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Electrochemistry of N-vinyl-2-pyrrolidone and a non polymerizable analogue

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According to previous studies, the electropolymerization of N-vinyl-2-pyrrolidone fits a cationic mechanism with grafting of the polymer onto the platinum anode.

However, this article shows that the pyrrolidone substituent of N-VP is also involved in the anodic reaction in addition to the polymerizable vinyl double bond. This additional reaction in the potential range of interest was confirmed by the electrochemical oxidation of a non polymerizable analogue of N-VP, i.e. N-methylpyrrolidone. Therefore, at least two mechanisms can contribute to the electrodeposition of a polymer film in a solvent of poly N-VP: electrografting and polymer branching and/or crosslinking by species stemming from the electrooxidation of the pyrrolidone rings. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The anodic electropolymerization of various monomers such as styrene and acrylamide was reported in aqueous solutions[1] and in organic media[2,3]. The initiating species that results from the electrooxidation of the monomer, propagates the polyaddition reaction either in solution[4] or as a polymer precipitated on the anode[5,6] depending on the polymer–solvent interactions.

Lécayon *et al.* have electropolymerized N-vinyl-2-pyrrolidone (N-VP) and claimed that the polymer grows according to a cationic mechanism and is grafted onto the platinum anode since it remains insoluble in acetonitrile (ACN) which is a good solvent for poly-N-vinylpyrrolidone (poly-N-VP)[7–9]. XPS, UPS and IRRAS spectroscopies also confirmed the presence of a thin poly-N-VP film on these surfaces. Further, a high resolution XPS analysis of the C_{1s} peak has concluded to the formation of carbon-metal bonds after the peak deconvolution[9].

These criteria for the N-VP electrografting are unambiguous as far as any side reactions of poly-N-VP (e.g. crosslinking) can be precluded. In their study of the electrooxidation of styrene, Akbulut *et al.*[2] have not observed the grafting of the growing chains onto the anode. They have proposed that the initiation step consits of the formation of soluble styrene radical-cations by direct oxidation of the monomer, followed by the very fast coupling of these radical-cations into dicationic species i.e., the actual initiators of the polyaddition reaction. This cationic mechanism was already reported for the electropolymerization of other monomers, such as N-vinylcarbazole (N-VC)[10]. In case of N-VC, it must be pointed out that Sacak *et al.*[11] have observed the deposition of poly-N-VC on the anode as result of the oxidation of the carbazole substituent and insolubility of the so-modified polymer.

We suggested in a previous article[12], that the electrografting of N-VP proposed by Lécayon *et al.*, is not the unique oxidation reaction that can occur. Indeed, the pyrrolidone substituent in N-VP might also be involved in the anodic reaction in addition to the polymerizable vinyl double bond. In order to clear up that problem, it is essential to investigate the electrochemical oxidation of a non polymerizable analogue of N-VP, e.g. N-methylpyrrolidone (MePy).

EXPERIMENTAL

All the experiments were carried out in a glove box under an inert and dried atmosphere at room temperature. The amount of residual water and oxygen in the glove box was continuously measured and kept below 2 and 10 ppm, respectively.

The electrolytic solution was prepared by dissolving the monomer (N-VP) and/or the polymer (poly-N-VP) in a solution consisting of the pure solvent, acetonitrile (ACN), and the supporting electrolyte, tetraethylammonium perchlorate (TEAP; 5×10^{-2} M).
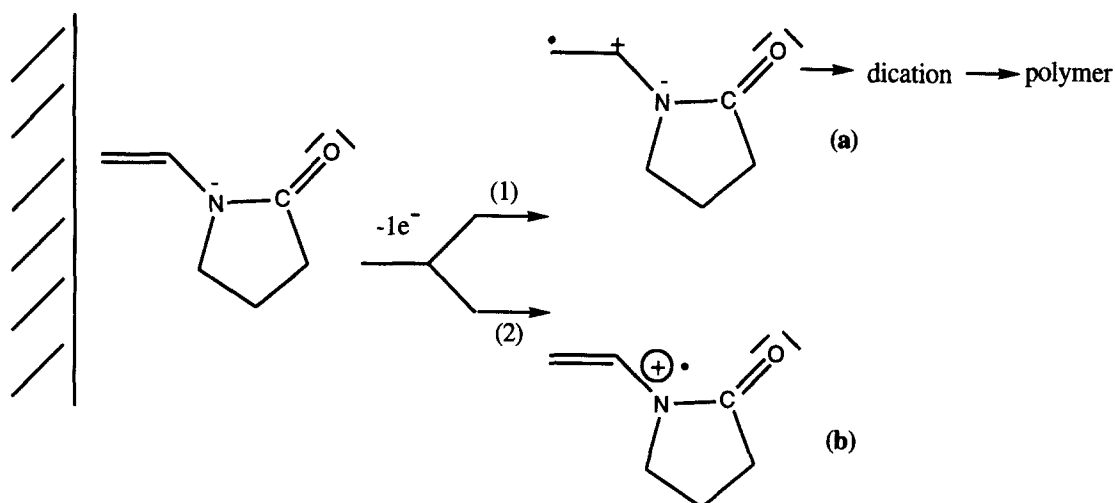
The electrochemical experiments were conducted by voltammetry using an electrolysis cell with the standard three-electrode configuration. A Pt foil, dipping in the solution, was used as a pseudo-reference electrode.

Pt working electrodes were treated by HCl (1 M, 2 min), and washed with H_2O (three times for 10 min, the last washing being carried out under ultrasonic agitation), heptane and acetone (5 min under ultrasonic treatment), respectively. Finally, they were dried in vacuo at 60°C for 12 h prior to use.

N-VP and MePy were dried over calcium hydride and distilled under reduced pressure. Purification of ACN, TEAP and 2,2-bis-(4-tert-octylphenyl)-1-picrylhydrazyl (DPPH) was detailed elsewhere[20]. Residual water content was titrated by the Karl–Fischer method and found to be less than 15 ppm for all the liquids.

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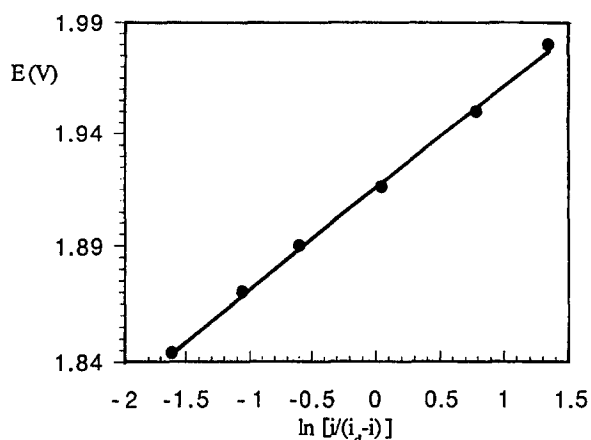† Research Associate of the Inter-University Institute for Nuclear Sciences

Homopolymerization of N-VP was carried out at 60°C for 18 h under nitrogen atmosphere by adding AIBN (0.6 wt% with respect to N-VP) to a monomer (20 ml) solution in ACN (200 ml). The polymer was precipitated into diethyl ether, washed and dried in vacuo at 40°C for two days. The purity of poly (N-VP) was ascertained by i.r. spectroscopy.

The electrochemical experiments were performed with a PAR 273A potentiostat-galvanostat coupled to a computer. XPS spectra were recorded with a SCIENTIA 300 ($hv = 1486.6$ ev) equipped with a rotating anode (4000 rpm).

RESULTS AND DISCUSSION

Figure 1 compares the anodic voltammetric scans for N-VP

Figure 1 Voltammetry on platinum in ACN: (A) N-VP = 5 × 10^{-3} M; (B) MePy = 10^{-2} M ($v = 50$ mV s^{-1})

I

Cationic path

Radical path

Scheme 1

Scheme 2

(*Figure 1A*) and MePy (*Figure 1B*). There is no noticeable difference between the two oxidation curves, which have the same general shape and extend over a large common potential range. That the potential at the peak maximum is not the same may be explained by the use of a pseudo-reference electrode for the potential measurements and a difference in the substituent of the pyrrolidone ring in position 2, i.e. a vinyl group in case of N-VP and a methyl group in MePy. *Figure 1A* shows that N-VP is oxidized by direct and irreversible electron transfer at the anode, in agreement with Lécayon et al.[7] who observed this oxidation in the 1.0 to 1.5 V versus Ag/Ag$^+$ range under the same experimental conditions as in this work. After 5 voltammetric scans up to 2.4 V, the oxidation curve remains unchanged, indicating that no deposition has occurred on the electrode.

The oxidation peak of MePy, is quite consistent with previous results published by Shono[13] and by Mann et al.[15], who have proved that an aliphatic amide, such as MePy, is irreversibly electro-oxidized in dry acetonitrile . Cyclic voltammetry of dilute solutions of aliphatic tertiary amides (2-5 × 10^{-3} M) in acetonitrile shows indeed a peak in the 1.2 to 1.5 V (versus SCE) potential range. According to the mechanism shown in *Scheme 1*, the cation-radical (I) is formed, which can react either by abstraction of one hydrogen atom from the solvent (radical path) or by loss of a second electron and a proton with formation of cationic species (cationic path).

The oxidation of cyclic aliphatic amides was also studied in the presence of a nucleophile, which was observed to react regioselectively on the endocyclic carbon atom in α position to nitrogen (*Scheme 2*). Okita et al. have reported that the oxidation of MePy at 2.2 V versus SCE in acetonitrile added with water (from 2% to 5%) formed the parent hydroxylactam as the main reaction product[16]. In methanol, the anodic oxidation of methyl N,Ndialkyl-carbamate yields the α-methoxylated compound[17]. Clearly, the scientific literature is rich in information about the oxidation of aliphatic amides and agrees with an oxidation potential in a range that includes the potentials used by Lécayon et al. for the N-VP electropolymerization. The shoulder observed on the solvent oxidation peak (region II in *Figure 1B*) might be the signature of an additionnal oxidation reaction of MePy, in a potential range more anodic than potentials scanned in *Figure 1A*. This shoulder is not observed in case of N-VP, which is not shown in *Figure 1A* but confirmed in Ref. [7].

According to the experimental data published previously[2,13,15], the electron transfer from the monomer to the anode could produce two species (*Scheme 3*): a radical-cation (a), as proposed by Akbulut et al. in case of the electro-oxidation of styrene[2], and a radical-cation (b) resulting from the electron transfer to the pyrrolidone substituent rather than to the C = C bond. Whatever the oxidized species, (a) or (b), they would be formed without any grafting onto the electrode and their subsequent reaction is then expected to occur in solution, but in the very close surrounding of the anode. In order to support this reaction

Scheme 3

Figure 2 *E* versus ln [i/(id-i)] for the polarography of a N-VP solution (5 × 10^{-3} M) in ACN added with TEAP (0.05 M). Anode: Pt and *v* = 1 mVs^{-1}

pathway, polarographic experiments have been conducted at a low scanning rate ($v = 1$ mVs^{-1}). The experimental data collected for a N-VP concentration of 5.10^{-3} M were plotted in *Figure 2* and fit equation (1), which is known to be valid for irreversible electrochemical reactions with formation of a soluble species[14].

$$E = E'_0 - R\frac{T}{nF\alpha_a}\ln\frac{i}{i_d - i} \qquad (1)$$

where α_a is the anodic transfer coefficient; *n*, the number of electrons involved in the electrochemical reaction; E'_0, the apparent standard potential of electrode; *T*, the temperature, *i*, the current intensity (A) and i_d the diffusion limited current (A). The slope of the straight line is 0.045 so that $(\alpha_a n) = 0.57$. Values of α are commonly found in the range of 0.3 to 0.7 [14]. From these data, the most probable value for *n* is one, supporting that the oxidation of N-VP is a faradic reaction and that a monoelectronic transfer occurs in agreement with *Scheme 3*.

These conclusions give no support to a grafting reaction onto the anode. In the case of a faradic reaction with 100% current yield, the density of grafted chains (d) can be calculated from equation (2) where *I* is the oxidation peak current (C), *F*, the Faraday constant (96487 C), *N*, the Avogadro constant and *S*, the actual

surface of the anode (Å^2)

$$d = \frac{I}{F}\frac{N}{S}\frac{1}{n} \qquad (2)$$

From the voltammetric data recorded for a 0.5 M N-VP solution in acetonitrile, a value of 5 chains/Å^2 was calculated which is unrealistic for a chain grafting process because of obvious steric hindrances. Therefore, it comes out that the carbocationic species (a) which is electrophilic enough to initiate the N-VP polymerization, is not grafted onto the electrode but rather follows the usual reaction way, which corresponds to the coupling with formation of the dicationic species, i.e. the actual initiator released in solution.

The N-VP concentration has a marked effect on the course of the electropolymerization. At low monomer concentration (< 0.5 M), the anode is not inhibited, in contrast to what happens at concentrations of 0.5 M and more. The intensity of the oxidation peak then becomes independent of the monomer concentration or even slightly decreases. Thus clearly an insulating film is deposited on the electrode in the presence of a solvent (ACN) for the polymer. According to Lécayon *et al.* this observation is evidence for the polymer grafting on the anode. An alternative proposal could however be found in the oxidation of the pyrrolidone substituent of both the monomer and the poly-N-VP chains. Indeed, in agreement with the results reported by Mann *et al.* for the electro-oxidation of aliphatic amides[15], a cationic branching reaction of poly-N-VP can occur (*Scheme 4*, route 1) and ultimately leads to insoluble hyperbranched and/or cross-linked polymer. It is also noteworthy that the protons formed are potential initiators for the cationic polymerization of N-VP in solution. Further, the radical transfer to ACN proposed in *Scheme 1* (radical path) may be responsible for a radical polymerization in solution (*Scheme 4*, route 2).

In order to prove that originally soluble chains are involved in the film formation on the anode, preformed poly-N-VP (0.5 M) was dissolved in a N-VP solution in acetonitrile (10^{-2} M) diluted enough to prevent the anode passivation from occurring. *Table 1* shows that the intensity of the oxidation peak decreases as the voltammetry is repeated at a scanning rate of 50 mV s^{-1}. XPS analysis of the anode was carried out in parallel and agrees with the
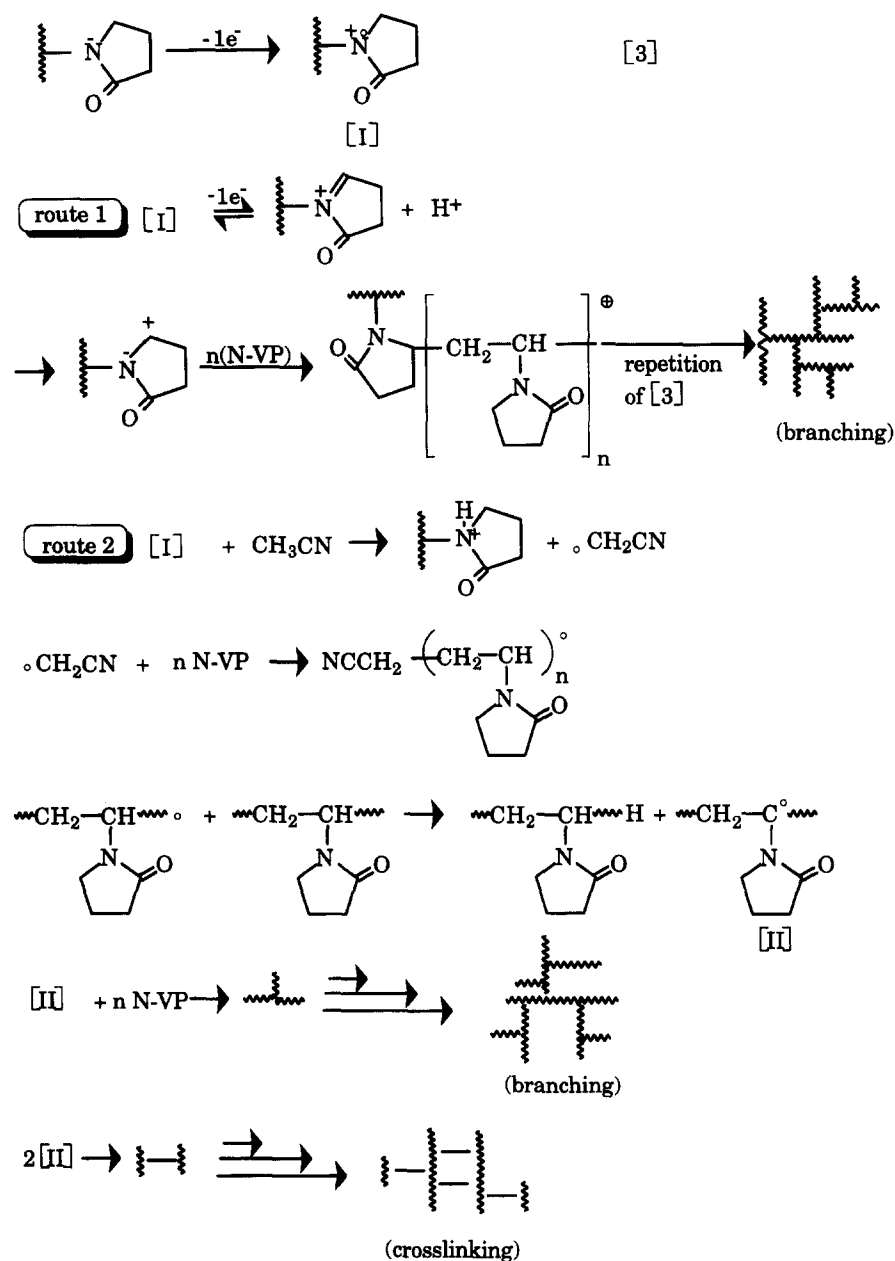
Scheme 4

schematizes a poly -N-VP segment.

Table 1

Experiment	$i(\mu a)$
1	600
2	470
3	400
4	225

Current intensity at the top of the N-VP oxidation peak for repeated voltammetric experiments on the same Pt electrode. Solution of N-VP (10^{-2} M) and poly-N-VP (5×10^{-1} M) in acetonitrile; $v = 50$ mV s^{-1}; anodic potential range: 0–2 V versus Pt.

deposition of a poly-N-VP film as discussed hereafter. Additional experiments were also carried out with solutions of the preformed poly-N-VP ($Mn = 10^4$) in ACN in the absence of N-VP. *Figure 3A* shows the anodic voltammetry of these solutions added with a conducting salt

(TEAP: 5×10^{-2} M) in the potential range used for the N-VP polymerization. The electrochemical scan observed at 50 mVs^{-1} is quite comparable to that reported in *Figure 1B* for MePy at the same scanning rate. The hump observed at a more anodic potential in *Figure 3A* is qualitatively in agreement with the shoulder (II) identified in *Figure 1B*. As already mentioned, the comparison of the potential values reported for independent experiments is not rigourous since a pseudoreference electrode, i.e. a large platinum foil dipping in the solution, is used. Nevertheless, the potential gap between the main oxidation peak and the hump or shoulder at the more anodic potential remains the same (ca. 0.8 V).

Finally, comparison of *Figure 1A, 1B* and *Figure 3A* shows that the oxidation potential at which N-VP is polymerized is anodic enough to trigger quite simultaneously the oxidation of the pyrrolidone substituent. The
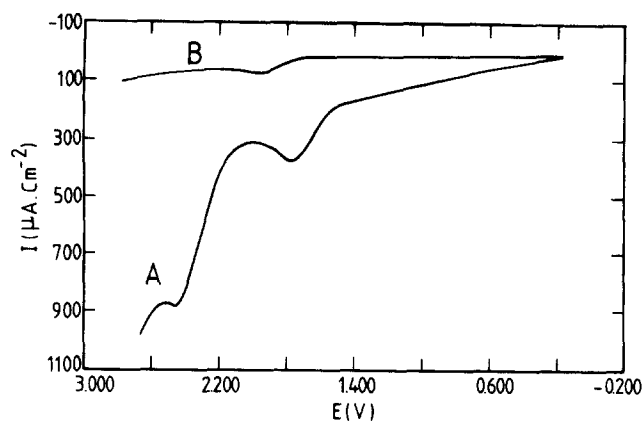
Figure 3 (A) Cyclic voltammetry of a poly-N-VP solution (6 g l^{-1} or 5 × 10^{-2} M in N-VP units) in ACN added with TEAP (0.05 M). Anode: Pt and $v = 50$ mV s^{-1}. (B) Cyclic voltammetry of a Pt anode coated with poly-N-VP dipped in ACN with TEAP (0.05 M). $v = 50$ mV s^{-1}
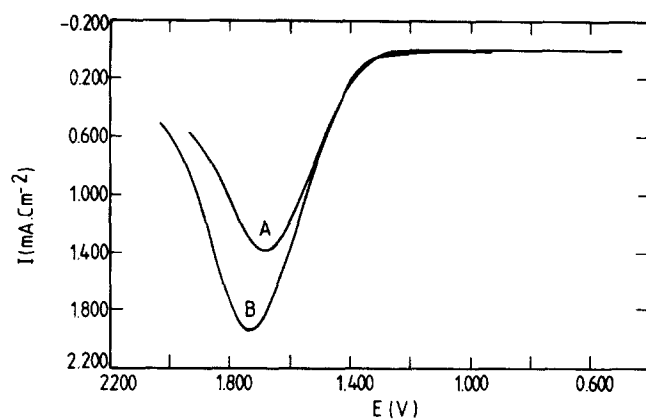
Figure 4 Voltametric of a N-VP solution (5 × 10^{-1} M) in ACN added with TEAP (0.05 M), $v = 50$ mV s^{-1} (A) without DPPH (B) with DPPH (= 10^{-4} M)

intensity of the poly-N-VP oxidation peak (5 × 10^{-2} M in N-VP : *Figure 3A*) is lower compared to the oxidation of N-VP (*Figure 1A*: 5 × 10^{-3} M) and MePy (*Figure 1B* 10^{-2} M) though the nominal concentration in N-VP is higher. This observation could merely reflect the smaller diffusion coefficient (*D*) of the pyrrolidone units in solution when they are part of polymer chains. Indeed, the Randles-Sevcik equation applicable to voltammetry[14], states that ip is proportional to $D^{1/2}$.

Interestingly enough, *Figure 3B* shows the voltammogram recorded when a platinum anode previously coated with poly-N-VP is dipped into TEAP (0.05 M) containing ACN. Comparison of *Figure 3A* and *Figure 3B* clearly shows that poly-N-VP is electroactive, would it be originally dissolved in the electrochemical bath or solvent cast on the anode. It is also observed that voltammetry triggers the insolubility of poly-N-VP deposited previously on the Pt anode.

From the experimental information collected until now, it appears that the electroinitiated cationic polymerization of N-VP is perturbed by side-oxidation reactions of the pyrrolidone substituent. Although the cationic polyaddition (through the vinyl double bond) is known to form oligomers[18], the reactions proposed in *Scheme 4* can account for the deposition of an insoluble polymer on the anode, even in a solvent for poly-N-VP. It must be noted that Haaf *et al.* reported that poly-N-VP radicals were prone to termination by H abstraction from the solvent or from

the chain backbone. In the first instance, the radical derived from the solvent initiates the N-VP polymerization, as assessed by the n.m.r. analysis of the chain ends[18]. Any radical transfer to the polymer then results in chain branching and ultimately crosslinking. This phenomenon was observed when poly-N-VP is added with persulfate which is a radical promoter[19]. In order to prove that radicals are operating when N-VP is electro-oxidized in acetonitrile, an electrochemically stable radical scavenger was added to the N-VP electropolymerization medium. 2,2-di-(4-t.octylphenyl)-1-picrylhydrazyl (DPPH) meets this requirement and is discoloured (from deep violet to yellow) upon reaction with radicals. Under the experimental conditions used in this study (ACN, 0.5 M N-VP), discoloration is observed (compared with a blank) at 1.5 V at low DPPH concentration (10^{-4} M). Increasing amount of DPPH has no effect on the general shape of the voltammetric curve, excepted for a noticeable increase in the intensity of the oxidation peak (*Figure 4*). This observation is consistent with a delay in the anode inhibition by a precipitated poly-N-VP film. Capture of free-radicals by DPPH in the reaction medium results in a decreased inhibition rate.

The explanation proposed for the anode inhibition by poly-N-VP could explain two observations reported by Lécayon *et al.* First, the film thickness starts to increase 100 s after the potential application[8]). This observation agrees with a polymerization reaction initiated in solution and followed by the electrode inhibition by polymer precipitation on the electrode, i.e. beyond the time required for the polymer insolubility. Léonard-Stibbe *et al.*[8] also detached a poly-N-VP film from the Pt anode and analyzed the polymer dissolved in a 50/50 (V/V) acetonitrile/water mixture by size exclusion chromatography. It is not clear whether the polymer was dissolved completely in this solvent mixture or only a fraction of it. The molecular weight was appromixated to 16 000 which was considered in an acceptable agreement with chains fully extended in a 50 nm thick film. However, authors were surprised by the relatively large polydispersity of a grafted polymer responsible for a film of a constant thickness. If radical polymerization and crosslinking of poly-N-VP in organic solvent is considered, it is known that water can dissolve a fraction of branched chains[18]. This could explain the choice by Léonard-Stibbe *et al.* of a 50/50 acetonitrile-water mixture to dissolve (part of?) poly-N-VP deposited on the anode, and finally account for the molecular characteristics of the analyzed poly-N-VP independently of any grafting.

If the cationic polymerization of N-VP is electro-initiated at the anode and rapidly perturbed by a cationic and/or radical process responsible for the polymer insolubility and deposition on the anode, no chemical modification of poly-N-VP could be detected e.g. by i.r. spectroscopy. In this respect, Haaf *et al.* have shown that Crospovidone, i.e. a completely insoluble and highly crosslinked poly-N-VP, has the same i.r. spectrum as linear poly-N-VP[18].

In order to probe the molecular structure of the polymer deposited on the anode more deeply, XPS analysis was carried out, and the C$_{1s}$ spectra were compared with the spectra published by Doneux *et al.*[9] for both poly-N-VP "grafted" onto Pt and commercially available poly-N-VP. Four samples were analyzed in this study: (i) poly-N-VP deposited on a Pt anode (2 V) from a poly-N-VP solution (0.5 M in repeat units) in ACN (5 min) (ii) poly-N-VP formed by repeated voltammetry (3 times at 5 mV/s) of a 1 M N-VP solution in ACN. The potential was scan up to
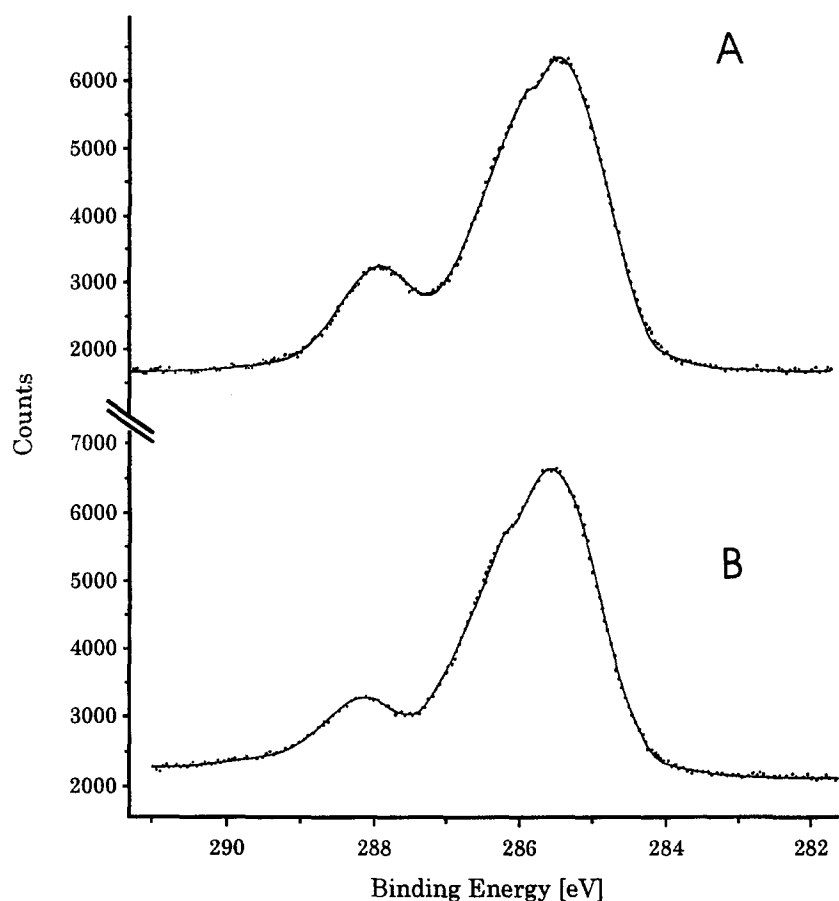
Figure 5 C$_{1s}$ XPS spectrum for poly-N-VP deposited on a Pt anode. (A) from a poly-N-VP solution in ACN (0.5 M repeat units, 2 V for 5 min), (B) from a 1M N-VP solution in ACN (3 scans at 5 mV s^{-1})

the maximum of the oxidation peak (minus 0.1 V) (iii) ibid for a mixture of N-VP (0.02 M) and poly-N-VP (0.5 M in repeat units): 5 scans at 50 mV s^{-1} and (iv) poly-N-VP spin coated on Pt and then polarized (2 V; 3 times for 10 s) in a TEAP solution (0.05 M). The C$_{1s}$ spectrum of all these samples has the same general shape as the reference spectra, which indicates that in all the cases a poly-N-VP film was deposited onto the anode in the presence of a good solvent (ACN) for the unmodified polymer. As an example, the spectra for samples (i) and (ii) which are reported in *Figure 5*, are in close agreement with the spectra reported by Doneux *et al.*[9]. From the C$_{1s}$XPS spectra for the investigated samples, it appears that the percentage of carbon atoms attached directly to an oxygen atom is systematically higher by 2%-3% than the expected value. Water contamination might account for this explanation, since H$_2$O can react as a nucleophile (*Scheme 2*) with formation of an alcohol which is nucleophilic enough to react with another carbonium ion resulting in the polymer cross-linking.

CONCLUSION

Consistently with the experimental observations, the species formed by the electrooxidation of the monomer used at low concentrations (< 0.5 M) are soluble in the reaction medium (ACN) as shown by polarography. At higher N-VP concentrations, a polymer film is deposited onto the anode, though it is expected to be soluble in ACN. The polymer insolubility is proposed to result from a grafting reaction by Lécayon *et al.*[8], though no electrochemical signature for the

grafting reaction was reported. An alternative explanation may be found in the oxidation of the pyrrolidone substituent of the monomer and/or of the already formed poly-N-VP. We have observed that this oxidation occurs in the same potential range as the N-VP electropolymerization. This additional reaction can lead to the formation of cationic species on the pyrrolidone rings of polyN-VP leading to a (hyper)branching reaction and/or to radicals by abstraction of a hydrogen atom from the solvent. These radicals can initiate the N-VP polymerization and the polymer insolubility by a series of transfer reactions to polymer chains as shown in *Scheme 4*. Experimental evidence confirmed the presence of radicals in the close vicinity of the anode. Therefore, two mechanisms could contribute to the formation of a poly N-VP film in ACN (i) the electrografting proposed by Lécayon *et al.* (ii) the electrooxidation of the pyrrolidone substituent responsible for the polymer insolubiltiy.

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