Solvent effect on the electrografting of acrylonitrile on nickel

M. Mertens [(1)], C. Calberg [(1)], N. Baute [(1)], R. Jérôme [(1)], L. Martinot [(2)]

[(1)] Center for Education and Research on Macromolecules (CERM), University of Liège, Sart Tilman, B6, 4000 Liège, Belgium
[(2)] Laboratory of Analytical Chemistry and Radiochemistry, University of Liège, Sart Tilman, B16, 4000 Liège, Belgium

Abstract

The effect of solvent on the reductive electrografting of acrylonitrile (AN) onto nickel cathodes has been studied in dimethylformamide (DMF), a solvent for polyacrylonitrile (PAN), and in non-solvents that include acetonitrile (ACN), propylene carbonate (PC) and pyridine (PY). Electrografting responsible for the cathode inhibition has been observed for the first time in PC and PY. Not only the polymer-solvent interactions but also the intrinsic polarity of the solvent have an effect on the intensity of the inhibition peak which is the signature of the electrografting reaction. Concentration of the monomer in the electrode double layer appears to decrease as the solvent polarity is increased, consistently with a more efficient displacement of the monomer by a more polar compound. That such a competition occurs is also supported by the effect of the nature and concentration of the conducting salt. The best quality films are formed in DMF, which is a solvent for PAN. Quarts: microbalance experiments have emphasized the crucial importance of the potential range used for the AN electroreduction, particularly in a solvent of the polymer.

Keywords: Electropolymerization; Acrylonitrile grafting; Solvent effect

1. Introduction

Metal coating by a polymer film is an efficient way to prevent corrosion, provided that this association is strong and permanent. Electropolymerization in organic [1] and aqueous media [2] is known as a useful method for the organic coating of metals. However, the long-term adhesion of the film deposited on the substrate is usually very disappointing, which is a severe limitation on this technique. Some years ago, a breakthrough was reported by Lecayon et al. [3] and Boiziau and Lécayon [4] who claimed that grafting (i.e., chemical bonding) of polyacrylonitrile (PAN) could be achieved at some common metals, particularly nickel, in dry acetonitrile (ACN). This result was in sharp contrast to previous studies on the electropolymerization of AN [5,6]. We have recently confirmed this quite unusual and very promising electrografting reaction of an organic polymer (PAN) onto a metal (Ni) and made clear that the peak I (often referred to as the 'inhibition peak') observed by voltammetry (Fig. 1) is the signature of the grafting reaction [7]. While the underlying mechanism of the electrografting is still a matter of controversy [4,7-9], some features are established. (i) Both mechanisms imply that the adsorption step of AN on the metal cathode under electrochemical conditions is fairly different from adsorption on a non-polarized metal from the gas phase, since it is well established that in the latter case, it is the nitrile group that essentially interacts with the metal [10-12]. Theoretical calculations [13] have confirmed that if the electric field is not too high, a stable configuration originates from a σ complex with AN linked via one bond between the β-vinylic carbon and a metal atom, while the nitrile group tends to align along the field. X-ray emission spectroscopy (EXES) measurements [14] have confirmed the existence of this C-Ni bond. Furthermore, experimental evidence for such a highly stable interaction between PAN and the metal in the potential range of peak I has been provided: a very adherent PAN film is deposited onto the Ni cathode not only in ACN, which is a non-solvent for the polymer, but also in dimethylformamide (DMF), which is a good solvent [8]. (ii) Dynamic mechanical thermal analyses (DMTA) recently performed by some of us [15] on PAN thin films, are in favor of a two-step AN electroreduction mechanism (Fig. 1), since the grafted polymer formed at the potential of peak I has not the same properties as the ungrafted one formed at the more negative potential (peak II).
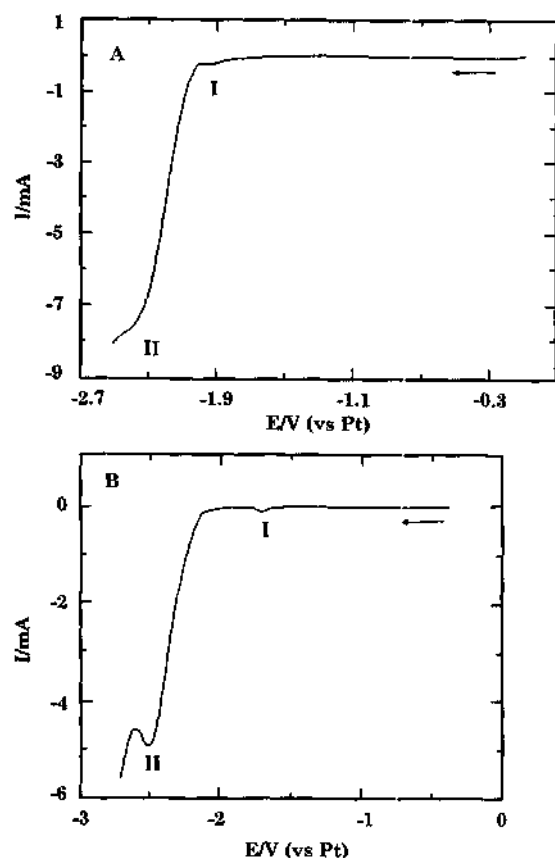
Fig. 1, Voltammetry of acrylonitrile at nickel in a 0.05 M TEAP solution in: (A) ACN, (B) DMF; AN = 0.1 M; v = 20 mV s⁻¹.

The possibility of extending the electrografting of AN to commonly used metals such as copper and steel [16,17], and to functionalize [18] the polymer coating have also been investigated. Hitherto, electrografting onto metals has been reported only for a few monomers, AN being the most representative one [3,19,20].

The purpose of the present paper is to report two distinct effects of the solvent on the electrografting reaction: (i) the effect of the polymer solvation on the electrochemical signature and the characteristics of the deposited film, and (ii) the influence of solvent polarity on the inhibition peak, the potential and intensity of which are directly related to the grafting reaction. In addition to ACN and DMF which have already been used in electrografting experiments [1-8], two other solvents (pyridine (PY), propylene carbonate (PC)) were considered for the first time.

In parallel with the electrochemical experiments, polymer deposition has been recorded in situ by means of a quartz crystal microbalance.

2. Experimental

Acrylonitrile (AN) and acetonitrile (ACN) were dried over calcium hydride and distilled under reduced pressure. *N, N*-dimethylformamide was dried over phosphorus pentoxide and distilled at 70°C under reduced pressure. Propylene carbonate was dried over molecular sieves for 24 h and distilled at 85°C under reduced pressure. Pyridine was dried over potassium hydroxide for 2 h at 120°C and distilled at 40°C under reduced pressure. Tetraethylammonium perchlorate (TEAP) and tetrabutylammonium perchlorate (TBAP) were heated in vacuo at 80°C for 12 h prior to use.

Electrochemical experiments, i.e., voltammetry (CV) and chronoamperometry (CA), were carried out with acrylonitrile (0.1 to 2 M) dissolved in acetonitrile, *N,N-di*-methylformamide, pyridine and propylene carbonate, respectively, containing tetraethylammonium perchlorate (5 X 10^{-2} M TEAP:) as the conducting electrolyte.

The water content was measured using the Karl-Fischer method (Tacussel aquaprocessor) and found to be lower than 5 ppm. At this level, no residual electrochemical signal attributable to water could be detected, both in the CV and CA experiments. All the experiments were carried out in a glove-box under an inert and dry atmosphere at room temperature.

The potentiostat, the electrochemical cell and the general procedure for the electrode preparation and

electropolymerization have been described elsewhere [8]. The nickel cathodes were subjected to a final polish with a 0.3 μm Al_2O_3 suspension in water, leading to reproducible electrochemical curves. Potentials were measured against a pseudo-reference Pt electrode. X-ray reflectivity measurements were carried out with a Siemens D5000 2-circle diffractometer. Ellipsometry measurements were carried out with a nulling scheme L117 ellipsometer (GAERTNER), at a wavelength of 6328 Å (helium-neon laser).

The quartz-crystal analyzer was a QCA917 model (PAR EG&G) equipped with a standard 9 MHz, AT-cut quartz crystal and a 0.2 cm^2 Pt electrode. Combining the balance with the potentiostat made it possible to measure simultaneously not only the current and potential ranges of an electrochemical reaction but also the associated changes in the resonant frequency of the quartz crystal with an accuracy of 0.1 Hz and at a sample period of 0.1 s. Subsequent examination of the collected data then allowed the identification of changes in both the mass and viscoelasticity of the reacting substances on the electrode surface.

3. Results and discussion

As mentioned in Section 1, the main purpose of this paper is to compare the electropolymerization of AN in four organic solvents: ACN, DMF, PY and PC, while keeping all the other conditions constant, i.e., cathode (Ni) and conducting salt (5 X 10^{-2} M, Et_4NClO_4).

Table 1
Peak I current (I_{p1}) for various AN concentrations in ACN, DMF, PC, and PY, respectively; v = 20 mV s^{-1}

	PAN solvent	Dipole moment (D)	$I_{p1}/\mu A$			
			AN = 0.02 M	AN = 0.1 M	AN = 2M	AN = 5M
ACN	No	3.47	a	370	25	b
DMF	Yes	3.86	a	95	15	b
PC	No	4.98	a	650	60	35
PY	No	2.2	85	16	b	b

a, peak 1 superimposed to peak II.
b, I_{p1} too weak to be detected.

In a limited series of AN electropolymerizations in DMF, the conducting salt was also changed. The choice of the solvent was determined by two criteria: (i) solubility of the polymer (PAN) and (ii) the relative polarity (dipole moment) of the solvent with respect to the monomer. DMF is a solvent for PAN, in contrast to ACN, PY and PC which precipitate PAN. Compared to the monomer (μ = 3.54 D), the dipole moments of ACN (3.47 D) and DMF (3.86 D) are quite similar, in sharp contrast to the much higher polarity of PC (4.98 D) and the lower polarity of PY (2.2 D) [21]. It is evident that these parameters do not give a complete account for the phenomena encountered but, they are 'easy to handle data'. It is also worth noting that the importance of the dipole moment of AN has been emphasized by Lécayon et al. [22], who proposed that the first step in the electrografting of AN onto Ni is the selective localization of the C-C double bond of AN in the very close vicinity of the cathode as result of the preferential orientation of the nitrile dipole in the electrical double layer. The solvents were selected so as to compare the effect of (i) a solvent (DMF) and a non-solvent (ACN) of similar polarity and (ii) the effect of three non-solvents of different polarities. Accordingly, the effect of the polymer solubility and the solvent polarity on the electropolymerization of AN can be studied independently.

3.1. Comparative reduction of AN in ACS and DMF

Fig. 1 compares the negative voltammetric scan of an AN solution in acetonitrile (ACN) and in DMF, respectively. Two peaks are observed, the origins of which have been discussed in a previous paper [8]. At the less negative potential, E_{p1} a peak of a relatively small height is observed. Since this peak is observed only when an insulating polymer is grafted onto the electrode, it has been referred to as an 'inhibition peak' and thus provides an electrochemical signature of the grafting reaction. As soon as the cathode is covered by this insulating film (cathodic inhibition), the current drops to zero. Therefore, the current at E_{p1} has to be inversely proportional to the rate at which the electrode is passivated (at a constant scanning rate).

The second peak at a more negative potential, E_{p2}, has been identified as a 'diffusion peak' since its intensity increases with $v^{1/2}$, (v is the potential scanning rate). For comparison, this relationship does not apply to the first peak [8]. Since a current is again observed beyond the potential of the inhibition peak, it is clear that new active sites become available on the cathode surface that allow continued reduction of AN to occur. The film is thought to be strained at this more negative potential with formation of cracks, as supported by microscopic observations [8]. However, at E_{p2}, no grafting occurs anymore on the cathode. In this potential range, the polymer precipitates

onto the metal as a non-adherent film in ACN, while no polymer deposition is observed in DMF, in contrast to what happens at potential E_{p1}. It is also worth noting that a PAN film grafted onto Ni at the potential of the first peak E_{p1} is removed from the electrode (degrafting) at a more negative potential for solvents in which the polymer is soluble. All these observations are of prime importance in order to control the highly desirable grafting of an organic polymer onto a metal but are not yet sufficient to extend it to a large range of useful polymer/metal pairs.

Although the absolute values of $Ep1$ and $Ep2$ in the two solvents cannot be compared in such different solvents because of the use of a pseudo-reference, it is seen in Fig. 1 that the two peaks are better resolved in DMF where the difference between E_{p1} and the onset of the rise of current to the second peak is 0.4 V compared to 0.1 V in ACN, with other conditions remaining the same. This is an important observation since the risk of contamination of the grafted polymer at E_{p1} by non-grafted chains formed at E_{p2} decreases as the resolution ($E_{p1} - E_{p2}$) is high.

Table 2
Dependence of the peak resolution ($E_{p2} - E_{p1}$) on the acrylonitrile concentration in DMF; v = 20 mV s^{-1}

AN/M	E_{p2} - E_{p1} / V
0.1	0.4
0.5	0.5
1	0.7
2	0.8

$E_{p2} - E_{p1}$ is measured from the top of peak I to the onset of the current rise of peak II.

Table 1 shows the dependence of the first peak height on the AN concentration. At very low monomer concentrations, only one peak is observed, however, as a result of the overlapping between peaks I and II. In fact, these peaks become steadily better resolved; thus, $E_{p1} - E_{p2}$ is observed to increase, as the AN concentration is increased (Table 2). In parallel, the height of peak I regularly decreases (Table 1). At a concentration of 5 M, both in ACN and DMF, the 'inhibition peak' is no longer observed because of its too low current, indicating a quasi-instantaneous passivation of the cathode by PAN. In addition to this similarity between the behavior in the two solvents, the peak intensity (I_{p1}) is systematically smaller in DMF compared to that for ACN. This observation indicates a more rapid formation of an insulating PAN layer as result of a much faster growth of the chains solvated by DMF rather than precipitation in ACN. According to ex situ ellipsometry and X-ray reflectivity measurements [23], the average thickness of a PAN film grafted onto Ni at E_{p1} in DMF is 120 nm (±20 nm), while it is only 25 nm (±2 nm) in ACN, when the AN concentration is 2 M in the two solvents. This observation reflects at least that the chain propagation is less rapidly perturbed by termination rate, when the chains growing from the electrode are solvated by DMF rather than being precipitated in ACN [8,23]. Chronoamperometric experiments carried out in ACN and for the first time in DMF, confirm the previous observations derived from voltammetry although the potential scanning rate is not the same [8,24]. In fact, in the potential range of peak I, Fig. 2a and Fig. 3a show that the current decreases rapidly down to a constant value near to zero after the time required for the complete inhibition of the electrode by the grafting of an insulating polymer layer. If the chronoamperometric experiment is stopped at this time, a grafted film is deposited on the cathode in both solvents. The current intensity arising in Fig. 3a (DMF) is much smaller than that in Fig. 2a (ACN) at the shortest observation times, which is consistent with the faster formation of the insulating layer on the cathode, as observed in the voltammetric experiments.
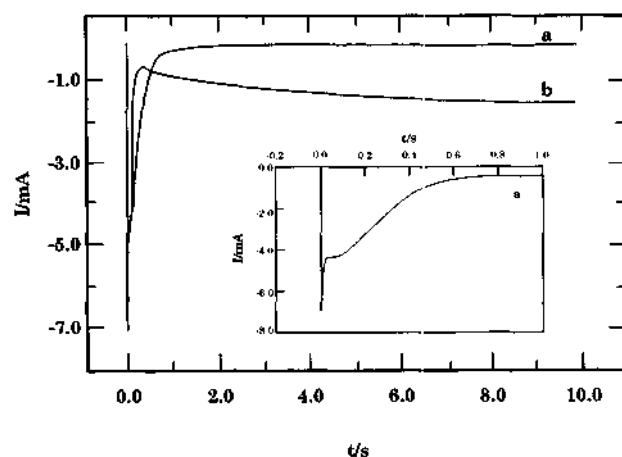
Fig. 2. Results of chronoamperometry experiments on AN (0.5 M) at nickel in a 0.05 M TEAP solution in ACN, (a) in the potential range of peak I; (b) at a potential beyond the origin of peak II.
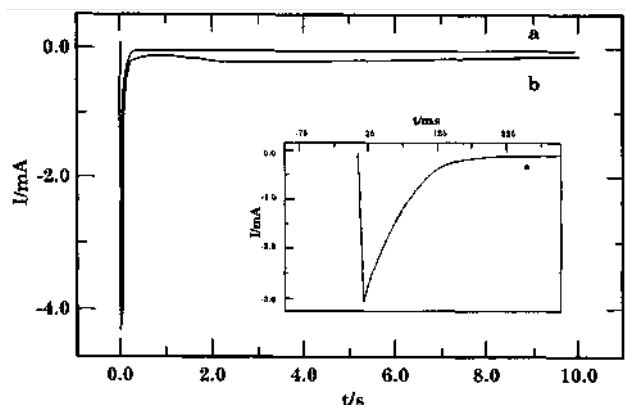

Fig. 3. Results of chronoamperometry experiments on AN (0.5 M) at nickel in a 0.05 M TEAP solution in DMF, (a) in the potential range of peak I; (b) at a potential beyond the origin of peak II.

The current observed at the very beginning of the chronoamperometric transient is basically a capacitive current to which a faradaic contribution associated with the AN reduction is superimposed. The shoulder observed on the experimental curve at the shortest time is thus the counterpart of the inhibition peak observed by voltammetry. The electrode inhibition occurs more rapidly in DMF (Fig. 3a) than in ACN (Fig. 2a), consistently with I_{p1} which is smaller in DMF compared to ACN (Table 1).

Fig. 2b and Fig. 3b show the chronoamperometric transients measured at a potential beyond the origin of the diffusion peak. Beyond the very fast auto-inhibition that occurs in ACN and DMF, the current increases. As discussed elsewhere for the AN reduction in ACN [8], a nucleation reaction with a constant number of active sites more likely occurs as a result of cracks initiated in the originally homogeneous PAN film when going to higher potentials. So, the reaction associated with peak II in voltammetry is also observed (as expected) by chronoamperometry and contributes to the current intensity and to the clearly observed increase in the thickness of the precipitated PAN film (see also the results of the quartz-crystal microbalance experiments). In DMF, the same general behavior occurs although the current is smaller and is observed over a much larger time scale (see Fig. 3b). The evidence for a well-defined nucleation process in ACN, is not observed in DMF, which is consistent with the solvation of the grafted PAN chains in DMF in relation to the precipitation of the chains and formation of a solid film in ACN.

3.2. AN reduction in PC and PY

Under the same dry conditions, the cathodic electropolymerization of AN in PC and PY has been compared to the behavior observed in the two previous solvents and particularly in ACN, which is also a non-solvent for PAN but has a quite different dipole moment.
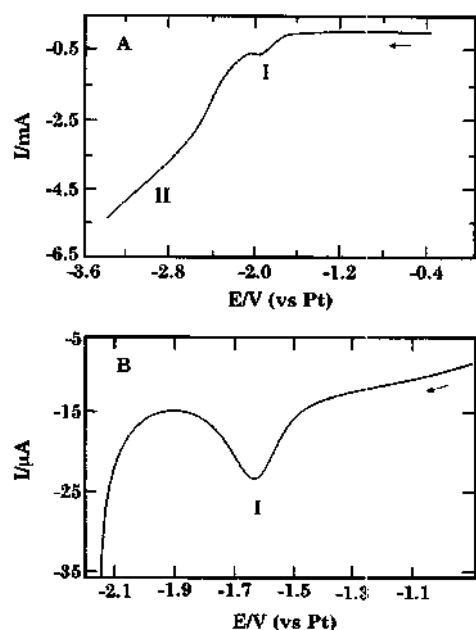
Fig. 4. Voltammetry of AN at nickel in a 0.05 M TEAP solution in PC; AN = 0.1 M; v = 20 mV s⁻¹; (A) in PC, (B) in PY.

Fig. 4A,B show that the negative scan is not basically different from that observed in ACN and DMF. The first peak, which is the electrochemical signature of the polymer grafting, is more easily observed in PC (Fig. 4A) because it is much higher compared with those in ACN and DMF. In sharp contrast, peak I is dramatically smaller in PY (Fig. 4B). Table 1 clearly shows that the current at peak I (I_{p1}) increases at constant AN concentration as the dipole moment of the three PAN non-solvents is increased. In each of these solvents, I_{p1} decreases when the AN concentration is increased. These data indicate that the cathode inhibition is controlled by the AN concentration in the same solvent. Therefore, if the time required for cathodic inhibition changes with the solvent, at a constant global AN concentration, the only reasonable explanation is that the local AN concentration in the electrical double layer is also different, and so must be the polymerization rate and the passivation time. From the experimental observations (Table 1), this local AN concentration must: increase from PC to ACN, and finally to PY. At AN = 0.02 M, peak I is observed only in PY to the exclusion of all the other solvents tested; this fact is consistent with the local AN concentration being higher in PY, which leads to such a fast inhibition that peak I is no longer observed at a monomer concentration of 2 M at a scanning rate of 20 mV s⁻¹.

As far as the second voltammetric peak is concerned (peak II), its origin is separated from the maximum of peak I by ca. 0.4 V to 0.5 V in PY (Fig. 4B) which is much more important than in ACN (0.1 V). In PC, the reverse situation is observed; peak II is so poorly defined that it seems to result from the overlapping of two contributions. At first sight, the gap between E_{p1} and E_{p2} decreases as the cathode inhibition is slower, thus from PY, to ACN and to PC; again, this is important information for optimizing the electrografting conditions.

The electrografting of the film deposited at the potential of the first peak in PC and PY has been confirmed. Indeed this film remains clearly insoluble when the cathode is carefully washed with a good solvent of PAN, e.g., DMF. XPS analysis of the cathode coating also gives a C/N atomic ratio of 3 and C/O ratio larger than 40, in agreement with the expected values for PAN. Similar observations were previously recorded for PAN grafted in ACN [8].

3.3. Effect of the conducting salt and solvent dryness

The experimental data collected in Table 1 are consistent with the competition between the solvent and the monomer for their localization in the double layer at the cathode. The solvent of higher dipole moment competes more efficiently which results in a local decrease of the AN concentration. In order to support this hypothesis, voltammetric experiments were carried out in the same given solvent (DMF), keeping the concentrations of the monomer and the conducting salt at constant values, but changing the molecular structure of this salt, i.e., substituting tetrabutylammonium perchlorate for the commonly used tetraethyl derivative).

Changing the size and hydrophobicity of the ammonium salt has a pronounced effect on the intensity of the inhibition peak, which is systematically higher when the conducting salt is TBAP rather than TEAP (Table 3). Furthermore, this effect is also increased when the concentration of the salt (whatever it is) is increased.

Table 3
Dependence of I_{p1} on the acrylonitrile concentration in DMF added with various amounts of two conducting salts: TEAP, TBAP (v = 20 mV s^{-1})

AN/M	I_{p1}/μA			
	TEAP/5 X 10^{-2} M	TEAP/5 X 10^{-3}M	TBAP/5 X 10^{-2} M	TBAP/5 X 10^{-3} M
0.2	50	31	120	95
0.5	26 (> 60 nm + 5 nm)	21	120 (23nm ± 2nm)	60 (25.5 nm ± 3 nm)
1	17	11	45	30
2	13		17	12

Values in parenthesis are the thickness of the PAN films.

Table 4
Evolution of I_{p1} versus the water content in ACN; v = 20 mV s^{-1}, AN= 1 M

H$_2$O/ppm	I_{p1}/μA
10	30
100	125
400	200

All these observations are again consistent with competition with the monomer for preferential localization in the very close vicinity of the electrode. This competition is more favorable to AN when both the conducting salt concentration and the tetra-alkyl-ammonium size are smaller. Although these experiments have been carried out in the same solvent, at the same temperature and at the same AN concentration (thus the same polymerization rate), the film thickness is much higher when TEAP is the conducting salt rather than TBAP. In fact, the PAN film is visible to the naked eye in the presence: of TEAP but not with TBAP. In this case, the extent of the chain growth would be basically controlled by the local AN concentration. The thickness measurements are in close agreement with the voltammetric observations as shown in Table 3.

It is worth pointing out that all the aforementioned experiments have been carried out under the best conditions of dryness (< 5 ppm H$_2$O) attainable in the electrochemical bath. For the sake of completeness, additional experiments were conducted with solvents contaminated by increasing amounts of water. Table 4 shows that the height of peak I (voltammetry experiments) increases with the water content in ACN and this observation has been confirmed in DMF. The origin of this effect has to be found in the reduction of water (H$^+$ + le$^-$ → H°) that occurs at a less negative potential than the first stage of electroreduction of AN. When the water content exceeds 400 ppm in ACN and 1000 ppm in DMF, the PAN grafting disappears in favor of the reduction of water.

3.4. In situ study of the grafting reaction in both DMF and ACN by means of the quartz-crystal microbalance

Convincing evidence for the electrografting, followed by the polymer desorption during a negative scan, has been found by probing the polymer deposition in DMF using a quartz microbalance. In these experiments, Pt cathodes were used to fit with the resonator requirements. It was found that the same cathodic behavior of AN is observed on both Pt and Ni electrodes [16]. Since the resonant frequency of the quartz-crystal varies with the changes in mass and viscosity at the quartz-crystal surface, it follows that a solid deposit will give rise to a frequency change from the initial resonant frequency. The comparison of the other experimental observations, i.e., voltammograms, and film deposition (or not), allows the changes associated with the mass and the viscoelasticity of the reacting substances on the electrode surface to be distinguished.

Fig. 5a shows how the quartz-crystal frequency depends on the cathode potential when the experiment is conducted in DMF. When the potential range of peak I is reached (ca. — 1.9 V), the resonant frequency decreases as a result of the polymer grafting. At this potential, a homogeneous and transparent PAN film becomes clearly fixed on the cathode, even in DMF, i.e., a good solvent for that polymer. Thus, this part of the response can be attributed to a mass increase. Between - 2.4 V and - 2.6 V (the second voltammetric peak range), a new shift in frequency is observed, which corresponds to the local formation and accumulation of soluble PAN chains in the very close vicinity of the cathode. A non-adherent, yellowish, gel-like polymer is then visible on the electrode withdrawn from the bath after that potential. Beyond - 2.6 V, thus upon increasing time (the potential scanning rate being 20 mV s^{-1}), the apparent mass increase is rapidly lost due to the diffusion of soluble PAN chains towards the bulk of the electrochemical medium. At -3.2 V, most of the originally grafted chains have been lost (see the dotted horizontal line in Fig. 5A) and the original resonant frequency is almost recovered as a result of the 'degrafting' reaction mentioned in the first part of this discussion.
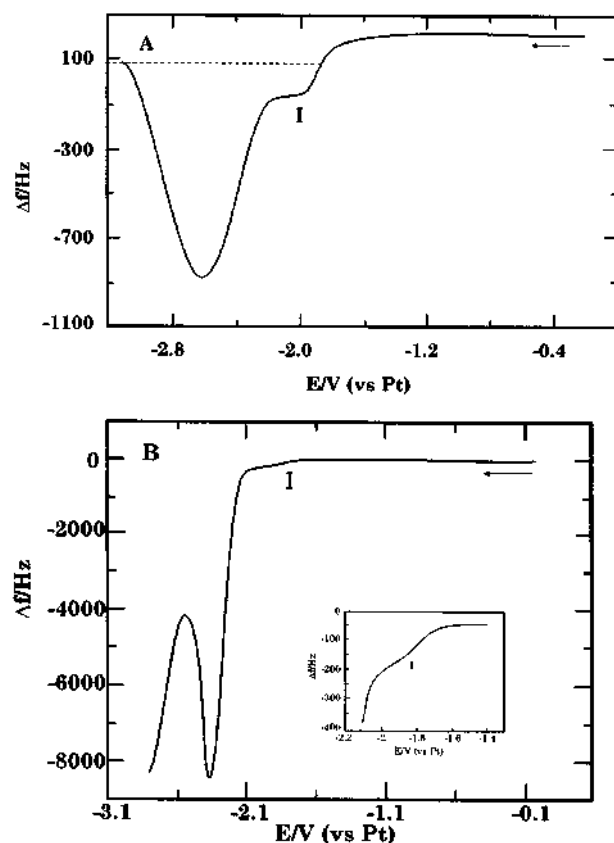
Fig. 5. Results of quartz microbalance experiments on AN at Pt in 0.05 M TEAP solution in (A) DMF; (B) ACN; AN = 0.2 M; v = 20 mV s^{-1}.

This conclusion is confirmed by a very simple experimental observation: after potential scanning up to - 3.2 V, polymer is no longer visible on the electrode by the naked eye. The same experiment was carried out in ACN (Fig. 5B). The first part of the recording is qualitatively the same as in Fig. 5a, i.e., a two-step decrease in frequency (the difference in the frequency scale must be noted). The first frequency change is consistent with the formation of an insulating PAN film in the potential range of peak I, whatever the solvent. It is followed by a more rapid and much more important change in ACN then in DMF in the potential range of the second voltammetric peak. This very dramatic difference between the behavior in these two solvents agrees with the formation of a polymer which is no longer 'grafted' to the cathode. As it is formed, this polymer becomes dissolved in DMF (which locally increases the viscosity [gel formation] and perturbs the quartz crystal frequency), whereas it is precipitated on the cathode causing the formation of a thicker, more compact and non-adherent yellowish polymer coating. The mass increase accounts for a frequency decrease in ACN, which is larger by one order of magnitude compared to DMF. The origin of the transient increase in frequency observed at — 2.4 V in ACN (without, however, reaching the initial frequency), followed by a new decrease in frequency is not clear yet. It might indicate some detachment of the film making some new cathode sites available for the further initiation and precipitation of the polymer.

4. Concluding remarks

From the whole set of experimental data collected in the four solvents under consideration, the solvation of the growing chains grafted onto Ni has a very favorable effect on the thickness of the achieved PAN film, measured ex situ. The greater thickness in a polymer solvent compared to that in a non-solvent might be explained by chain growth continuity for a longer period of time, thus consuming the monomer at the expense of initiation at the cathode surface. The use of a solvent for PAN has also the advantage of enhancing the resolution between E_{p1} and E_{p2}, which decreases the risk of perturbing the formation of the strongly adherent film at E_{p1} by formation of non-grafted chains at E_{p2}. Comparison of behavior in the three non-solvents with different dipole moments leads to the conclusion that the higher is the solvent polarity, the smaller the local concentration of AN in the electrical double layer at the cathode compared to the global concentration. Competition is thus occurring at the cathode between the solvent and the monomer that determines the local concentration of the monomer, the polymerization rate and thus the cathode inhibition rate. An extra competition between the monomer and the

conducting salt has also been demonstrated.

As shown in Tables 1 and 2, the AN concentration is a key parameter since when it is too small, peak I (grafting) and peak II (AN polymerization without grafting) become superimposed. As a result, a non-adherent film is deposited on the electrode. Therefore, any experimental conditions (solvent, conducting salt, etc.) that decrease the local concentration of the monomer in the double layer (where the polymerization is initiated), must have a detrimental effect on the occurrence of the electrografting reaction. Since most of the experiments reported so far have been conducted only in ACN, this might explain why changing the only monomer (and not the solvent), as well as only a few monomers such as acrylonitrile [3], *p*-chlorostyrene [19] and methacrylonitrile [20] have been successfully grafted. As an indication of this, Tanguy et al. [20,25] have recently reported that the appearance of the so-called prepeak (the signature of the grafting reaction) of methacrylonitrile in ACN occurs only at very high concentrations. This observation also suggests a competition between the solvent and the monomer for their localization at the electrode. This paper, therefore, provides an important guideline in the search for new monomers to be grafted onto metals, i.e., such monomer-solvent pairs that the monomer takes precedence over the solvent (and any chemicals in the reaction medium) for the occupation of the cathode sites leading to adherent polymer film formation. Preliminary results that support the validity of this concept will be published in the near future.

Acknowledgements

References

[1] G. Mengoli, B.M. Tidswell, Polymer 16 (1975) 881.
[2] G. Mengoli, Adv. Polym. Sci. 33 (1979) 2.
[3] G. Lécayon, C. Le Gressus, A. Le Moel, Eur. Patent n° 0038 244 (1981).
[4] C. Boiziau, G. Lecayon, La Recherche 19 (1988) 888.
[5] B. Yurttas, L. Toppare, V. Akbulut, J. Macromol. Sci. A25 (2) (1988) 219.
[6] S.N. Bhadani, Q. Ansari, S.K.S. Gupta, J. Appl. Polym. Sci. 44 (1992) 121.
[7] R. Jérôme, M. Mertens, L. Martinot, Adv. Mater. 7 (9) (1995) 807.
[8] M. Mertens, C. Calberg, L. Martinot, R. Jérôme, Macromolecules 29 (1996) 4910.
[9] C. Bureau. G. Deniau, P. Viel, G. Lécayon, Macromolecules 30 (1997) 333.
[10] J. Perreau, C. Reynaud, C. Boiziau, Surf. Sci. 162 (1985) 776.
[11] G. Xue, J. Dong, J. Zhang, Y. Sun, Polymer 35 (1994) 723.
[12] P. Parent, C. Laffon, G. Tourillon, A. Cassuto, J. Phys. Chem. 99 (1995) 5058.
[13] V. Geskin, R. Lazzaroni, M. Mertens, R. Jérôme, J.L. Brédas, J. Chem. Phys. 105 (1996) 3278.
[14] P. Jonnard, F. Vergand, P.F. Staub, C. Bonnelle, G. Deniau, C. Bureau, G. Lécayon, Surf. Interface Anal. 24 (1996) 339.
[15] C. Calberg, M. Mertens, N. Baute, R. Jérôme. V. Carlier, M. Sclavons. R. Legras, J. Polym. Sci., Part B: Polym. Phys (accepted for publication).
[16] M. Mertens, Ph.D. Thesis, University of Liège, Belgium (1995).
[17] C. Fredriksson, R. Lazzaroni, J.L. Brédas, M. Mertens, R. Jérôme, Chem. Phys. Lett. 258 (1996) 356.
[18] M. Mertens, C. Calberg, L. Martinot, R. Jérôme, J. Schrijnemackers, U.S. Patent n° 5,567,297 (1996).
[19] G. Deniau, G. Lécayon, G. Zalczer, C. Boiziau, G. Hennico, J. Delhalle, J. Chem. Perkin. Trans. 2 (1990) 1433.
[20] J. Tanguy, G. Deniau, C. Augé, G. Zalczer, G. Lécayon, J. Electroanal. Chem. 377 (1994) 115-123.
[21] A.L. McClellan, Tables of experimental dipole moments, W.H. Freeman (1963).
[22] G. Lecayon, Y. Bouizem, C. Le Gressus, C. Reynaud, C. Boiziau, C. Juret, Chem. Phys. Lett. 91 (1982) 506.
[23] C. Calberg, M. Mertens, R. Jérôme, X. Arys, A.M. Jonas, R. Legras, Thin Solid Films (accepted for publication).
[24] P. Viel, Ph.D. Thesis, Paris VI, France (1990). [25] J. Tanguy, G. Deniau, G. Zalczer, G. Lecayon, J. Electroanal. Chem. 417 (1996) 175.