm^{-2}	*Q* /C dm^{-2}
12	−1.26	50	0.28 after 10 min	210
15	−1.26	50	0.28 after 10 min	257

Table 3. Influence of electropolymerization duration on the covering quality of the films (zinc plate cathode)

Results of the porosity test (% of surface covered with copper) for various electropolymerization conditions or durations (porosity test with $CuSO_4$ 0.1 M during 30 s).

Duration /min	*Porosity test* /% of the surface covered with Cu	*Electropolymerization conditions*	
		Potential /V vs NHE	*Temperature* /° C
3	3% Cu	-1.36	50
5	7.6% Cu	-1.36	50
10	1.3% Cu	-1.36	50
20	9% Cu	-1.36	50
15, 6	–	-1.26	50
12	–	-1.26	50
15	–	-1.26	50

Duration /min	*Porosity test*	*Current density* /A dm^{-2}	*Temperature* /° C
11	–	-0.2	50

Duration /min	*Porosity test*	*Potential between Pt and Zn* /V	*Temperature* /° C
60	–	-5.5	25
60	–	-4	25
60	–	-4 + curing 30 min at 120° C	25

greater than in the monomer ($C/N_{\text{in the monomer}} = 7$; $C/N_{\text{in the polymer}} \approx 13$).

The u.v.–visible spectrum for the monomer dissolved in methanol showed two peaks, at 234 and 278 nm. For the electropolymerized film and the cured film, also dissolved in methanol, these peaks completely disappeared and a new one at 262 nm appeared (see Fig. 6). The peak at 234 nm was assigned to the $\Pi - \Pi^*$ electron transition of the vinyl group [17] and that at 278 nm to the same transition for the pyridine group. The peak at 262 nm was consistent with a poly(2-vinylpyridine) structure [17]. A sample of polymer obtained by radical polymerization showed a peak at about the same wavelength as that of the electropolymerized film (256 nm).

The infrared spectrum of a film obtained on zinc at −1.26 V vs NHE, 50° C after 3 h electropolymerization is shown on Fig. 7. The peaks correspond to the peaks of poly(2-vinylpyridine) obtained by radical polymerization (2920, 1580, 1560, 1470, 1430, 980, 920, 790 and 740 cm^{-1}).

In a preliminary experiment performed at 50° C and −1.56 V vs NHE, the volume of hydrogen evolved after 20 min electropolymerization was measured and found to be 0.2 ml. The corresponding yield for polymer formation was thus approximately 80%, based on the assumption of a one electron reduction for each monomer. All other current yields were eval-

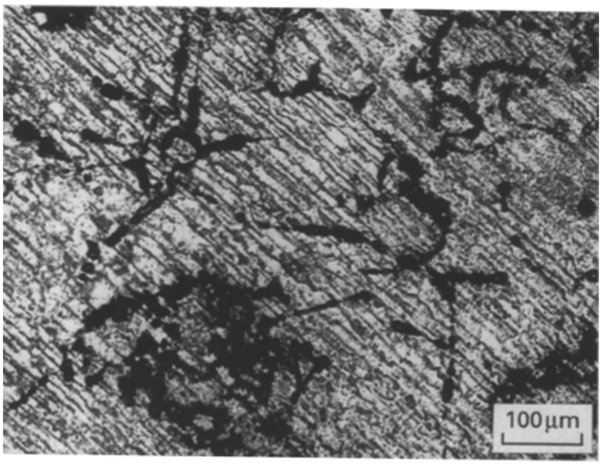

Fig. 5. Optical microscopy of porosity test (20 min electropolymerization at −1.36 V vs NHE; 50 ° C). The black dots are the copper deposits in the pores of the coating.

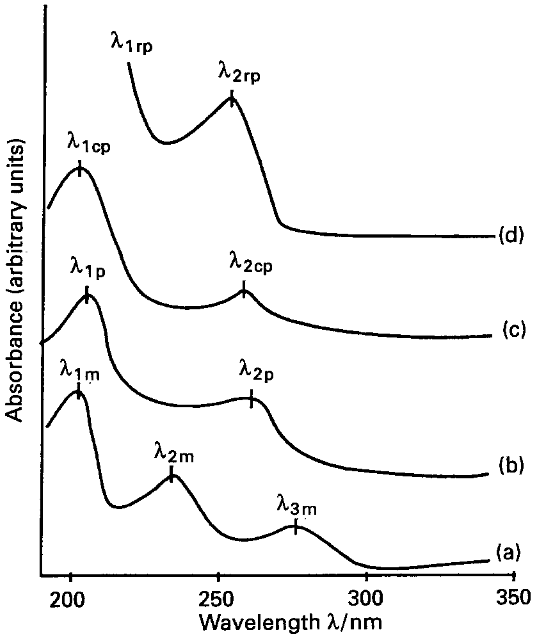

Fig. 6. U.v. spectra (range 190–350 nm); blank = air; all the samples were dissolved in CH_3OH. (a) monomer; (b) polymer; (c) polymer cured for 30 min at 120 ° C; (d) polymer obtained by radical polymerization. $\lambda_{1m} = 200$ nm (CH_3OH), $\lambda_{2m} = 234$ nm, $\lambda_{3m} = 278$ nm; $\lambda_{1p} = 206$ nm (CH_3OH), $\lambda_{2p} = 262$ nm; $\lambda_{1cp} = 202$ nm (CH_3OH), $\lambda_{2cp} = 262$ nm; λ_{1rp}: CH_3OH, $\lambda_{2rp} = 256$ nm.

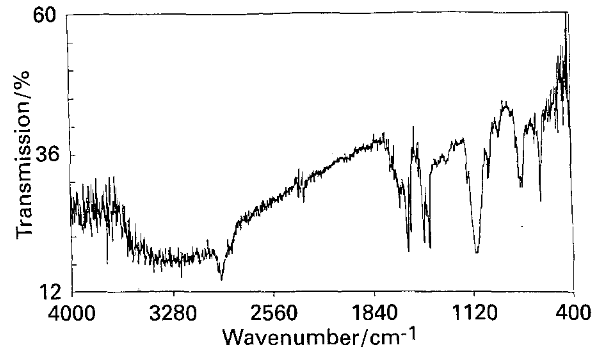

Fig. 7. I.r. spectrum of an electropolymerized film on zinc (–1.26 V vs NHE, 50° C, 3 h).

uated by calculating the ratio between the actual and the theoretical weight of polymer based on the one electron per monomer hypothesis. The error is important because the polymer weight is in the range of a few milligrams and the weight of the sample (substrate + resin) in the range of 10 g. Yields, were, however, quite good (Table 4). In the same conditions, the yield decreased as the electropolymerization duration increased. For all other parameters kept constant, the yield increased with increasing temperature (from 40 to 50° C) or more cathodic potentials (from –1.16 to –1.36 V vs NHE).

Some GPC measurements were attempted but the formed polymer was not very soluble in trichlorobenzene and it was necessary to filter before introducing the solution into the column. The concentration in solution was low and, consequently, only a very weak peak could be observed at about 500 for the mean molecular mass, $\bar{M}$.

The transverse resistivity of the films was measured after drying using the following method: ten samples were piled upon each other and the resistivity was measured as a function of the pressure applied on the pile. The electrical resistance was found to be infinite whatever the imposed pressure. We concluded that the polymer films were not conducting in the transverse direction after drying. However they were probably conducting in the solution because electropolymerization continued.

4. Discussion

The XPS results obtained on a relatively good film (–1.36 V vs NHE, 50° C and 5 min) showed that the composition of the film was very different from the initial compositon of the monomer. There was a large excess of carbon versus nitrogen. This result is in contradiction with the u.v.–visible spectra showing agreement with a poly(2-vinylpyridine) structure. For thick deposits, the coating thickness was calculated by weighing (film specific gravity estimated as 1 kg dm^{-3}).

The XPS results showed no signal corresponding to zinc, inferring that the deposits completely covered the surface. The thickness of the deposits was greater than the depth of analysis by XPS (more or less 6 nm).

The results obtained by porosity tests gave different conclusions with regard to the covering. This gives information about the diameter of the pores: they are much smaller than the diameter of the analysing spot of the XPS equipment.

Sekine *et al.* [17] obtained completely polymerized films after curing only, as shown by u.v.–visible spectra. In the present study, the spectra for cured and uncured films were approximately identical. This is probably due to the higher electropolymerization temperature (50° C instead of 25° C).

The electropolymerized films were brown in colour while the polymer obtained by the radical mechanism is white. The former is probably a mixture of polymers with different yellow or brown oligomers. After curing, the colour of the polymer films became darker. The polymer films were insoluble in hexane but partly soluble in methanol. It was difficult to detach the films from the zinc substrate.

The quantity of electrons consumed in each experiment was calculated from the curve of current against time of electropolymerization. This quantity, Q, was too high compared with that needed for the synthesis of the polymer assuming a one electron mechanism for each monomer. This may be explained by the formation of compounds other than poly(2-vinylpyridine), and these compounds may be in solution as well as on the metallic sample. This question is still unanswered.

5. Conclusion

The best conditions to generate poly(2-vinylpyridine) films by electropolymerization on a zinc substrate were the following: potentiostatic deposition at –1.26 V vs NHE at 50° C for about 15 min. Stirring was necessary to avoid covering of the zinc surface by bubbles.

Table 4. Influence of the electopolymerization conditions (D = duration; T = temperature) on the thickness (μm) and yield (%) – magnetic stirring (zinc plate cathode)

Electropolymerization conditions							
D /min	*T* /°C	*Potential* /V vs NHE	*Measured weight* /mg	*Thickness* /μm	*Measured Q* /C	*Theoretical weight* /mg	*Yield* /%
90	50	-1.36	44.4	90.6	30	32.6	136
90	40	-1.36	20.8	42.4	24.8	27	77
48	40	-1.36	16	32.7	15.6	17	94
90	50	-1.16	19.9	41	22.6	24.6	81

The films obtained were brown, while poly(2-vinylpyridine) synthesized by a radical mechanism was white. Product compositions were different for the monomer and the polymer but contradictory results were obtained by XPS and u.v. or i.r. techniques.

GPC measurements gave a value of more or less 500 for the molecular weight of the polymer.

The films were not electronically conducting after drying but were most probably electronically conducting during the electropolymerization process.

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References

[1] G. Troch-Nagels, R. Winand, A . Weymeersch and L. Renard, *J. Appl. Electrochem.* **22** (1992) 756.

[2] K. Honda, T. Iyoda and T. Shimidzu, Abstract IL 3-3 in 42nd Meeting of the International Society of Electrochemistry in Montreux (Switzerland), Aug. (1991).

[3] K. G. Ellis, P. O. Fogarty, M. N. Mahmood and D. J. Pearce, Abstract 3-16 in 42nd Meeting of the International Society of Electrochemistry in Montreux (Switzerland), Aug. (1991).

[4] J. C. Michaelson, A. J. McEvoy, N. Kuramoto and M. Gratzel, Abstract 3-44 in 42nd Meeting of the International Society of Electrochemistry in Montreux (Switzerland), Aug. (1991).

[5] J. C. Mesquita and L. M. Abrantes, Abstract 3-33 in 42nd Meeting of the International Society of Electrochemistry in Montreux (Switzerland), Aug. (1991).

[6] F. T. A. Vork and L. J. J. Janssen, *Electrochim. Acta* **33** (1988) 1513.

[7] L. F. Warren and D. P. Anderson, *J. Electrochem. Soc.* **134** (1987) 101.

[8] F. T. A. Vork, B. C. A. M. Schuermans and E. Barendrecht, *Electrochim. Acta* **35** (1990) 567.

[9] J.-Fr. Fauvarque, A. Digua, M.-A. Petit and J. Savard, *Makromol. Chem.* **186** (1985) 2415.

[10] J.-Fr. Fauvarque, M.-A. Petit and A. Digua, *ibid.* **188** (1987) 1833.

[11] G. Schiavon, G. Zotti and G. Bontempelli, *J. Electroanal. Chem.* **161** (1984) 323.

[12] G. Zotti and G. Schiavon, *ibid.* **163** (1984) 385.

[13] Z. Xu, G. Horowitz and F. Garnier, *ibid.* **246** (1988) 467.

[14] A. Siove, D. Ades and C. Chevrot, *Makromol. Chem.* **190** (1989) 1361.

[15] H. D. Abruna, P. Denisevich, M. Umana, T. Meyer and R. W. Murray, *J. Am. Chem. Soc.* **103** (1981) 1.

[16] R. L. Carley, R. E. Thomas, E. A. Irene and R. W. Murray, *J. Electrochem. Soc.* **137** (1990) 1485.

[17] I. Sekine, K. Kohara, T. Sugiyama and M. Yuasa, *ibid.* **139** (1992) 3090.

[18] 'Encyclopedia of Polymer Science and Engineering', Vol. 17, John Wiley & Sons, New York (1989) p. 567.

[19] B. Noirhomme, ULB thesis, Faculté des Sciences (Chimie organique physique), Sept. (1980).

[20] J. C. Salamone, A. W. Wisniewsky and E. J. Ellis, *Polym. Prepr. Am. Soc. Div. Polym. Chem.* **16** (1975) 727.