The Electroreduction of Acrylonitrile: A New Insight into the Mechanism

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ABSTRACT: Several complementary electrochemical techniques have been used in order to clear up the mechanism of the electrochemical reduction of acrylonitrile (AN) on nickel. According to Lecayon et al., the electropolymerization of AN occurs in acetonitrile in the presence of tetraethylammonium perchlorate in such a way that polyacrylonitrile (PAN) is “grafted” onto the cathode. This electrochemical reaction has been reinvestigated both in acetonitrile, a nonsolvent of PAN, and in *N*,*N*-dimethylformamide (DMF), a good solvent for the polymer. The key role of the reduction potential on the electrografting reaction has been emphasized. The two electrochemical phenomena previously reported by Lecayon et al. have indeed been confirmed, but now it is clear that the “electrografting” of PAN selectively occurs at the less cathodic potential. At this potential, a PAN film is formed by a radical process and firmly secured onto the electrode, even in DMF. If the cathodic potential is further increased, the PAN film is easily removed from the metal and dissolves quickly in DMF. The transfer of one electron from the metal to the monomer occurs when the reduction is carried out at the more cathodic potential. A nonadherent PAN film is then formed onto Ni in acetonitrile, although the AN polymerization occurs in solution when acetonitrile is replaced by DMF. The AN polymerization is then consistent with an anionic process.

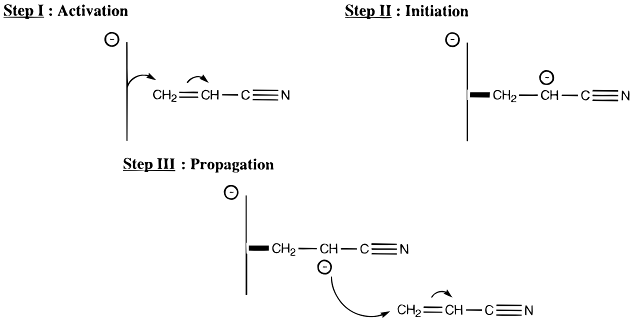
Introduction

During the last decade, increasing attention has been paid to electrochemistry as an interesting technique to polymerize different monomers.[1−4] Electropolymerization is now emerging as a branch of electrochemistry that combines the potentiality of that discipline and the characteristic features of polymer science.

More than 15 years ago, Mengoli reviewed the potentiality of electropolymerization in polymer coating,[5] which is however limited by the long term instability of the polymer/solid substrate interface. In 1988, C. Boiziau and G. Lecayon[6] raised a great prospect by claiming that polyacrylonitrile (PAN) could be grafted onto the usual metals (e.g., Ni) by electropolymerization. Scheme 1 shows the anionic mechanism proposed for the grafting. This result differs from previous studies that pointed out acrylonitrile dimerization[7] and anionic polymerization in solution.[8,9] The observation of two reduction steps for the AN reduction was also reported for the very first time. Furthermore, P. Viel described the two reduction peaks corresponding to a passivation peak at the less cathodic potential and to a diffusion peak, at the second potential.[10] Finally, the grafting reaction of PAN was claimed to occur onto Ni when the electropolymerization is carried out at a potential lying between these two peaks.

In our opinion, the intimate mechanism of the AN electropolymerization is still unclear. Indeed, Lecayon et al. propose a unique mechanism although two reduction reactions are observed. It might also be argued that the PAN film deposited onto the cathode results from the intrinsic insolubility of the growing PAN chains in acetonitrile (ACN), the unique solvent used up to now for “electrografting”. Because of these uncertainties and the huge interest in the possible grafting of a polymer onto a metal, we have revised the cathodic reaction of AN. One of the main issues is to know at which potential the grafting of the PAN on Ni occurs: is it at the potential of peak I, of peak II, or in the whole range of potentials between the two peaks? No clear answer has ever been given by Lecayon et al. Furthermore, the species grafted to the cathode has never been identified. The question of the radical or anionic electrografting reaction is thus considered in this paper.

Scheme 1



Experimental Section

Acrylonitrile (AN), acetonitrile (ACN), and ϵ-caprolactone (ϵ-CL) were dried over calcium hydride and distilled under reduced pressure. *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. 2,2-Bis-(4-*tert*-octylphenyl)-1-picrylhydrazyl (DPPH) (Janssen, >98%) was dried under reduced pressure for a week prior to use.

Electrochemical experiments, i.e., voltammetry, chronoamperometry, chronopotentiometry, and differential pulse polarography, were carried out with acrylonitrile solutions in acetonitrile or *N*,*N*-dimethylformamide (0.1−2 M) containing tetraethylammonium perchlorate (5×10^{-2} M) as a conducting salt. The water content was measured according to the Karl−Fischer method (Tacussel Aquaprocessor) and fixed any time below 5 ppm. All the experiments were carried out in a

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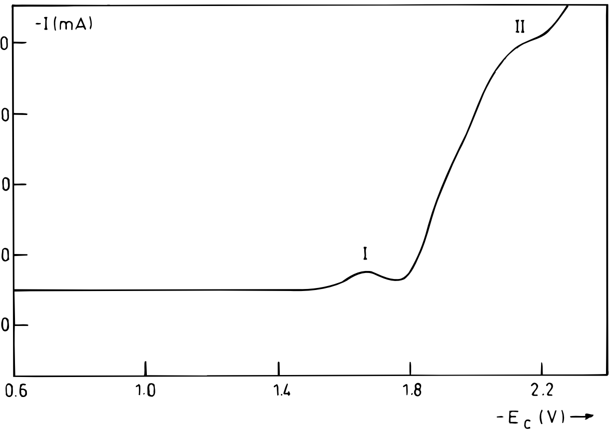


Figure 1. Voltammetry of AN on nickel in a 0.05 M TEAP solution in ACN. [AN] = 0.05 M; $v = 5$ mV s^{-1}.

glovebox under a dried inert atmosphere at room temperature. A PAR-E.G. and G. potentiostat (Model 273A) was used for this purpose. Electrolytic polymerization of AN was achieved in a one-compartment cell (150 mL of solution), and the potentials were measured against a Pt pseudo reference electrode. The two counter-electrodes were platinum foils (10 cm^2 each).

Nickel or zinc plates (3 cm^2) were mechanically polished with an alumina suspension in water, washed with heptane and acetone, and finally treated overnight in vacuo at 180 °C. Just before use, the superficial oxides were electrochemically reduced in ACN containing TEAP (5 × 10^{-2} M). Ni or Zn plates were used as working electrodes. After each electrochemical run, the cathode was carefully washed with ACN before characterization.

Secondary ion mass spectrometry (SIMS) analysis was set out with a Q156-CAMECARIBER spectrometer, and X-photoelectron spectroscopy measurements (XPS) were performed with HP 5950A equipment. IR spectra were recorded with a Bruker (Model Equinox IFS28) FTIR spectrometer equipped with a grazing angle accessory. PAN films were observed with a scanning electron microscope (SEM) (Cambridge Leica) and with a Digital Instruments Nanoscope II atomic force microscope (AFM), operating in contact mode with a commercial Si_3N_4 tip.

Results and Discussion

Figure 1 confirms the existence of the two reduction peaks previously reported for the AN reaction in ACN on nickel. The shape and low intensity of peak I which was referred to as an inhibition peak by Lecayon et al.[11,12] are consistent with an irreversible change of the electrode surface. Consistently, when the electrolysis is carried out at the potential of peak I, a thin and colorless PAN film is formed onto the cathode as confirmed by FTIR spectroscopy (Figure 2).

Figure 3 displays the voltammograms recorded in the very close vicinity of potential of peak I at two different AN concentrations: (a) [AN] = 0.1 M, (b) [AN] = 0.5 M. Any increase in the AN concentration has two major effects, i.e., a decrease in the peak intensity (i_{p1}) and an apparent shift of peak I toward a less cathodic potential (E_{p1}). This abnormal dependence of the inhibition peak on the AN concentration is in sharp contrast to the behavior of peak II, the intensity of which (i_{p2}) increases with the AN concentration, whereas the potential (E_{p2}) becomes more cathodic. Therefore, the voltammogram strongly depends on the monomer concentration.

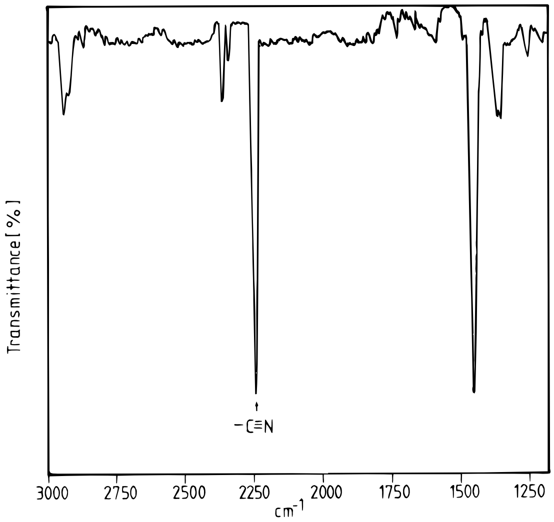


Figure 2. IR spectrum of a PAN film grafted onto Ni in a TEAP (0.05 M) solution in ACN. [AN] = 1 M.

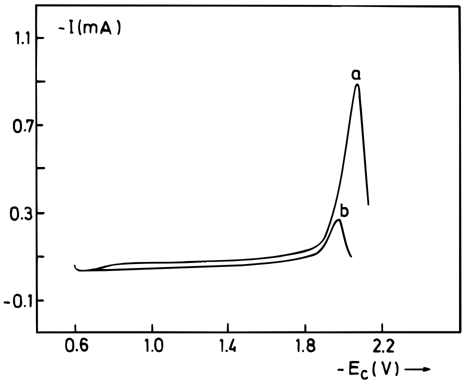


Figure 3. Voltammograms recorded at the potential of peak I for two AN concentrations: (a) [AN] = 0.1 M, (b) [AN] = 0.5 M. ACN/TEAP/Ni system.

As a rule, at low AN concentration (10^{-2} M), only one peak is observed which actually results from the overlapping of two peaks. This originally unique peak splits indeed into two steadily better resolved components upon increasing AN concentrations. In a similar way, the relative intensity of the inhibition peak decreases to the point where it becomes unobserved at AN concentrations higher than 2 M. All these observations perfectly agree with the facts previously reported by Viel.[10] The conclusion is that kinetics of the AN polymerization (chemical process) is controlled by the monomer concentration: when this concentration increases, the inhibition time, thus the time required for the formation of a nonconducting PAN film onto the cathode, decreases and so does the intensity of peak I as shown by voltammetry (Figure 3).

On the assumption of PAN grafting onto Ni,[6] the grafted chain density (D) can be calculated for a faradic reaction according to:

$$D = \frac{I}{F} \times \frac{N}{S} \times \frac{1}{n} \qquad (1)$$

where I = current quantity associated with the reduction peak (C), F = Faraday constant (96 487 C), n = number of electrons involved, N = Avogadro constant, and S = actual surface (Å^2). The high intensity of peak II leads to such an exceedingly high value ($D \geq 10$ chains/Å^2, for $n = 1$) that the "grafting" hypothesis is unacceptable.

D is much smaller (0.2 chain/Å^2) when the reaction is supposed to occur at the first reduction potential, but still too high for being consistent with the "grafting" of

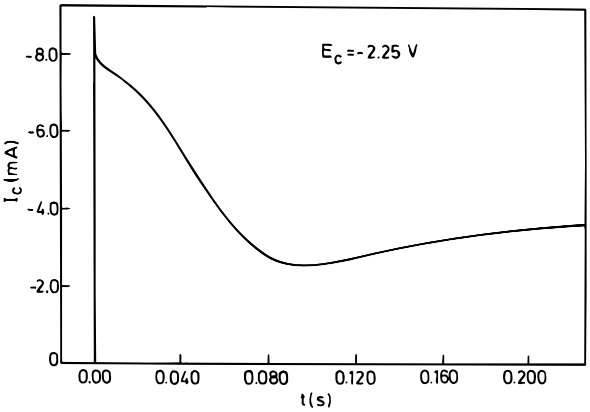


Figure 4. Chronoamperometry experiment of AN on nickel in a 0.05 M TEAP solution in ACN. [AN] = 0.5 M; $E_c = -2.25$ V.

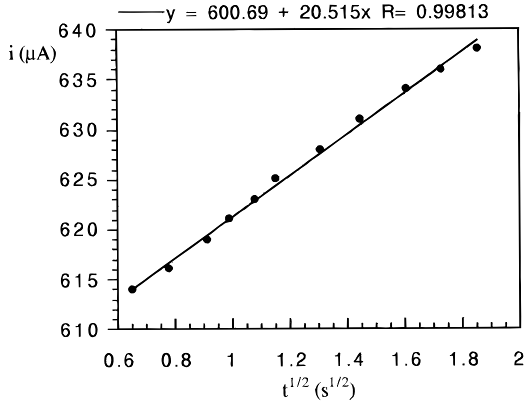


Figure 5. Chronoamperometry experiment of AN on Ni in a 0.05 M TEAP solution in ACN. $E_c = -1.85$ V, i.e., an intermediate value between potentials of peaks I and II. Time dependence of the current intensity in the region of intensity recovery. [AN] = 0.5 M.

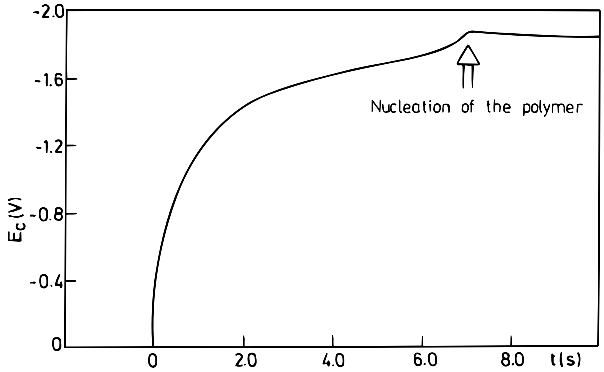


Figure 6. Chronopotentiometry experiment of AN on nickel in a 0.05 M TEAP solution in ACN. [AN] = 0.5 M; $i = 150$ µA.

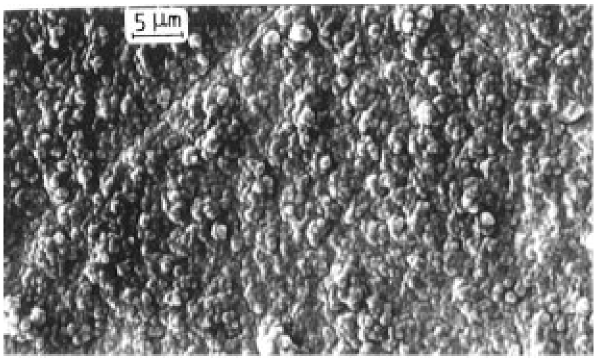


Figure 7. Scanning electron micrograph of PAN film deposited on Ni in a 0.05 M TEAP solution in ACN at potentials between peaks I and II.

PAN chains onto the metal. This latter chain density is ca. 4 times larger than the value observed by Ries and Favis et al.[13,14] for the stacking of stearic acid molecules perpendicular to the air/water interface.

If more than one electron is involved in the reduction process, the calculated grafting density is proportionally smaller, so that the PAN grafting might be a reasonable hypothesis if the reaction at the potential of peak I occurs according to a purely faradic reaction.

Chronoamperometry experiments confirm that two phenomena occur beyond the potential of peak I (Figure 4). Viel[10] has also observed an auto-inhibition phenomenon between 40 and 80 ms, which is the signature of the first reaction observed in voltammetry.

Beyond that point, the current is further increasing according to a linear dependence of i vs $t^{1/2}$ (Figure 5). This observation is consistent with a nucleation reaction with a constant number of active sites.[15] The sites for the nucleation process are likely defects triggered in the original PAN film by a cathodic potential high enough to strain the film. The reaction associated with peak II can then occur on the metal surface locally restored. Thus, Figure 5 implies that the AN polymerization is also initiated at a more cathodic potential than peak I, but according to a different mechanism as supported by the colorless and thin film originally formed at the potential of peak I (voltammetry experiment) which becomes yellow and thicker at a more cathodic potential.

The chronopotentiometric response of the system has also been investigated, although it is known that galvanostatic electrolysis can lead to some unexpected phenomena such as side reactions over a large range of potentials.[16,17] Figure 6 confirms that the nucleation of the polymer film results from "superpolarization" after ca. 7 s: this observation is usually reported in the case of metal deposition preferentially initiated from nucleation sites as evidenced by Fleischman and Thirsk.[18] The "superpolarization" observed in Figure 6 would reflect the increase in potential required for the strain of the insulating PAN film formed at lower potentials.

This nucleation phenomenon has been clearly demonstrated by scanning electron microscopy (SEM). Indeed, the PAN film formed at the potential of peak I is very thin, transparent, and unobserved by SEM, but detected by IR. Figure 7, however, shows a clear nucleation of PAN chains at peak II, which gives to the film a visible cauliflower aspect.

From the aforementioned results, it appears that the electrolysis of the AN/Ni/ACN system is more complex than previously proposed by G. Lecayon et al. The intimate mechanism of AN reduction in ACN is still unclear and requires a more detailed and systematic analysis.

For this purpose, we have considered a larger range of experimental conditions compared with the previous studies. In a nonsolvent for PAN, such as ACN, a polymer deposition is expected to occur whatever the polymerization mechanism: grafting or not. Substitution of a PAN solvent, e.g., DMF, for ACN is thus worthwhile. Furthermore, the use of a Zn cathode also deserves interest, since the inhibition peak is no longer observed (Figure 8), and this fact allows the study of the electrochemical reaction that occurred at the potential of peak II on nickel to be studied quite independently of any preceding reaction.

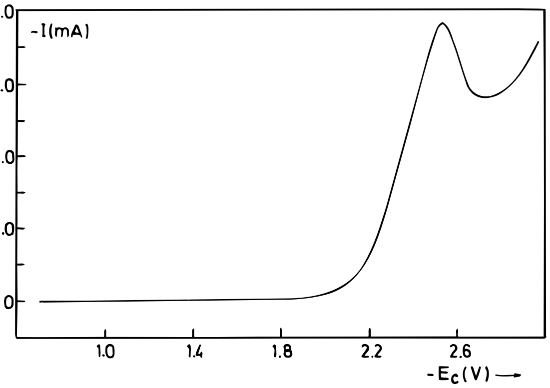


Figure 8. Voltammetry of AN on zinc in a 0.05 M TEAP solution in ACN. [AN] = 5 × 10^{-1} M; $v = 20$ mV s^{-1}.

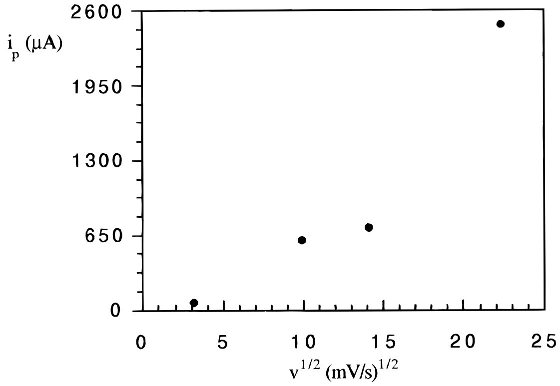


Figure 9. i_{p1} vs $v^{1/2}$ relationship observed by voltammetry on nickel in a 0.05 M TEAP solution in ACN. v is the scanning rate, and i_{p1} is the intensity of the inhibition peak. [AN] = 0.5 M.

Reduction of AN in ACN onto Ni at the Potential of Peak I. Cyclic voltammetry clearly points out that the AN reduction is an irreversible process since no peak is observed when the potential scan is reversed. Nevertheless, the irreversibility of peak I might only be apparent because the AN reduction product, whatever it is, initiates the AN polymerization and is so far consumed in the process.

It is noticeable that the AN polymerization at the potential of peak I produces an insulating PAN film (Figure 1), which is insoluble in any good solvent for the polymer, such as dried DMF. This observation is in favor of a strong adhesion of the PAN film onto the cathode and is consistent with the polymer grafting claimed by G. Lecayon et al.,[16] although a cross-linking reaction of PAN cannot be precluded.

For the sake of comparison, a PAN film spin-coated on nickel is rapidly dissolved in dry DMF.

In order to get some insight into the mechanism of the irreversible reaction at potential of peak I, the peak current (i_p) has been plotted against $v^{1/2}$, where v is the potential scanning rate. No linear relationship is observed (Figure 9), indicating that the reaction is not faradic.[19] Differential pulse polarography (Table 1), however, agrees with a faradic process since the peak intensity is proportional to the pulse height. Finally, from the following equation, which is valid for an irreversible reaction with formation of an insoluble product[19] (100% faradic process), the number of electrons involved in the reaction (n_c) can be figured out:

$$E_p - E_{p/2} = 47.7/(\alpha n_c) \tag{2}$$

Table 1. Dependence of the Inhibition Peak Intensity (i_{p1}) (μA) on the Pulse Height As Observed by Differential Pulse Polarography; ACN/TEAP/Ni; [AN] = 0.1 M

	pulse height		
scanning rate (mV s^{-1})	25 mV	50 mV	100 mV
2	82 ± 5	155 ± 10	340 ± 15
5	73 ± 5	162 ± 10	
10	195 ± 10	395 ± 15	

Table 2. Number of Electrons (n_c) Involved in the Inhibition Process (Peak I); ACN/TEAP/Ni; [AN] = 0.15 M

V (mV s^{-1})	E_p (V)	$E_{p/2}$ (V)	αn_c[a]
5	−1.70	−1.61	0.53
50	−1.85	−1.76	0.53
200	−1.95	−1.85	0.48

[a] α is usually in the range of 0.3−0.7[19] so that $n_c = 1$.

Table 3. Dependence of the Inhibition Peak Intensity (i_{p1}) on the DPPH Concentration; ACN/TEAP/Ni; [AN] = 0.2 M; $V = 20$ mV s^{-1}

[DPPH]	i_{p1} (μA)
0	78
3×10^{-4}	410
10^{-3}	680

where E_p = peak potential (mV), $E_{p/2}$ = half-peak potential (mV), α = charge transfer coefficient, and n_c = number of electrons that participate to the reaction.

Table 2 shows that $\alpha n_c = 0.5$. Since α currently lies in the range of 0.3−0.7 (although the extreme limits are 0.1 and 0.9), $n_c = 1$ would be a reasonable hypothesis, which however requires that the oxidation at the anode does not create or consume any charged species, since the transfer of one electron to AN and bonding of this monomer to the metal must form a radical species. From this discussion, the only reasonable conclusion is that the intimate electronic mechanism responsible for the inhibition peak does not clearly fit a faradic process.

In order to identify the active species (radical or anion) formed when the AN solution in ACN is electrolyzed at the potential of peak I, appropriate chemicals have been added into the electrochemical bath.

DPPH has been used as a probe molecule for the formation of radical species. DDPH is indeed a colored radical (violet) stable under ambient conditions which immediately loses its color in the presence of short-life radicals. ε-Caprolactone (ε-CL) is a cyclic aliphatic ester (7-membered ring) known for *selective ionic* ring-opening reaction.[20] It has been used as a probe for an anionic AN polymerization. These two additives have proved to be electrochemically inert in the investigated range of potentials.

Addition of DPPH to AN solutions has two major effects on the electropolymerization carried out at the potential of peak I. Table 3 shows that the intensity of the inhibition peak (i_{p1}) increases with the DPPH concentration ([AN] = 0.2 M, $v = 20$ mV s^{-1}), whereas the film thickness decreases. These data are consistent with deactivation of "grafted" PAN radicals by DPPH radicals. Accordingly, the PAN chain length (thus the film thickness) decreases, delaying so the inhibition of the Ni cathode. As a consequence of the earlier termination of the growing PAN chains, more monomer is available for initiation and thus for "grafting".

Figure 10 confirms that the density of PAN chains "grafted" onto Ni is higher in the presence of DPPH. This figure is a comparison of a first and a second potential scan on the same electrode either in the

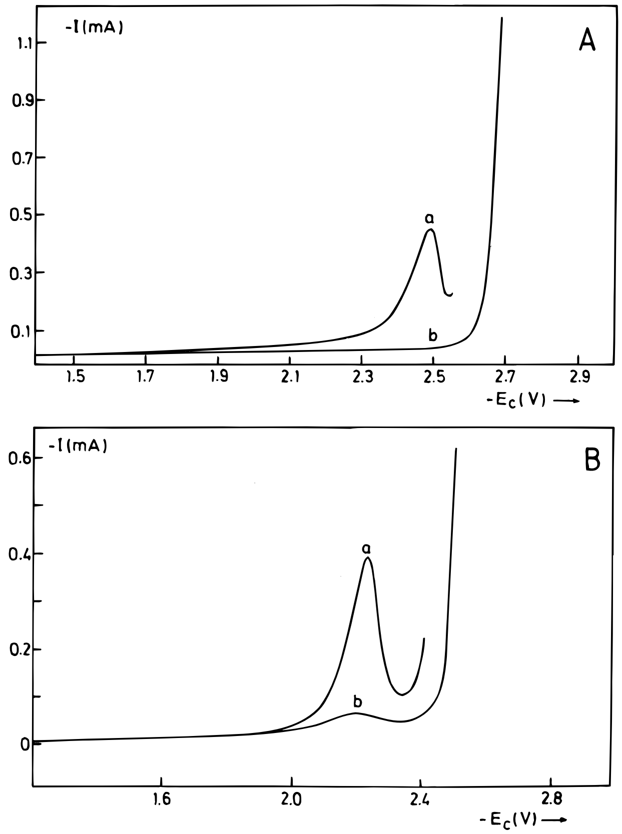
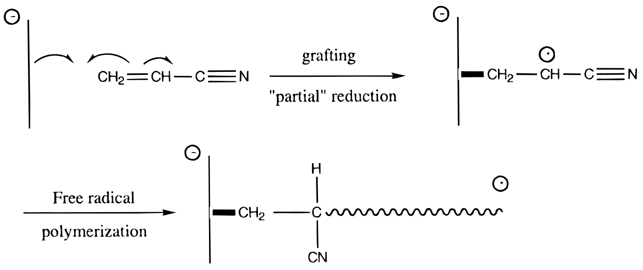


Figure 10. Comparison of first (a) and second (b) potential scan on the same nickel cathode in a 0.05 M TEAP solution in ACN: (A) with DPPH (10^{-3} M), (B) without DPPH. [AN] = 0.1 M; $v = 20$ mV s^{-1}.

presence (Figure 10A) or in the absence (Figure 10B) of DPPH. When DPPH is dissolved in the electrochemical bath (10^{-3} M), no inhibition peak is observed during a second potential scan (b), in contrast to what happens in the absence of DPPH, all the other conditions being the same. This observation agrees with a higher density of "grafted" chains and a more efficient inhibition of the cathode as result of the DPPH addition. It also accounts for the higher current intensity reported in Table 3.

Scheme 2



When the DPPH concentration is higher than 10^{-3} M, the PAN film is so thin that it cannot be observed by the naked eye anymore.

If DPPH is a terminating agent for the PAN radicals growing from the Ni cathode, this molecule should be chemically bonded to the "grafted" PAN film. After careful washing of the cathode with ACN (solvent for DPPH), secondary ion mass spectrometry (SIMS) shows signals for species of 57, 71, and 133 amu, which are not observed when the electrolysis is carried out in the absence of DPPH (Figure 11). These signals are consistent with the $(CH_3)_3C^+$, $(CH_3)_3CCH_2^+$, and $Ar(CH_2)_4^+$ ions, respectively, derived from the *tert*-octylphenyl substituent of DPPH.

Furthermore, the original violet color of DPPH (3 × 10^{-5} M) disappears in the very close vicinity of the cathode as soon as the potential of peak I is applied. This is in sharp contrast to the persistent color of the DPPH solution in acetonitrile when no AN is added. All these experimental observations agree with the formation of acrylonitrile radicals which are firmly linked to the cathode and propagate the radical polymerization of AN (Scheme 2).

In agreement with a radical mechanism, addition of ε-CL does not perturb the AN polymerization at the potential of peak I. Indeed, the intensity of the inhibition peak (i_{p1}) is independent of the ε-CL concentration, all other conditions being the same (Table 4). Thus ε-CL, known for unreactivity toward radical species,[20] does not participate to the electrochemical reaction at the less cathodic potential for the AN reduction. Ac-

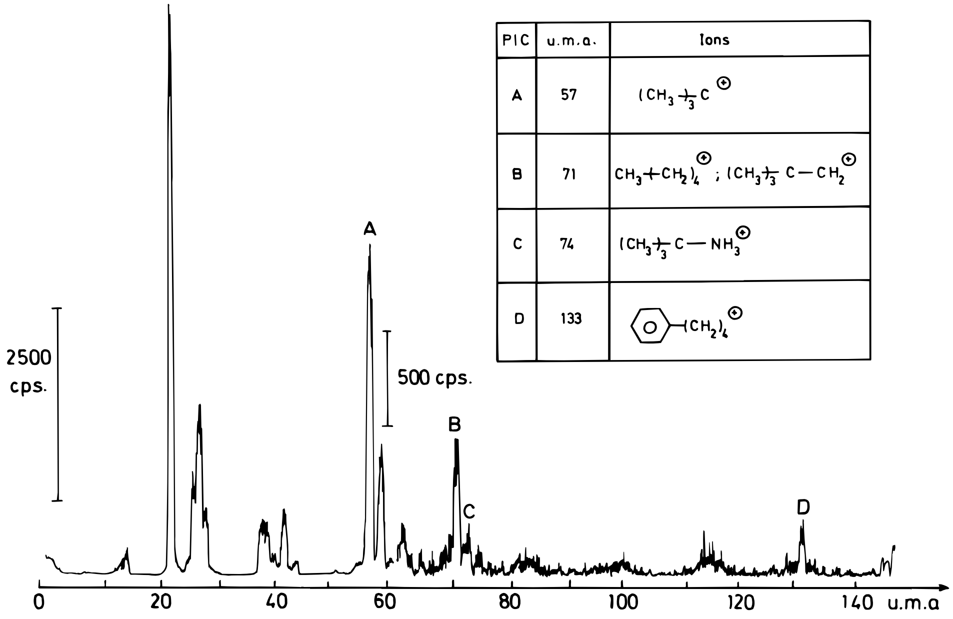
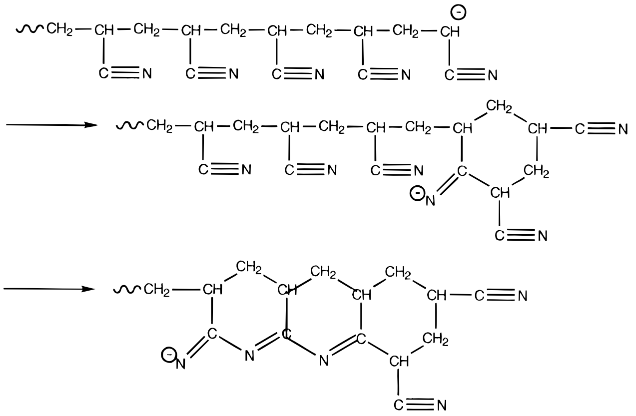


Figure 11. Secondary ion mass spectrometry analysis of a PAN film deposited on Ni in the presence of DPPH in a 0.05 M TEAP solution in ACN. [AN] = 0.1 M; [DPPH] = 3 × 10^{-5} M.

Table 4. Dependence of the Inhibition Peak Intensity (i_{p1}) on the ϵ-CL Concentration; ACN/TEAP/Ni; [AN] = 0.5 M; $V = 5$ mV s^{-1}

[ϵ-CL] (M)	i_{p1} (μA)
0	30
0.25	27
0.5	32
0.75	30

Scheme 3



cordingly, SIMS and FTIR confirm that no ϵ-CL moiety is attached to the PAN film.

In conclusion, the AN reduction at the potential of peak I results in the grafting of a radical species, which then propagates the AN polymerization. This process, which involves the transfer of one electron to AN, is not clearly faradic, and there is no obvious reason for it to be capacitive. Indeed, it would then be quite a problem to account for the strong and irreversible "chemisorption" of the PAN chains on the nickel cathode, since the usual models for capacitive reactions rely upon some reversibility.[19] Actually, the grafted acrylonitrile radical formed as result of the reduction reaction is instantaneously consumed—since it initiates the AN polymerization—which prevents any reliable analysis of the reduction process.

Reduction of AN in ACN onto Ni at the Potential of Peak II. When the electropolymerization is carried out in ACN at a potential of −2.4 V, a PAN film is also deposited onto the Ni cathode. In contrast to the film formed at the potential of peak I, this film is thicker, yellowish, and completely soluble in dry DMF. The yellow color is typical of PAN formed according to an anionic mechanism as reported by Funt et al.[21] for the cathodic AN electropolymerization initiated by a radical anion (Scheme 3). It is worth noting that this coloration disappears when the electrolysis is carried out at a temperature low enough (e.g., −30 °C) to avoid the nucleophilic attack of the nitrile substituents. Undoubtedly, AN can be electropolymerized at two distinct potentials, but according to two different mechanisms as supported by the completely different electrochemical signatures. This explains why the film characteristics change so much when the potential of electrolysis is more cathodic.

Reduction of AN in DMF onto Ni. Deposition of a PAN film onto the cathode when an electrolysis is carried out in a solvent of PAN would undoubtedly be strong evidence for polymer "grafting" onto the metal. It is the reason why the electropolymerization of AN has been repeated in DMF, i.e., a solvent for PAN. DMF is an aprotic solvent quite comparable to ACN with respect to the dielectric constant ($\epsilon = 37-38$) and to the cathodic potential window.

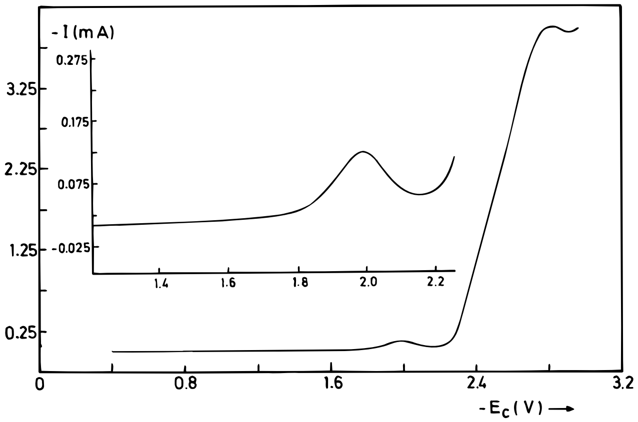


Figure 12. Voltammetry of AN on nickel in a 0.05 M TEAP solution in DMF. [AN] = 0.1 M. $v = 50$ mV s^{-1}.

Under these conditions that were not previously described by G. Lecayon et al., two reduction peaks are again observed by voltammetry on nickel (Figure 12). The peak observed at the less cathodic potential has all the characteristics of an inhibition peak, including the abnormal dependence of the peak intensity (i_{p1}) on the AN concentration. A PAN film is clearly fixed to the Ni electrode and is responsible for the cathodic passivation. This observation is the signature of the strong adhesion of PAN onto Ni. This adhesion is maintained when the electrolysis is carried out under ultrasonic irradiation at the same potential.

It is noteworthy that the PAN film electrodeposited on Ni in DMF shows improved properties compared with the film formed in ACN at the potential of peak I. For instance, the polarization resistance in an aqueous KNO_3 solution (0.1 M) is increased by a factor of 2.5 (2.5 MΩ·cm^2 instead of 1 MΩ·cm^2) when the film is "grafted" in DMF. This beneficial effect could result from a chain propagation for a longer period of time in relation with the solvation of PAN in DMF.

This conclusion is consistent with the film morphology which can be observed by atomic force microscopy (AFM). For this purpose, films have been deposited at the potential of peak I from ca. 1−2 M AN solutions. AFM shows different surface morphologies depending on the solvent (Figure 13). In ACN, precipitation of PAN results in a rough surface instead of a smooth one for films deposited in DMF.

Upon potentiostatic electrolysis at the potential of peak II in DMF, no film is deposited onto the cathode and no irreversible modification of this electrode occurs as evidenced by the duplication of the voltammogram. It appears from the quoted experimental observations that, although AN is polymerized at the potentials of the two voltammetric peaks, the PAN chains are strongly bonded onto the cathode at the less cathodic potential only. Consistently, the film deposited in ACN at the more cathodic potential shows no adhesion to the metal. It is easily peeled off the Ni plate. Furthermore, this film is not responsible for the cathode passivation, which indicates that the electrochemically active sites on Ni remain available, i.e., they are not occupied by "grafted" chains.

It is of the utmost importance that a PAN film originally formed at the potential of peak I no longer adheres onto the Ni cathode when the potential is further increased up to potential of peak II. This observation is consistent with the "debonding" of previ-

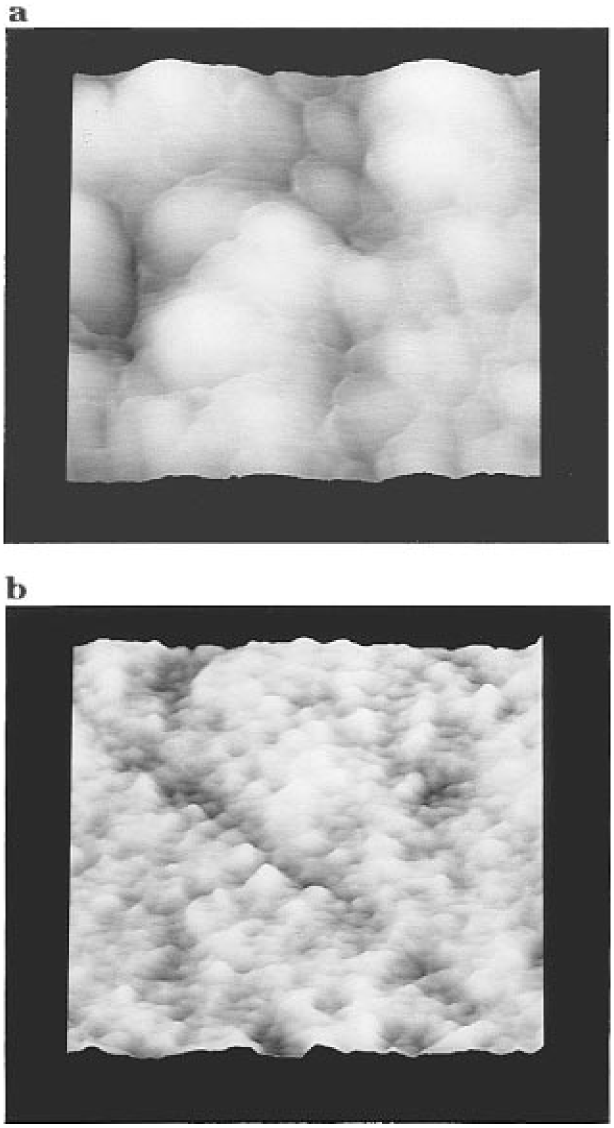


Figure 13. Atomic force micrographs of PAN films deposited on Ni at potential of peak I: (a) in DMF, (b) in ACN; 3-D surface plot with a scan area of 950 × 950 nm^2; vertical scale 1 cm = 31 nm.

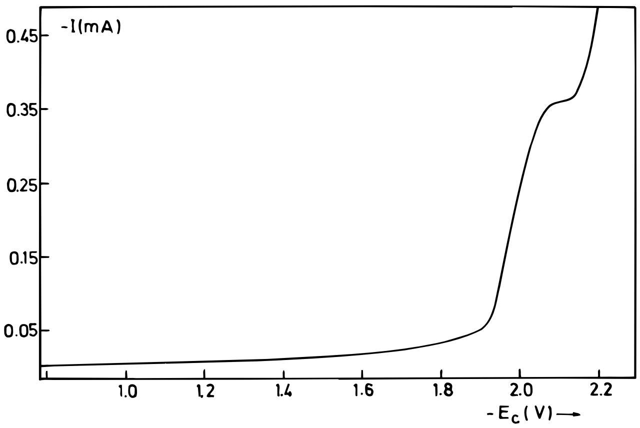


Figure 14. Voltammogram of a PAN film previously deposited on nickel in ACN at the potential of peak I and cathodically polarized in a 0.05 M TEAP solution in DMF. $v = 50$ mV s^{-1}.

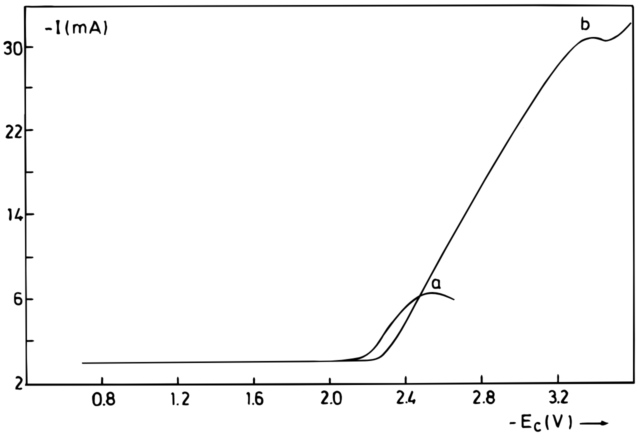


Figure 15. Dependence of the diffusion peak intensity on the AN concentration: (a) [AN] = 0.1 M, (b) [AN] = 0.5 M, for the ACN/TEAP (0.05 M)/Zn system. $v = 10$ mV s^{-1}.

Table 5. Dependence of the Diffusion Peak Intensity on the Pulse Height As Observed by Differential Pulse Polarography; ACN/TEAP/Zn; [AN] = 0.1 M; $V = 2$ mV s^{-1}

pulse height (mV)	i_p (μA)
25	430
30	510
50	900

ously “grafted” chains, at a potential close to potential of peak II.

In order to support this hypothesis, a PAN film deposited on nickel in ACN at the potential of peak I has been cathodically polarized at the peak II potential in DMF containing the usual conducting salt. Figure 14 shows the corresponding voltammogram of the cathodic polarization. During the scan, an unidentified shoulder is observed, and this shoulder is no longer observed when the voltage scan is duplicated.

SIMS analysis of the Ni cathode does not detect anymore the signal at 26 amu typical of the CN$^-$ ion.

Clearly, PAN has been completely dissolved in DMF during the first scan. There is now enough evidence to state that PAN is selectively “electrografted” onto Ni at the less cathodic of the two reduction potentials of AN. The electrode passivation is the signature of the strong anchoring of the polymer film onto the cathode. When the electropolymerization of AN is carried out at the more cathodic reduction potential, no inhibition occurs and the film deposited on Ni in a nonsolvent has no adhesion to the metal. This very clear-cut situation is confirmed by the debonding of an originally “grafted” PAN film, which is demonstrated by the electrochemical signal reported in Figure 14. This signal might actually be responsible for the shoulder observed on the voltammogram in Figure 1 in the potential range between peak I and peak II.

Clearly, the choice of ACN as a solvent for electrolysis may lead to erroneous conclusions about the PAN “grafting” since a film can be merely deposited on the cathode as result of insolubility in the reaction medium.

Reduction of AN in ACN and DMF onto Zn. When Zn is used instead of Ni, all the other conditions being the same, comparison of Figures 1 and 8 clearly shows that the metal used as a cathode has a critical effect on the AN reduction. Only one reduction peak is indeed observed for the reduction on Zn (Figure 8). This peak has the same characteristics as peak II on nickel (Figure 1). The current intensity is indeed much higher than an inhibition peak (such as peak I), and its intensity increases with the AN concentration (Figure 15). Moreover, differential pulse polarography analysis evidences a faradic reaction since the peak intensity is proportional to the pulse height (Table 5). In voltammetry experiments, the peak intensity is proportional

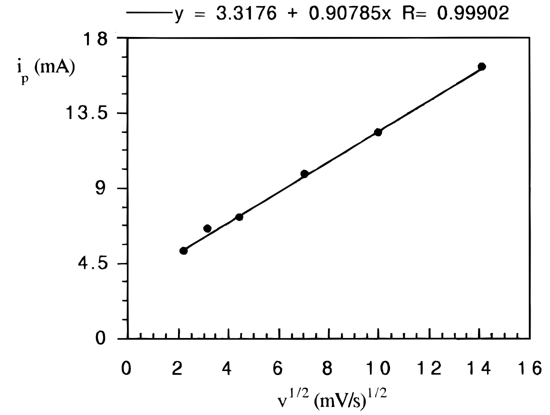


Figure 16. i_p vs $v^{1/2}$ relationship observed by voltammetry for the ACN/TEAP (0.05 M)/Zn system. i_p is the intensity of the diffusion peak, and v is the scanning rate.

Table 6. Number of Electrons (n_c) Involved in the Diffusion Process (Peak II); ACN/TEAP/Zn; [AN] = 0.1 M

V (mV s^{-1})	E_p (V)	$E_{p/2}$ (V)	αn_c[a]
5	−2.526	−2.304	0.21
10	−2.536	−2.311	0.21
50	−2.756	−2.513	0.20
200	−2.844	−2.578	0.18

[a] See eq 2, where the extreme limits for α are 0.1 and 0.9.

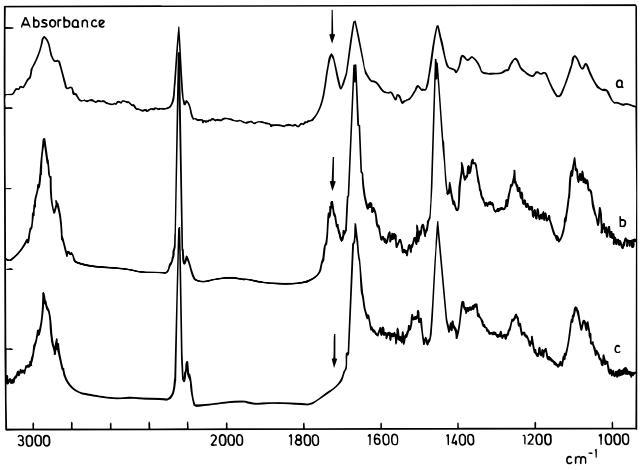


Figure 17. IR spectra of: (a) AN/ϵ-CL copolymer synthesized at the potential of the diffusion peak, [AN] = 2 M, [ϵ-CL] = 1 M; (b) the same copolymer after repeated precipitation in toluene; (c) blend of preformed PAN and poly ϵ-CL (5 wt %) after precipitation in toluene.

to the square root of the scanning rate (Figure 16). Nevertheless, the straight line does not pass through the origin, which is indicative of some kinetic problems. The transfer of one electron at potential of peak II may be supported by eq 2 and data in Table 6, in agreement with Viel's results for the unique peak observed on nickel in the low AN concentration regime ($\leq 5 \times 10^{-3}$ M).[10]

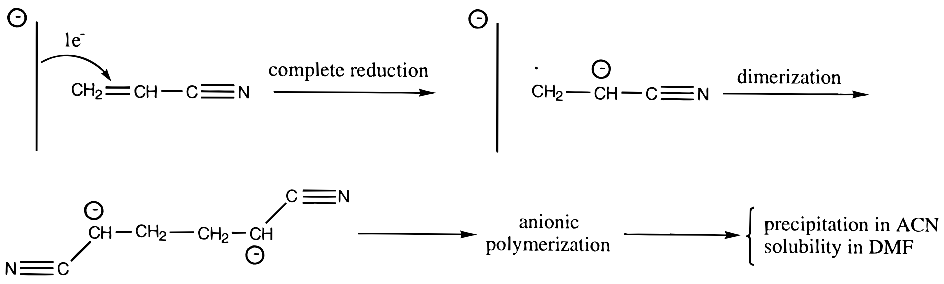
The unique reduction peak observed in ACN is similarly observed in DMF. A solution of AN (2 M) and ϵ-CL (1 M) in DMF has been electrolyzed at a constant current (5 mA) at −20 °C for 1 h. A yellowish polymer has been formed in solution and afterward precipitated into methanol. The IR spectrum of this polymer (Figure 17a) shows an absorption at 1725 cm^{-1}, characteristic of the carbonyl group of ϵ-CL units. The ^{1}H NMR analysis confirms this observation and concludes with a composition of 5 wt % poly ϵ-CL.

The formation of an AN/ϵ-CL copolymer has been independently confirmed by the persistent absorption at 1725 cm^{-1} upon the repeated precipitation of the polymer in toluene, which is a solvent for poly ϵ-CL and a nonsolvent for PAN (Figure 17b). This observation is in sharp contrast to the IR analysis of a mixture of preformed PAN and poly ϵ-CL (5 wt %): the precipitation of this mixture in toluene is responsible for the complete disappearance of the IR absorption of the carbonyl group of ϵ-CL units (Figure 17c). Since the propensity of ϵ-CL to be anionically polymerized is well-known,[20] the AN copolymerization with ϵ-CL demonstrates the formation of AN anions. It is essential to mention that ϵ-CL is electrochemically inert within the same potential range. On the basis of these data, we propose to consider the reduction of AN at the highest potential (peak II) as a faradic process that involves the transfer of one electron from the metal to AN with formation of a radical anion (n_c = 1) followed by a very fast dimerization and anionic polymerization of AN (Scheme 4).

Proposal of a Mechanism for the Electrochemical Polymerization of AN onto Nickel. Undoubtedly, AN is polymerized at two different reduction potentials, according to a specific mechanism at each of them. However, "electrografting" of PAN onto nickel selectively occurs at the less cathodic potential. The unique mechanism proposed by G. Lecayon et al. (Scheme 1) has thus to be revised. Consistently with the experimental observations, the three following proposals are put forward for the AN electropolymerization mechanism.

At the less cathodic reduction potential of AN, a radical species is "grafted" onto Ni as shown in Scheme 2. This process is quite unusual as depicted by the abnormal characteristics of the electrochemical peak observed by voltammetry. The strong interaction between the metal and the growing PAN chains explains why PAN remains bound to the metal even in a solvent of PAN. The film is colorless as is usually the case for PAN formed by a radical process. The film thickness is small (<1 μm) as a result of a more or less rapid termination of the growing radicals by bimolecular recombination or disproportionation.

Scheme 4



At the second cathodic peak, a faradic reaction occurs which depends on the transfer of one electron from the metal to the monomer.[22] As shown in Scheme 4, an AN radical anion is formed in agreement with the recent proposal by Bhadani et al.[8] This active species is not grafted onto the metal as evidenced by the absence of passivation, but it rather forms a dimer in solution by radical coupling. The dianionic species then propagates the AN polymerization independently of the metal. In ACN, the insoluble PAN is deposited onto the metal as a yellowish film, i.e., the same color as a PAN film formed by anionic polymerization where secondary nucleophilic attack of the nitrile substituents occurs (Scheme 3).

Polarization of a previously “grafted” PAN film at a potential more cathodic than peak I is responsible for polymer debonding and for restoration of the electrode conductivity.

Conclusion

A thorough analysis of the electropolymerization of AN in relation to the metal cathode (Ni and Zn) and the organic solvent (ACN and DMF) has contributed to improve the understanding of the underlying mechanism.

Under the experimental conditions previously described by G. Lecayon et al. (Ni and ACN), the AN reduction at two distinct potentials is confirmed by voltammetry. Electropolymerization occurs at each of these potentials but according to a different mechanism. At the less cathodic potential, an inhibition peak is observed as the result of a complex mechanism since it does not fit with classical standards: neither with a faradic process nor with a fully capacitive process.

The most important observation is the deposition of a strongly adhering film onto the Ni cathode even in a solvent for PAN (DMF). The addition of either DPPH or ϵ-CL to the AN solution leads to a clear evidence for the formation of a radical species that initiates and propagates PAN chains firmly attached to the Ni cathode. At the more cathodic potential, reduction of AN is a faradic process based on the transfer of one electron to the monomer and the formation of an anion radical that rapidly dimerizes and initiates the AN polymerization independently of the cathode. As a result, no film is deposited onto this electrode in a solvent for PAN (DMF). In a nonsolvent (ACN), the polymer is merely precipitated onto the electrode as a nonadherent film.

When Zn is used as a cathode, only one reduction is observed at such a potential that the faradic process occurs and the PAN chains are not bonded to the metal.

The inhibition peak observed with Ni is the actual signature for a very strong adhesion of PAN chains to the cathode, which is referred to as a chain grafting by Lecayon et al., who paid attention to elucidate the nature of the chain−metal interaction.[11]

In addition to the dual mechanism proposed above, a possible debonding of originally “grafted” PAN chains has to be considered when the potential is increased beyond the value requested for their formation. An increasingly more cathodic potential can also be responsible for the strain of the originally “grafted” film, so that the conductivity of the cathode is very locally restored, and this allows the anionic polymerization of AN to occur and to lead to PAN films with a cauliflower aspect in ACN.

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