

## Investigation of the cathodic electropolymerization of acrylonitrile, ethylacrylate and methylmethacrylate by coupled quartz crystal microbalance analysis and cyclic voltammetry

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### Abstract

The cathodic electropolymerization of acrylonitrile (AN), ethylacrylate (EA) and methylmethacrylate (MMA), has been monitored for the first time by coupled electrochemical quartz crystal microbalance (QCM) and cyclic voltammetry analyses. These data have been compared to the previously published analyses for methacrylonitrile (MAN). At the potential  $E_{p1}$  of the less cathodic of the two voltammetric peaks observed (peak I), the polymer formed is anchored firmly to the cathode even in a good solvent for it, and it remains adsorbed when the voltammetric scan is repeated up to  $E_{p1}$ . In parallel, a linear relationship is observed between the frequency change recorded in situ by the QCM up to  $E_{p1}$  and the PAN film thickness measured ex-situ by ellipsometry. However, when potentials more negative than peak I are scanned, the polymer desorption (degrafting) occurs as assessed by solubilization in a good solvent. Polymerization is also resumed but in solution and no longer as grafted chains. The major difference between the acrylic monomers (AN and EA) and the methacrylic ones (MMA and MAN) is that part of the methacrylic chains are not grafted at  $E_{p1}$ . This coexistence of adsorbed and desorbed chains is not observed for the polyacrylic chains in that potential range. The mass of PAN deposited onto the cathode has been approximated from the film thickness and the Sauerbrey equation, so allowing the  $M_n$  of the grafted chains to be estimated.

**Keywords:** Acrylonitrile; Ethylacrylate; Methylmethacrylate; Electrografting; Quartz crystal microbalance; Ellipsometry; Electrocoating

### 1. Introduction

Coating of metals by organic films is a valuable strategy for changing the surface properties and protecting it from corrosion. The electropolymerization of acrylonitrile and some vinyl monomers has been proposed as a valuable strategy for this purpose [1-2]. In this respect, the report by Lécayon et al. [3] that acrylonitrile (AN) can be electrografted (i.e. strongly chemisorbed) onto usual metals in dry acetonitrile (ACN), is a very promising approach to improve the usually poor adhesion of organic coating onto metals.

When the reduction of AN is carried out under voltammetric conditions, the voltammograms show two peaks. Viel [4] ascribed the peak of very low intensity at the less negative potential ( $E_{p1}$ ) to passivation (peak I) and the peak at the second potential ( $E_{p2}$ ) to diffusion control (peak II). The mechanism that was proposed originally [5] is as follows: (i) dipole orientation and activation of the monomer molecule in the strong electric field in the close vicinity of the

polarized electrode; (ii) vinyl-end chemisorption of the monomer and electron transfer from the cathode to the monomer, yielding a  $\sigma$ -bound intermediate; (iii) chemical propagation of the AN polymerization from this grafted intermediate.

Later on, Tanguy et al. [6] suggested that peak I is a pre-peak resulting from the adsorption of the monomer reduction product, but more likely of oligomers initiated by the monomer reduction product in solution. This assumption was based on experimental observations reported for the electrografting of methacrylonitrile (MAN) in ACN [6-7] and in reference to the observation [8-9] and prediction [10] of more than one voltammetric peak as result of a single electrochemical reaction.

Previous work from this laboratory confirmed the feasibility of the cathodic electrografting of AN, and came to the conclusion that peak I is the critical potential range in which the 'electrografting' reaction occurs [11]. At more negative potential ( $E_{p2}$ ), chain propagation occurs in solution and chain 'grafting' is no longer observed. More importantly, we have proposed recently a guideline for the extension of the electrografting reaction to new monomers [12]. Therefore, in addition to the two monomers that have been known for electrografting for a long time (AN and MAN), a series of alkyl acrylates and methacrylates can now be grafted successfully onto nickel [13-14]. In the case of methacrylates such as MAN and methylmethacrylate (MMA), only part of the chains are grafted to the cathode, even when the potential range of peak I is not exceeded [13]. Furthermore, the passivation peak I is observed only at high monomer concentration. These limitations are not observed in the case of acrylic monomers, such as AN and ethylacrylate (EA) [13].

The coupling of quartz crystal microbalance analysis (QCM) and cyclic voltammetry is a very powerful tool in the analysis of how the electrode and its very close environment are changed simultaneously with the progress of the electrochemical reaction. This strategy has been used in the specific case of MAN. The purpose of this paper being the extension of this analytical strategy to the electroreduction of acrylic (AN and EA) and methacrylic (MMA) monomers, so as to compare the electrochemical behavior of these two families of monomers on a reliable basis.

## 2. Experimental

Acrylonitrile (AN), ethylacrylate (EA), methylmethacrylate (MMA) and acetonitrile (ACN) were dried over calcium hydride and distilled under reduced pressure just before use. *N,N*-dimethylformamide (DMF) was dried over phosphorus pentoxide and distilled at 70°C under reduced pressure. Tetraethylammonium perchlorate (TEAP) was heated in vacuo at 80°C for 12 h prior to use.

Electrochemical experiments were carried out with acrylonitrile (0.2–2 M) dissolved in acetonitrile and *N,N*-dimethylformamide, respectively, and with methylmethacrylate (2 M) dissolved in *N,N*-dimethylformamide. All these solutions contained tetraethylammonium perchlorate ( $5 \times 10^{-2}$  M TEAP) as a conducting salt.

The water content was measured by the Karl–Fischer method (Tacussel aquaprocessor) and ascertained to be lower than 5 ppm. No residual electrochemical signal characteristic of water could be detected. All the experiments were carried out in a glove-box, under an inert and dried atmosphere at room temperature.

The potentiostat, the electrochemical cell and the general procedure for the electrode preparation and electropolymerization were described elsewhere [11]. Potentials were measured against a Pt pseudo-reference electrode.

Film thickness was measured ex-situ using a nulling scheme L117 ellipsometer (Gaertner), at a wavelength of 6328 Å (helium-neon laser) [15]. Two zone measurements were performed, in order to remove residual alignment errors. A model consisting of a homogeneous layer on a flat substrate was used to fit all the data available for PAN films prepared under different experimental conditions at once. The parameters for the model were the film thickness, the refractive index of the nickel substrate, and the refractive index of PAN. The thickness of some samples was measured independently using X-ray reflectometry. These thickness values were held constant while fitting the ellipsometric data. This allowed the optical parameters to be obtained with high accuracy. The values found for the refractive indexes were in the range of the values reported in the scientific literature.

The samples were prepared during a potential scan of  $20 \text{ mV s}^{-1}$  up to the potential of the maximum of peak I, followed by a voltage hold of 20 s. The electrografted films were then washed carefully with DMF in order to dissolve any ungrafted chains, then with ACN and dried finally in vacuo before measurement.

The quartz crystal analyzer was a QCA917 model (PAR EG&G) equipped with a standard 9 MHz, AT-cut quartz crystal and a  $0.2 \text{ cm}^2$  Pt electrode. The sample period was 0.1 s. Combination of this balance with the potentiostat makes it possible to measure simultaneously the current and the potential of an electrochemical reaction and the associated changes in the resonant frequency of the quartz crystal with an accuracy of 0.1 Hz.

### 3. Results

In most QCM investigations, the frequency changes are discussed with reference to the Sauerbrey equation [16], which assumes an ideal rigid layer behavior. Nevertheless, the QCM measures frequency variations and not mass variations, thus taking into account changes in the viscoelasticity of the deposited film and the liquid layer at the quartz-crystal surface. In this respect, Buttry and Ward [17] have shown how the thickness of the organic coating measured ex-situ affects the experimental frequency changes, a linear dependence giving credit to the validity of the Sauerbrey equation.

#### 3.1. Simultaneous cyclic voltammetry and quartz crystal analysis of AN electroreduction

##### 3.1.1. AN electroreduction in a solvent (DMF) and in a non-solvent (ACN) for the polymer.

Fig. 1 shows how the reduction current and the quartz crystal frequency depends on the negative potential in the case of AN solution in a solvent (DMF) and in a non-solvent (ACN) for the polymer. The whole potential range of interest (peaks I and II) was scanned, and the monomer concentration was kept low enough (0.2 M), for the upper limit of the QCM sensitivity (20 MHz) not to be exceeded. Data previously reported for the forward scan [12] are confirmed by Fig. 1 and completed now by data collected during the backward scan.

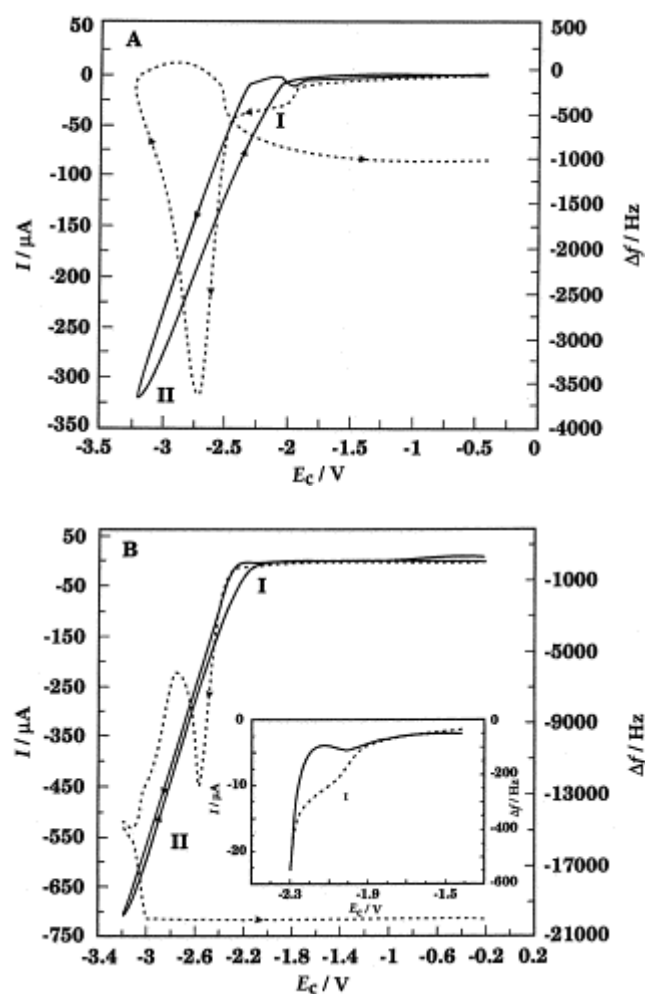


Fig. 1. Simultaneous plot of the AN reduction current (—) and the quartz crystal frequency (---) versus the potential. Solution in (A) DMF; (B) ACN; [AN]=0.2 M; [TEAP]=0.05 M;  $\nu=20\text{ mV s}^{-1}$

In DMF (Fig. 1(A)), a first negative frequency shift associated with the current rise at  $E_{p1}$  (ca.  $-1.9\text{ V}$ ) was observed, consistent with the visible ‘grafting’ of a homogeneous and transparent insulating PAN film. As a result, the current dropped down to zero, and the QCM response was observed as a plateau. When the potential was increased further beyond  $-2.4\text{ V}$ , an additional negative shift in frequency was found, associated with the onset of the current of peak II, consistent with the local formation of a non-adherent, yellowish, gel-like polymer quite visible to the naked eye in the very close vicinity of the cathode. Beyond this potential, thus upon increasing time (the potential scan rate being  $20\text{ mV s}^{-1}$ ), the apparent mass increase was lost rapidly due to the diffusion of PAN chains from the cathode surface to the solution. This observation is evidence that the polymer formed at a potential more negative than  $E_{p1}$  is not ‘grafted’ (chemisorbed) to the metal, since it dissolves rapidly in DMF. The frequency went on increasing with more negative potential until the original resonant frequency was recovered at  $-3.2\text{ V}$ . This observation is most important, since it proves that the PAN chains that were grafted originally at  $E_{p1}$  are released from the cathode (degrafting reaction) at the more negative potential  $E_{p2}$ . This phenomenon was confirmed convincingly by the backward scan. Indeed, a negative frequency shift was observed when the potential of peak I was approached, indicating that the cathode sites made available by the degrafting reaction contributed again to the electrografting of new chains in this critical potential range.

The same experiment was repeated in ACN (Fig. 1(B)) instead of DMF, all the other conditions being the same. Although a large difference in the frequency scale was noted, the response of the system was qualitatively independent of the solvent until  $-2.5$  V (comparison of Fig. 1(A and B)). When the potential range of the second voltammetric peak was scanned, the frequency changed more rapidly and much more markedly in ACN than in DMF. Indeed, polymer chains were not grafted in this potential range and being insoluble in ACN, they precipitated on the cathode as a compact yellowish film. This continuous deposition of insoluble PAN accounts for the mass increase and thus for the frequency decrease that rapidly exceeded the upper limit of the equipment response. No change may be expected in the QCM trace when the potential scanning is reversed as result of the polymer insolubility. The origin of the positive frequency transient observed beyond  $-2.6$  V is not clear. What we know is that the chains originally grafted at  $E_{p1}$  were degrafted at more negative potential [11]. However, they are insoluble in ACN, so that the original film may remain on the cathode, but its morphology has to change so as to make cathode sites available to AN in agreement with the continuous polymer deposition beyond  $E_{p1}$ . These modifications might affect the frequency response in an unpredictable way.

### 3.1.2. AN electroreduction in the potential range of peak I

In the specific case of MAN, the amplitude of peak I decreased very slowly as the cyclic voltammetry of 80% monomer solution (10 M) in ACN (a solvent for the polymer) was repeated, whereas a small reverse peak was observed [6 and 7]. Partial desorption of the originally adsorbed PMAN during the reverse scan was proposed as the explanation for the surface reactivation during the next scan [7]. The same experiment was carried out with AN as a monomer. Fig. 2 shows a typical cyclic voltammogram recorded in DMF for 0.2 M AN solution at  $20 \text{ mV s}^{-1}$ , on a quartz crystal metallized with platinum. The forward curve shows a well defined current peak at  $-1.9$  V. Simultaneously, the quartz frequency was shifted continuously towards negative values, at least until the electrode became passivated. Beyond  $-1.9$  V, the current decreased rapidly, in contrast to the QCM response which did not change very significantly. A thin polymer film was then visible on the cathode when it was withdrawn from the electrochemical bath. During the reverse scan, in contrast to what happens when MAN is concerned, no reverse current peak was recorded and no partial desorption of the polymer is observed by QCM, although DMF is a good solvent for PAN. Rather, the frequency tended to decrease slowly, which indicates that the cathode was not fully passivated and that some grafting occurs when scanning backward in the potential range of peak I.

When the potential scan was repeated, the forward scan showed a significant decrease in the intensity of peak I in agreement with the quasi-complete passivation of the cathode by the insulating PAN layer formed during the first scan. The frequency change was small, which confirms that only a small part of the cathode sites were available for the second reduction step. Once again in contrast to what happened in the case of MAN, no reverse voltammetric peak and no polymer release were observed.

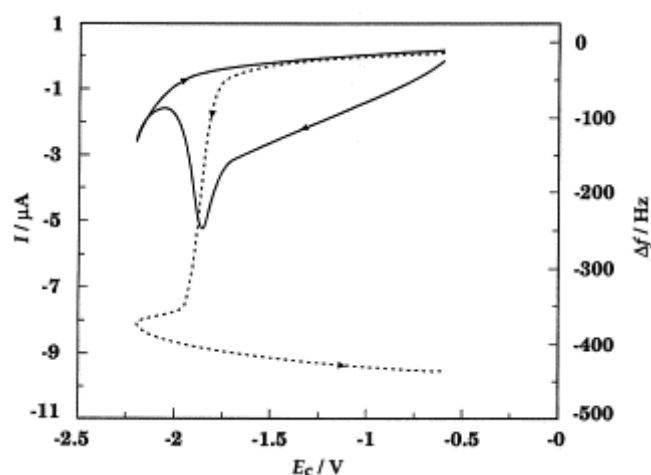


Fig. 2. Simultaneous plot of the AN reduction current (—) and the quartz crystal frequency (---) versus the potential, in the range of peak I, and in DMF. [AN]=0.2 M; [TEAP]=0.05 M;  $\nu=20 \text{ mV s}^{-1}$ .

### 3.2. Simultaneous cyclic voltammetry and quartz crystal analysis of the EA electroreduction

#### 3.2.1. EA electroreduction in a solvent for the polymer (DMF)

Fig. 3 compares the voltammogram and the QCM response when 0.5 M EA solution in DMF is scanned. The QCM response shows again a two-step decrease in frequency when the potential reaches more negative values, consistently with the voltammetric peaks I and II which overlap each other. When potentials higher than  $-2.5 \text{ V}$  were scanned, the frequency increased slowly, indicating that the polymer formed diffused to the solution. In agreement with the behavior of AN in DMF (see Fig. 1(A)), the PEA chains formed in the potential range of peak II, were not 'grafted' to the cathode.

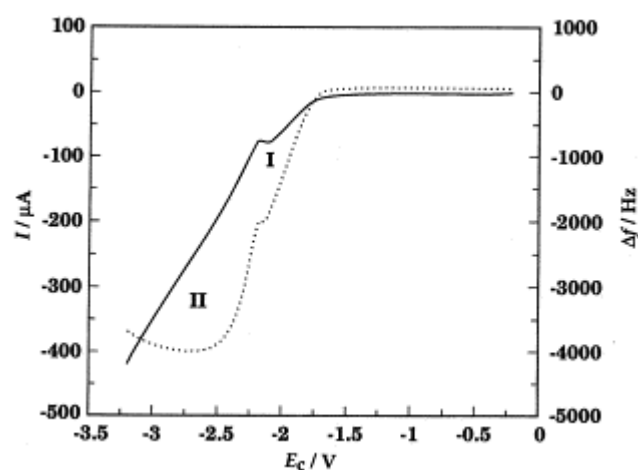


Fig. 3. Simultaneous plot of the EA reduction current (—) and the quartz crystal frequency (---) versus the potential, in DMF; [EA]=0.5 M; [TEAP]=0.05 M;  $\nu=20 \text{ mV s}^{-1}$

### 3.2.2. EA electroreduction in the potential range of peak I

Fig. 4 shows the cyclic voltammogram and the related QCM response when 0.5 M EA solution in DMF is scanned in the potential range of peak I. The cyclic voltammogram remained basically the same when the EA concentration was increased up to 2 M. No reverse current peak was recorded and no significant polymer desorption was observed during the backward scan. These observations are quite consistent with the AN behavior.

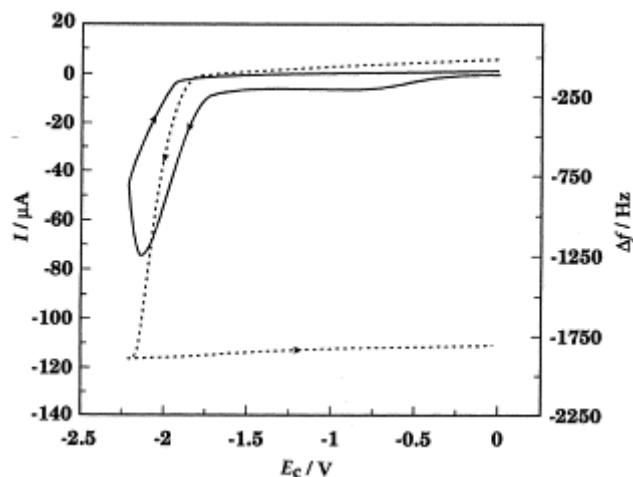


Fig. 4. Simultaneous plot of the EA reduction current (—) and the quartz crystal frequency (---) versus the potential, in the range of peak I and in DMF; [EA]=0.5 M; [TEAP]=0.05 M;  $\nu=20 \text{ mV s}^{-1}$ .

### 3.3. Simultaneous cyclic voltammetry and quartz crystal analysis of the MMA electroreduction

#### 3.3.1. MMA electroreduction in a solvent for the polymer (DMF)

It must be pointed out that peak I was observed only at high monomer concentration when methacrylic derivatives (MAN and MMA) were used rather than acrylic ones (EA and AN) [13]. For instance, Tanguy et al. used MAN concentrations in the range 50 vol.% (6 M) in ACN to 100% (pure MAN) [6 and 7]. Similarly, the electrografting of MMA was reported to occur at concentrations higher than 20 vol.% (2 M) in DMF [13]. A competition between monomer and solvent for adsorption onto the cathode in the very first step of the grafting reaction has been proposed to account for this experimental observation [13 and 14].

Fig. 5 shows a typical voltammogram and QCM response when 2M MMA solution in DMF was scanned at  $20 \text{ mV s}^{-1}$ . An initial negative frequency shift was observed in parallel to the current of peak I ( $-1.8 \text{ V}$ ). Beyond this potential, the current decreased rapidly as result of the cathode passivation by an insulating film. At the same time, the QCM response showed a small positive transient, which was not observed when a solution of AN or EA in DMF was scanned. This small transient followed by a plateau suggests that a small part of the PMMA chains formed at  $E_{p1}$  diffuses slowly to the bulk (DMF is a solvent for PMMA). Beyond  $-2.4 \text{ V}$  (potential range of peak II), an additional negative frequency shift was observed, which corresponds to the MMA polymerization and accumulation of soluble PMMA chains in the very close vicinity of the cathode (a non-adherent gel-like polymer was visible on the cathode when withdrawn from the reaction medium). As result of the high monomer concentration

required, an excessive amount of polymer was formed and the upper limit of the QCM was rapidly reached.

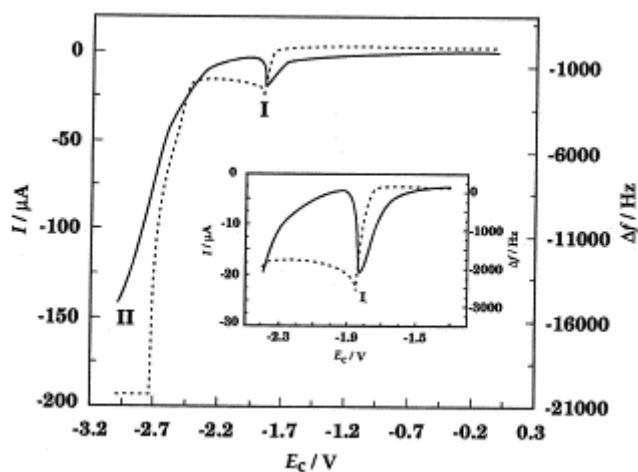


Fig. 5. Simultaneous plot of the MMA reduction current (—) and the quartz crystal frequency (---) versus the potential, in DMF; [MMA]=2 M; [TEAP]=0.05 M;  $\nu=20 \text{ mV s}^{-1}$

### 3.3.2. MMA electroreduction in the potential range of peak I

Fig. 6 shows the cyclic voltammogram of the 2 M MMA solution in DMF restricted to the potential range of peak I (thus until  $-1.9 \text{ V}$ ). The forward scan does not deserve specific comments. On the backward scan, a small 'reverse' cathodic current peak was observed. The QCM response was a positive shift which agrees with desorption of a large amount of polymer from the cathode towards the solution. Nevertheless, part of PMMA remained bound to the electrode when the reverse scan was complete (ca. 45% of the total frequency shift is preserved). This general behavior (Fig. 6) should be compared to Fig. 2 which is characteristic of AN treated under the same conditions (complete absence of degrafting).

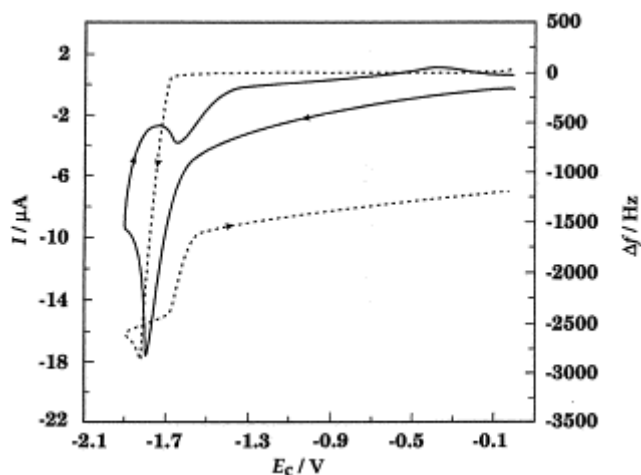


Fig. 6. Simultaneous plot of the MMA reduction current (—) and the quartz crystal frequency (---) versus the potential, in the range of peak I, and in DMF; [MMA]=2 M; [TEAP]=0.05 M;  $\nu=20 \text{ mV s}^{-1}$ .

When the same potential scan was repeated, the cyclic voltammogram was basically unchanged, except for a slight decrease in the intensity of peak I and a comparatively smaller



negative frequency shift. Compared to the first scan, a much smaller amount of PMMA remained anchored to the cathode at the end of the reverse scan (the final frequency shift was about 1200 Hz for the first scan and about 250 Hz for the second one). The amount of polymer grafted during the second scan was smaller than during the first one, as a result of the blockage of part of the cathode sites by the polymer formed during the first scan. These observations (reverse peak and polymer adsorption-desorption process) are in complete agreement with those reported by Tanguy et al. for the electroreduction of MAN [7], but in sharp contrast to the electrochemical behavior of AN and EA.

### 3.4. Relationship between the frequency change associated with peak I and the film thickness measured by ellipsometry

In order to give credit to the above discussion, it is essential to confirm that the frequency shift observed in the potential range of peak I is associated to a mass change. For this purpose, the dependence of the frequency change (measured in-situ by QCM) on the AN concentration has been compared to the same dependence of the PAN film thickness (measured ex-situ by ellipsometry) [15].

Fig. 7 shows how the QCM data depend on the monomer concentration in ACN and DMF, respectively. The frequency shifts recorded at  $E_{p1}$  were highly reproducible and they increased with the monomer concentration in a way that, however, depended on the solvent used. As a rule, the QCM response in ACN was much smaller than in DMF and tended to level off rapidly with increasing AN concentration. In contrast, this response increased regularly with the monomer concentration in DMF, at least up to 2 M. As soon as the PAN chains reach some critical length in ACN, they precipitate on the electrode, which is detrimental to the chain propagation. In DMF, the growing tethered PAN chains are solvated, which preserves their reactivity for a longer period of time.

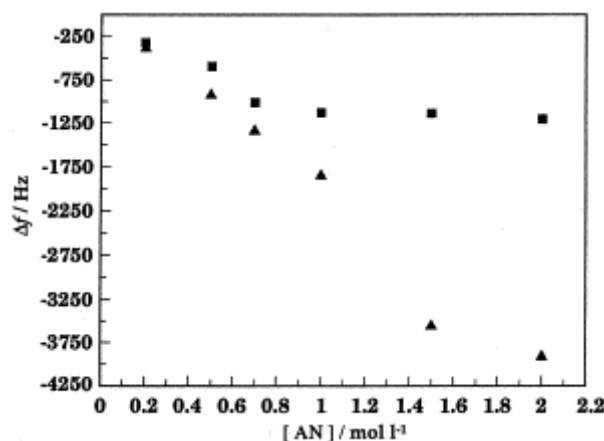


Fig. 7. Dependence of the frequency change (QCM) associated with peak I on the AN concentration in (▲) DMF and (◻) ACN.

The frequency changes recorded in the potential range of peak I in both ACN and DMF have been plotted vs. the thickness of the grafted film measured ex-situ by ellipsometry. Fig. 8 confirms the linearity of the relationship between the frequency changes and the thickness of the films prepared at the potential of peak I. In agreement with Buttry and Ward [17], this linearity indicates that the QCM response is dominated by a mass effect since the film

thickness, which has been measured after drying, is representative of the amount of polymer deposited on the cathode, ruling out any additional contribution.

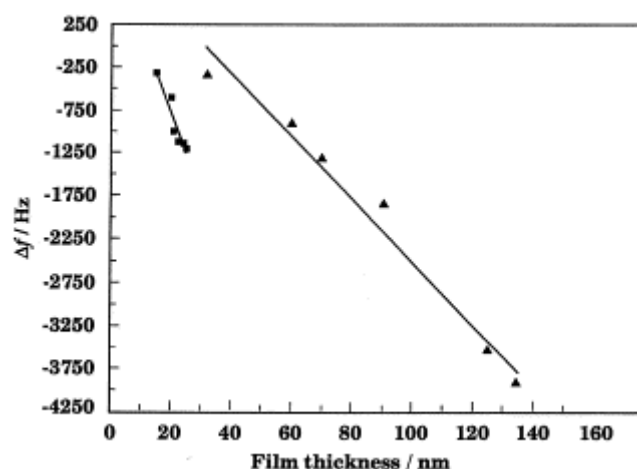


Fig. 8. Relationship between the frequency change (QCM) associated with peak I and the PAN film thickness measured by ellipsometry for samples prepared at this potential ( $E_{p1}$ ) for various AN concentrations in ( $\blacktriangle$ ) DMF and ( $\blacksquare$ ) ACN.

The mass of PAN deposited at  $E_{p1}$  was calculated by two methods. The first method is based on the film volume, (i.e. electrode area and film thickness measured by ellipsometry) and the density of commercially available PAN ( $1.18 \text{ g cm}^{-3}$  [18]). The second method relies upon the Sauerbrey equation [16].

$$\Delta M = -\Delta f A (\rho_q \mu_q)^{1/2} / 2f_o^2$$

where  $\Delta M$  is the mass change,  $\Delta f$  the frequency change,  $A$  the electrode area ( $1 \text{ cm}^2$ ),  $\rho_q$  the quartz density ( $2.648 \text{ g cm}^{-3}$ ),  $\mu_q$  the quartz shear modulus ( $2.947 \times 10^{11} \text{ dyn cm}^{-2}$ ) and  $f_o$  the resonant frequency ( $8.88 \times 10^6 \text{ Hz}$ ).

Table 1 shows that the two calculation methods give comparable results, particularly in DMF, which confirms that the QCM response in this solvent is due basically to the grafted PAN chains and not to some contribution from solvent molecules.

Table 1. Deposition of PAN on the cathode in the potential range of peak I

Solvent	[AN]/mol l <sup>-1</sup>	Film thickness/nm	Frequency change/Hz	10 <sup>6</sup> × Deposited mass/g cm <sup>-3</sup>	
				From film thickness	From the Sauerbrey equation
DMF	0.2	32	350	3.8	2
	1	90	1850	1.1	1.0
	2	135	3910	1.6	2.2
CAN	0.2	15	320	1.8	1.8
	1	22	1130	2.6	6.3
	2	25	1200	3.0	6.7

In a previous paper the PAN grafting density was estimated from the current quantity associated with peak I to ca.  $10^{-9}$  mol of grafted polymer chain per  $\text{cm}^2$  [11]. On that basis

and from data in Table 1, the molar mass of the grafted chains formed in 2M AN solution in DMF has been calculated to be in the range  $16\ 000 < M_n < 22\ 000$ .

#### 4. Conclusions

The coupling of quartz crystal microbalance measurements and cyclic voltammetry has confirmed substantial differences in the electroreduction of acrylic (AN and EA) and methacrylic (MMA and MAN) monomers. When acrylic monomers are concerned, polymer electrografting at the less negative potential  $E_{p1}$  has been assessed by the linear relationship between the frequency changes associated with peak I and the thickness of the polymer film (Fig. 8). That peak I is the actual signature for the grafting reaction, can also be found in the lack of polymer desorption, when the cyclic voltammetry is carried out strictly in the potential range of this peak ( Fig. 2 and Fig. 4). In sharp contrast, desorption and dissolution of the polymer in a good solvent is the rule at potentials more negative than peak I ( Fig. 1 and Fig. 3). Indeed, in the case of AN, the initial resonant frequency is recovered rapidly when the potential of peak II is reached ( Fig. 1(A)). Furthermore the cathode becomes reactivated and a new grafting reaction is observed when  $E_{p1}$  is scanned backward. This situation however changes when a non-solvent for PAN (ACN) is substituted for DMF (Fig. 1(B)). Indeed, as a result of PAN precipitation, the frequency shift has no tendency to come back to the initial value when scanning backward, but rather to decrease further as expected.

The major difference between acrylics (AN and EA) and methacrylics (MMA and MAN) is the formation of nongrafted chains in the potential range of peak I when the methacrylic monomers are reduced. Furthermore, when a solution of methacrylate is scanned backward in the potential range of peak I, a small reverse peak (grafting) is observed which compensates to some extent the partial release of previously grafted chains (Fig. 6). Recent experimental [13] and theoretical [14] data have shown that the success or failure of the electrografting reaction depends on the issue of the competition of the solvent and monomer for their adsorption onto the cathode sites, so confirming that chemisorption of the monomer is the prerequisite for the grafting reaction. At least for the acrylic monomer/solvent pairs considered in this work, the issue of the adsorption competition is very clear, since either no electrografting occurs or it is observed even at low monomer concentrations. In the case of the methacrylic monomer/solvent pairs studied, high monomer concentrations are required, emphasizing that the monomer adsorption is not inherently stronger than that of the solvent. In other words, the average lifetime of the adsorbed monomer and parent growing chains would be much shorter in the case of methacrylics than acrylics at least in the solvents used until now. Thus, depending on the dynamics of the chemisorption, chains appear strongly bonded to the cathode or involved in a grafting-degrafting process. All these observations indicate that the detailed mechanism for the electrografting of (meth)acrylate monomers is dependent strongly on the experimental conditions (solvent, cathodic potential), so that it is very hazardous to propose a general mechanism from the analysis of only one monomer in one solvent as was proposed recently [7].

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## 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 no. 0038 244* (1981).
- [4] P. Viel, Ph.D. Thesis, Paris VI, France, 1990. [5] G. Lécayon, Y Bouizem, C. Le Gressus, C. Reynaud, C. Boiziau, C. Juret, *Chem. Phys. Lett.* 91 (1982) 506. [6] J. Tanguy, G. Deniau, C. Auge', G. Zalczer, G. Le'cayon, *J. Electroanal. Chem.* 377 (1994) 115. [7] J. Tanguy, G. Deniau, G. Zalczer, G. Le'cayon, *J. Electroanal. Chem.* 417 (1996) 175.
- [8] R. Brdicka, *Collect. Czech. Chem. Commun.* 12 (1947) 522. [9] W. Kemula, Z. Kublik, A. Axt, *Roczn. Chem* 35 (1961) 1009.
- [10] R.H. Wopshall, I. Shain, *Anal. Chem* 39 (1967) 1514.
- [11] M. Mertens, C. Calberg, L. Martinot, R. Jérôme, *Macro-molecules* 29 (1996) 4910.
- [12] M. Mertens, C. Calberg, N. Baute, R. Jérôme, L. Martinot, *J. Electroanal. Chem.* 441 (1998) 237.
- [13] N. Baute, P. Teyssié, L. Martinot, M. Mertens, P. Dubois, R. Jérôme, *Eur. J. Inorg. Chem.* (1998) 1711.
- [14] X. Crispin, R. Lazzaroni, V. Geskin, N. Baute, P. Dubois, R. Jérôme, J.L. Brédas, *J. Am. Chem. Soc.* 121 (1999) 176.
- [15] C. Calberg, M. Mertens, R. Jérôme, X. Arys, A.M. Jonas, R. Legras, *Thin Solid Films* 310 (1997) 148.
- [16] G.Z. Sauerbrey, *Physik* 155 (1959) 206.
- [17] D.A. Buttry, M.D. Ward, *Chem. Rev.* 92 (1992) 1355.
- [18] J. Bandrup, E.H. Immergut, *Polymer Handbook*, Third ed., Wiley, New York, 1989, p. V/57.