Electrografting of Acrylic and Methacrylic Monomers onto Metals: Influence of the Relative Polarity and Donor–Acceptor Properties of the Monomer and the Solvent

Noëlle Baute[a], Philippe Teyssié[a], Lucien Martinot[b][+], Marc Mertens[a][++], Philippe Dubois[a][+++], and Robert Jérôme*[a]

University of Liège, Center for Education and Research on Macromolecules (CERM)[a],
Sart Tilman, B6, B-4000 Liège, Belgium

University of Liège, Laboratory of Analytical Chemistry and Radiochemistry[b],
Sart Tilman, B16, B-4000 Liège, Belgium

Received April 14, 1998

Keywords: Materials science / Surface chemistry / Electrochemistry / Organic-inorganic hybrid composites / Donor-acceptor systems

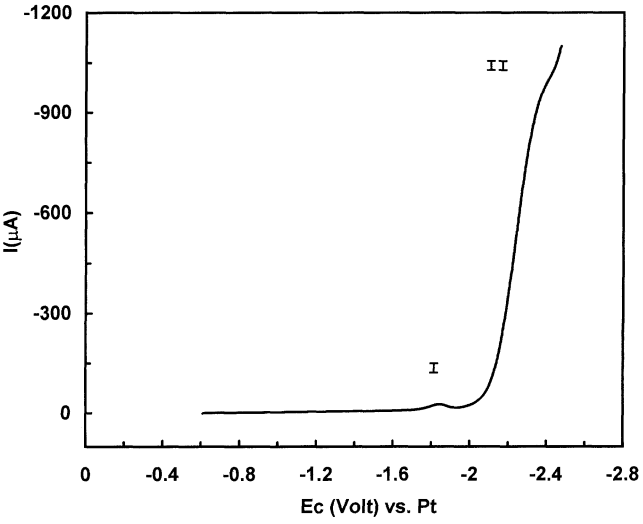
The possibility of grafting a series of alkyl polyacrylates and polymethacrylates onto a nickel cathode by electropolymerization of the parent monomers has been investigated and has emphasized the critical importance of the solvent used. Indeed, the intensity of the inhibition peak, which is the electrochemical mark of the cathode passivation as result of the polymer grafting, clearly depends on both the polarity and the donor-acceptor properties of the solvent. The Gutmann concept is used to account for these experimental results. An increase in the donicity of the solvent used for the electrochemical medium has allowed, for the very first time, several polyacrylates and polymethacrylates [such as poly(ethyl acrylate), poly(methyl methacrylate), and poly(2-trimethylsilyloxyethyl methacrylate)] to be electrografted onto Ni. This observation is consistent with a competition process between the monomer and the solvent for being adsorbed on the cathode and amassing in its very close vicinity. The outcome of this competition is controlled by the relative polarity (in case of low donicity) and the relative donor-acceptor properties (when the difference is high enough) of the monomer/solvent pair, and by the monomer concentration (in case of weak competition). A semi-quantitative relationship has also been observed between the monomer ability to be electrografted and the electron-accepting character of the vinyl β-carbon atom as measured by ^{13}C NMR.

Introduction

Although electrochemistry is a well-known technique for coating various conducting substrates by an organic polymer, the achievement of a stable polymer-metal association is usually a challenge, since a poor and short-lived interfacial adhesion is the rule[1][2].

According to the pioneering work by Lécayon et al.[3][4], we have confirmed in a previous paper[5] that polyacrylonitrile (PAN) could be cathodically electrografted onto several transition metals (Ni, Cu, Fe), and made clear that peak I, observed by voltammetry (Figure 1) is the mark of the grafting reaction. The term grafting, which implies a chemical bonding of the polymer to the metal, has been used by these authors on the basis of X-ray emission spectroscopy (EXES) analysis[6]. This quite unusual and promising reaction, originally reported in acetonitrile (ACN), which is a nonsolvent for the polymer (PAN), has been confirmed in a good solvent such as dimethylformamide (DMF)[5]. This observation is a convincing evidence for a highly stable interaction between PAN and the metal in the potential range of peak I. When this potential is increased further (Figure 1, peak II), the originally "grafted" PAN is debonded and dissolved in DMF and the polymerization occurs in solution[7][8].

Figure 1. Voltammetry of AN on nickel in a 0.05 M TEAP solution in DMF; [AN] 0.5 M; $v = 20$ mVs^{-1}



[+] Research associate of the Inter-University Institute for Nuclear Sciences (Brussels).
[++] Current address: Norton Performance Plastics, avenue du Parc 18, B-4650 Chaîneux, Belgium.
[+++] Current address: Laboratory of Polymeric Materials and Composites, University of Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium.

  1434–1948/98/1111–1711 $ 17.50+.50/0

Until now, only very few monomers are known for their capability of being grafted onto a metallic cathode. In addition to polyacrylonitrile that has been most extensively studied, grafting of poly(*p*-chlorostyrene) has been reported some years ago by Deniau et al.[9]. This conclusion might, however, be distorted by the parasitic loss of the chlorine atom simultaneously observed. A cross-linking reaction[10] gives a better account for the intrinsic insolubility of that polymer in the solvent used (ACN) and thus for the presence of the deposited film. The case of polymethacrylonitrile, recently reported by Tanguy et al.[11][12], is less ambiguous, since this polymer is known to be soluble in the reaction medium (ACN). Furthermore, according to these authors, infrared spectra did not show any structural modification indicating cross-linking[11]. Nevertheless, they noted that the electrografting of polymethacrylonitrile in acetonitrile strongly depended on the monomer concentration, without giving a satisfactory explanation for this experimental observation.

It is clear from the "state of the art" that the actual weakness of the electrografting reaction is the severe restriction on the choice of the polymer to be grafted. Discovery of new monomers prone to electrografting and able to make a stable organic coating reactive is highly desirable for specific technological applications (adhesion in composite materials, ...). The purpose of this paper is to search for experimental conditions under which the electrografting reaction known for acrylonitrile and methacrylonitrile could be extended to a large set of vinyl monomers. There is indeed a complete lack of information that could serve as a guideline for increasing the range of electrografted organic coating. It is interesting to note that the problem of polymer adhesion on various surfaces in different solvents has been discussed in terms of acid-base interactions between polymer and solid, polymer and solvent, and solvent and solid, in order to explain polymer deposition in a particular medium[13][14]. The problem is, however, more complex when the polymer is formed in situ by electropolymerization, since an additional partner has to be considered, i.e. the monomer. Furthermore, at the very first step of the process, only monomer and solvent may compete for adsorption on the metal, which is actually the electrode where electropolymerization is initiated. Once a polymer is formed, sites originally available to polymerization initiation would be progressively occupied until the complete passivation of the electrode. Nevertheless, during the whole process, a competitive monomer/solvent adsorption on sites left unoccupied has to be operative and to control the electrochemical reaction. It is therefore of prime importance to focus on the monomer adsorption on the cathode, a prerequisite step for the polymer grafting according to the early works by Lécayon et al.[15]. In line with these considerations, the adsorption of acrylonitrile ($CH_2=CH_3-CN$, the most widely studied monomer) from gas phase and liquid phase has been experimentally studied in case of metal substrates, i.e. copper[16], gold[17], platinum[18], silver[19], and nickel[20]. According to theoretical models, acrylonitrile interacts with the surface of copper, nickel, and iron[8][21] through both nitrile group and vinyl end, whereas it does not interact strongly with zinc[22]. These authors have also shown that formation of a σ complex between the β-carbon atom of the acrylonitrile C−C double bond and the metal atom is favorable in a moderate electric field, the nitrile substituent of the monomer being aligned along the field[8]. All these results emphasize the importance of the monomer adsorption. The voltammetric curves also suggest that an adsorbed species is involved in the charge-transfer step[23]. The important role played by the solvent in interfacial adsorption processes has been known for a long time in electrochemical experiments[24]. Displacement of solvent molecules by an electroactive molecule is the rule[25] and competitive adsorption of different species is a phenomenon commonly observed in these experiments[26]. Consistently, we have recently reported on the influence of the solvent polarity on the acrylonitrile electrografting, in particular on the monomer concentration in the electrical double layer of the electrode[7]. In this paper, we will discuss the problem of the competitive monomer/solvent adsorption for a series of solvent/monomer pairs, in reference to the well-known Gutmann donor−acceptor concept[27][28], which is a widely accepted criterion in electrochemical processes[29][30]. It will be shown, that the adequate choice of the solvent donor−acceptor properties with respect to the monomer, is a very powerful tool for qualitatively predicting the electrografting of a series of polymers widely used for technological applications [such as poly(ethyl acrylate), poly(methyl methacrylate) and poly(2-trimethylsilyloxyethyl methacrylate)] (Scheme 1), and known as "ungraftable" until now. A semiquantitative criterion will be proposed to evaluate the grafting capacity of new monomers and which solvent would be most appropriate to this purpose.

Results and Discussion

It has been observed for the first time that an acrylate other than acrylonitrile, i.e. ethyl acrylate, could be grafted onto nickel, just by substituting DMF for the commonly used ACN solvent. This observation has led to the detailed analysis reported in this paper.

For the sake of completeness, it must be noted that the widely described behavior of acrylonitrile will serve as a reference to establish whether the grafting of the monomers considered in this work, occurs or not. Numerous criteria have thus to be considered and have been systematically checked for each monomer considered in this study. Since the aim of this paper is to report on the critical effect of the solvent on the electrografting course, this systematic part of the work is not detailed here, but summarized as follows[5].(i) Both passivation (peak I) and diffusion (peak II) peaks can be observed in the recorded voltammograms (see Figure 1 as an example). (ii) When electrolysis is carried out in the potential range of peak I (Ep1), a thin polymer film is formed on the cathode, even in a good solvent for the polymer. No cross-linking reaction may account for this insolubility. When a second forward scan is carried out in this

potential range, the current intensity cannot be recovered as a consequence of the cathode passivation. Except when mentioned in the discussion, no unbound polymer is formed in the potential range of peak I, as attested by a lack of polymer precipitation when the electrochemical bath is poured into a nonsolvent for this polymer. The intensity of peak I (ip1) decreases when the monomer concentration is increased as result of a more rapid formation of an insulating film. No linear relationship between ip1 and $v^{1/2}$ can be found (v is the potential scanning rate). (iii) ip2 increases with the monomer concentration and a linear relationship between ip2 and $v^{1/2}$ confirms the diffusion-controlled origin of peak II. Chain propagation then occurs independently of the cathode (as confirmed by precipitation of the polymer from the electrochemical bath).

Ethyl Acrylate (EA) Reduction in Acetonitrile (ACN) and in Dimethylformamide (DMF)

Cathodic scans have been carried out in an extended range of EA concentration ($5{\cdot}10^{-2}$ to 2 M) in ACN, and only one reduction peak of high intensity is observed (Figure 2a). This unique peak has been previously identified as a diffusion peak, since the peak intensity (ip2) linearly increases with the square root of the potential scanning rate[5]. ip2 is also observed to increase upon increasing EA concentration, while its potential (Ep2) becomes more cathodic. Polymerization then occurs in the electrochemical solution.

The experiments have been repeated in DMF. Starting from the lowest concentration (10^{-2} M), as in ACN, the diffusion peak alone was noticed. Above 0.5 M EA concentration, this unique peak splits in two resolved components of highly different intensity, as shown by voltammetry on nickel in Figure 2b. Actually, the resolution of the two peaks (thus the distance they are apart from each other) increases and the intensity of peak I (ip1) decreases, when the monomer concentration is increased (Table 1). As previously concluded from the AN electrografting[5], the voltammogram strongly depends on the monomer concentration and on the polymerization kinetics. When the EA concentration is increased, the time required for the formation of an insulating film onto the cathode decreases, and so does ip1 since the inhibition occurs faster. When electrolysis is carried out in the potential range of peak I, the current drops down to zero and only a residual current is observed when the potential scan is repeated. Even though the experiment was conducted in DMF, a good solvent for poly(ethyl acrylate) (PEA), a film is clearly bound on the nickel electrode and is responsible for the cathodic passivation. Infrared spectroscopy carried out ex situ confirms the deposition of a PEA film (Figure 3a), since the IR spectrum is identical to the one recorded for a reference PEA film prepared by free-radical polymerization (Figure 3b). The four main bands at 2983, 1740, 1456 and 1183 cm^{-1} have been assigned to $\nu_{as}(CH_2)$, $\nu(C{=}O)$, $\delta(CH_2)$, and $\nu(C{-}O)$.

As discussed in a previous paper[7], the solvent polarity has a critical effect on the electrografting and this has been

Figure 2. Voltammetry of EA on nickel in a 0.05 M TEAP solution in: a) ACN, [EA] = $5{\cdot}10^{-2}$ M; b) DMF, [EA] = 2 M; v = 20 mVs^{-1}

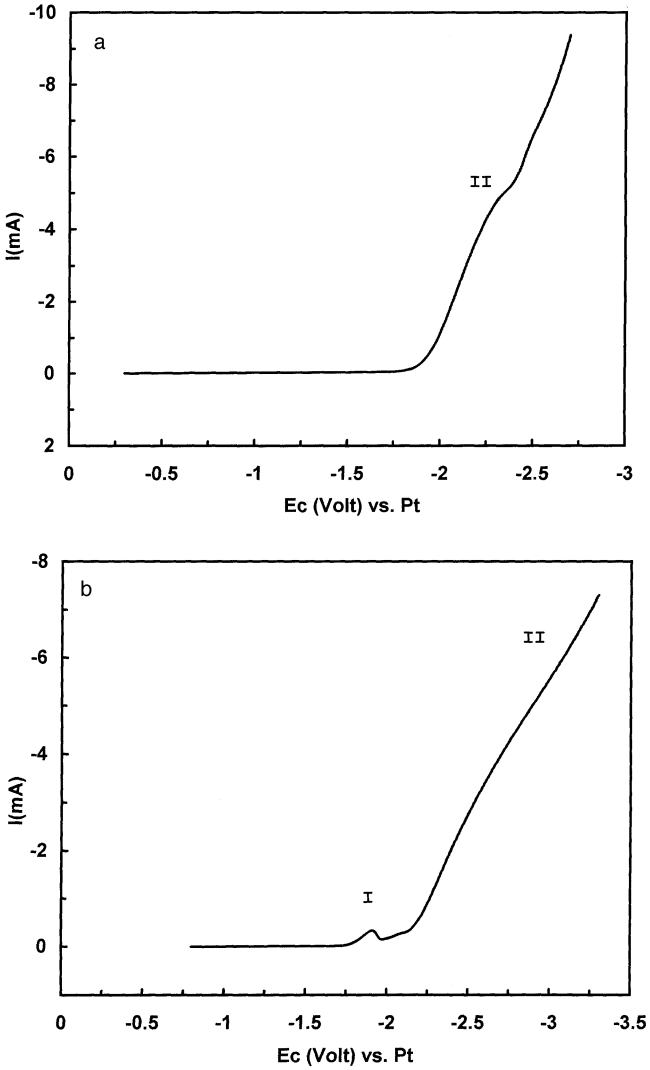


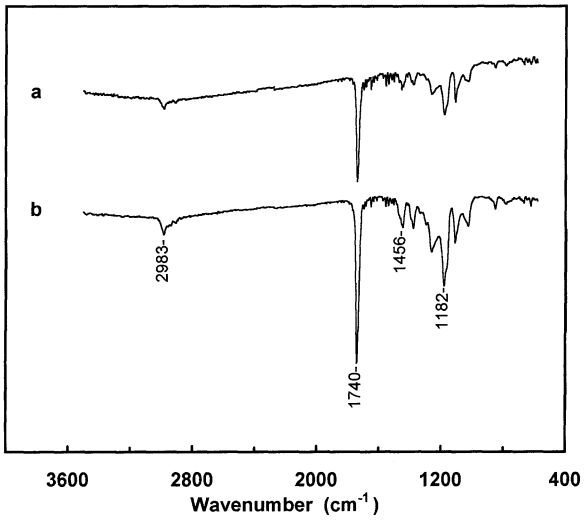
Table 1. Intensities of peak I (ip1) for various EA concentrations in DMF; v = 20mVs^{-1}

Solvent	[EA] = 0.1 M	[EA] = 0.5 M	[EA] = 1 M	[EA] = 2 M
DMF	[a]	500 μA	400 μA	300 μA

[a] Peak I superimposed to peak II.

explained by a competition between the solvent and the monomer. Depending on this competition, the actual monomer concentration at the cathode will be or will not be high enough for observing the cathode passivation. Since ACN and DMF have a very comparable polarity [ε(ACN) = 38.0; ε(DMF) = 36.1], this parameter cannot explain why EA is not electrografted to the cathode in ACN, although it is in DMF above a defined concentration, all the other conditions being the same. The Gutmann donor-acceptor approach[27][28] could however be a better basis for the qualitative comparison of the solvent and the

Figure 3. Infrared spectrum of a) a PEA film deposited on Ni from a solution of [EA] = 2 M in DMF at potential of peak I; b) a free-radically prepared PEA casted onto a Ni plate



monomer and their possible competition for the occupancy of the cathode surface. The donor number is characteristic of the solvation, coordination, and adsorption properties of the solvent. It is defined for each solvent as the numerical value of the enthalpic variation that occurs when the donor is added to the reference acceptor. Quantitative measurements have been carried out by Gutmann et al.[33], in case of a number of O- and certain N-containing solvent molecules added to antimony(V) chloride as the reference acceptor in 1,2-dichloroethane (the donor number of which has been assigned to 0). The acceptor number[28] is defined as a dimensionless number related to the relative chemical shift of ^{31}P in Et_3PO dissolved in the particular solvent. Hexane and $Et_3PO-SbCl_5$ in 1,2-dichloroethane are the references, to which the acceptor numbers 0 and 100, respectively, have been assigned. Antimony(V) chloride has been used as a standard for both acceptor number and donor number, in order to emphasize the relationship between acceptor properties and their conjugate donicity. Table 2 lists the donor number, the acceptor number and dielectric constant for the solvents which are used in this study. It is interesting to note that the acceptor number decreases from ACN to HMPA, thus in the reverse order to that of the donor number, although this observation is not the rule within the Gutmann scale. Under these specific conditions, the tendency of the solvents (used in this study) to be adsorbed may be discussed in terms of either donor numbers or acceptor numbers. Since the donor number of these solvents (Table 2) extend over ca. half the donor number scale (0−38.8) whereas the acceptor number (Table 2) cover a very short range of the acceptor number scale (0−129), the main discussion will refer to the donor number of the solvent without losing sense. DMF is clearly a stronger donor and a poorer acceptor than ACN. When AN and EA are compared (Scheme 1), the ester substituent of the polymerizable C−C double bond in EA is less efficient than the nitrile substituent in AN in triggering an electron delocalization. In the chemisorption model proposed by Lécayon et al.[15], AN would be properly oriented in the electric field at the cathode, as a result of the strong electron-withdrawing nitrile substituent. The acidic extremity (i.e. the β-carbon atom) of AN would accordingly be in an ideal position with respect to the reactive sites on the cathode (considered as a Lewis base). The β-carbon atom of EA has a lower acceptor capability than AN, which may be a key issue, since adsorption in electrochemistry (here on the cathode) is always a competitive process[24] between the adsorbate (the monomer in this case) and the solvent. Indeed, for an adsorbate molecule to occupy a surface site, a number of solvent molecules have to be displaced. It is therefore quite reasonable to assume that the electrografting of a monomer can only occur in a solvent which has a lower tendency to be adsorbed onto the cathode site, i.e. a solvent which is a poorer acceptor and/or a better donor.

Scheme 1

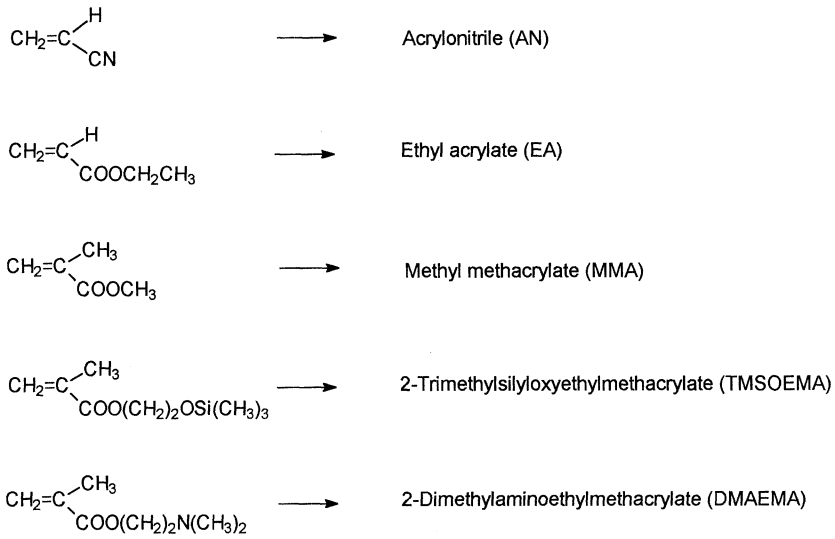


Table 2. Donor number, acceptor number, and dielectric constant of different solvents

Solvents	Donor number[28]	Acceptor number[28]	Dielectric constant[28]
ACN	14.1	19.3	38.0
PC	15.1	18.3	65.0
DMF	26.6	16.0	36.1
PY	33.1	14.2	12.3
HMPA	38.8	10.6	30.0

Several series of experiments are proposed in this paper to support this hypothesis. In a first step, the EA/DMF solution has been added with ACN in order to check the extent to which the electrochemical mark of the electrografting is perturbed.

In a second step, the electropolymerization of AN will be compared in four solvents: ACN, PC, PY, and HMPA, that are all nonsolvents for PAN. ACN and PC have a low and similar donicity, but highly different polarity. The donicity of PY and HMPA is high and quite comparable, whereas the polarity is very different (Table 2). The same cathode (Ni) and the same conducting salt (Et_4NClO_4, $5\cdot10^{-2}$ M) will be used in all the experiments.

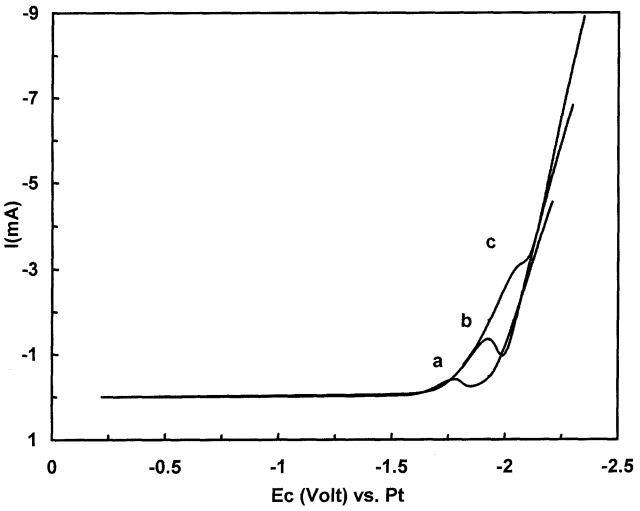
Finally, three methacrylic monomers: methyl methacrylate (MMA), 2-dimethylaminoethyl methacrylate (DMAEMA), and 2-trimethylsilyloxyethyl methacrylate (TMSOEMA) will be studied for investigating the possible effect of the monomer structure on their ability to be grafted onto the cathode.

Ethyl Acrylate (EA) Reduction in a Mixture of DMF and ACN

Figure 4 compares the voltammetric cathodic scans of a 1M EA solution in DMF modified by an increasing percentage of ACN. The monomer concentration is kept unchanged in all the experiments. When EA is electrografted in DMF, the intensity of the inhibition peak is ca. −400μA (Figure 4a). When the relative amount of ACN in the EA/DMF solution is increased, the intensity of peak I increases, whereas the resolution between peak I and peak II decreases (Figure 4 b, c). The dependence of ip1 on the ACN percentage in the EA/DMF solution is such that the cathode is more slowly inhibited, in agreement with a lower EA concentration at the cathode. This observation suggests that the co-solvent (ACN in this case) competes with the monomer for adsorption on the cathode. Since ACN and DMF have the same polarity and are both good solvents for PEA, only a significant difference in the donor-acceptor properties can explain the experimental observations in Figure 4.

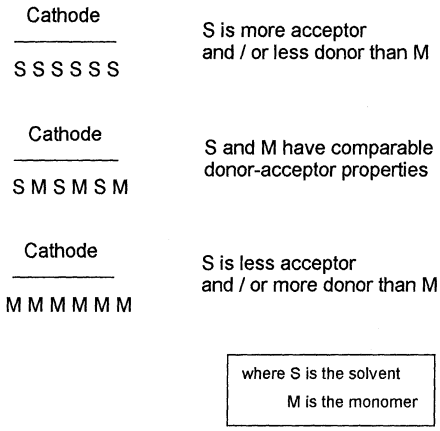
Scheme 2 illustrates this extreme situation where the monomer (e.g. EA) is a poorer acceptor than the solvent (e.g. ACN) and is so far unable to displace the solvent molecules in order to be adsorbed on the cathode sites. No inhibition peak is observed on the voltammogram but only a diffusion peak: this indicates that the monomer reduction

Figure 4. Voltammetry of EA on nickel (v = 20 mVs^{-1}) in a DMF solution, [EA] = 1 M, Ip1 dependence on the addition of ACN: a) without ACN; b) + 3% of the volume; c) + 12% of the volume



can occur at a more cathodic potential, as confirmed by the polymer formation in solution.

Scheme 2



Comparative Reduction of Acrylonitrile (AN) in ACN and PC, in PY and HMPA

Table 3 shows that the intensity of peak I (ip1) increases when PC is substituted for ACN at constant monomer (AN) concentration, thus when polarity is increased in case of solvents of low donicity. Figure 5 shows voltammograms of AN in PY. The intensity of peak I is much lower than in ACN and PC for the same monomer concentration (Table 3). As a rule, the cathode inhibition is controlled by the monomer concentration and ip1 systematically decreases as the AN concentration is increased[5]. So, the small ip1 value in PY might be explained by a high local AN concentration in the electrical double layer and a more rapid formation of an insulating film. As previously discussed the low polarity may account for the experimental observations[6], but the

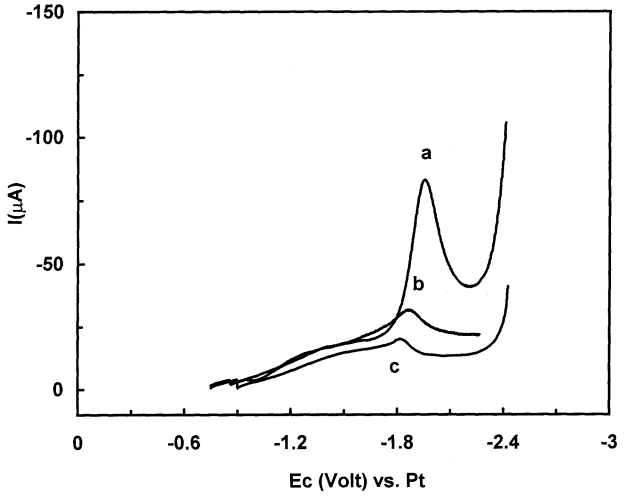
effect of the solvent donicity may not be ignored. In order to appreciate the relative importance of solvent polarity and solvent donicity, hexamethylphosphoramide (HMPA) which has a high and comparable donicity as PY, but which is 2.5 times more polar has been used. Table 3 shows that there is no significant difference in the voltammograms in PY and HMPA since ip1 remains almost unchanged when HMPA is substituted for PY, all the other conditions being the same. From Table 3, we can draw the conclusion that the solvent polarity has a decisive effect on the AN electrografting only when the solvent is a good enough acceptor and a poor donor (see ACN/PC pair). When the solvent is a poor acceptor and a good enough donor (PY/HMPA pair), the polarity has no longer a significant influence, since that solvent has a small tendency to be adsorbed onto the cathode. Although neglected until now, the relative donor-acceptor properties of the monomer/solvent pair must be considered when the monomer electrografting is concerned.

Table 3. Intensity of peak I (ip1) for various AN concentrations in ACN, PC, PY, HMPA; $\nu = 20$ mVs^{-1}

Solvents	[AN] = $5\cdot10^{-2}$ M	[AN] = 0.1 M	[AN] = 0.5 M	[AN] = 2 M
ACN	[a]	370 μA	30 μA	25 μA
PC	[a]	650 μA	90 μA	60 μA
PY	25−30 μA	15−20 μA	[b]	[b]
HMPA	30−35 μA	15−17 μA	[b]	[b]

[a] Peak I superimposed to peak II. − [b] Peak I intensity to weak to be detected.

Figure 5. Voltammetry of AN on nickel in a 0.05 M TEAP solution in PY: a) [AN] = $2\cdot10^{-2}$ M; b) [AN] = $5\cdot10^{-2}$ M; c) [AN] = 0.1 M; $\nu = 20$ mVs^{-1}



Scheme 2 summarizes the main experimental observations, that lead to the following conclusions: (i) As previously pointed out, no electrografting occurs when the solvent is a better acceptor than the monomer, to the point where the solvent is preferably adsorbed on the cathode to the exclusion of the monomer. (ii) When the monomer and the solvent have quite comparable donor-acceptor properties, the adsorption on the cathode is controlled by their relative polarity, the more polar compound being preferably adsorbed. (iii) If the solvent is a better donor and a poor acceptor (compared to the monomer), its tendency to adsorption is low, and any difference in polarity has no remarkable effect on the inhibition peak. The propensity of the monomer to be electrografted will be enhanced by increasing its electron acceptor capability compared to the solvent. Then the inhibition could be so fast that peak I is no longer observed because of an extremely low intensity. The only way to observe it, would be to decrease the monomer concentration.

Methyl Methacrylate (MMA) Reduction in ACN and in DMF

Although donor and acceptor numbers are available for a series of traditional solvents, no pertinent information has been reported in case of monomers, at least to our best knowledge. This situation has prompted us to compare three methacrylate monomers, different by the substituent in the ester group and accordingly by the acceptor properties of the β-carbon of the polymerizable double bond (Scheme 1). The monomers have also been selected on the basis of the "reactivity" of the ester group in order to provide the final organic coating with adhesive properties towards a polymeric matrix, e.g. for producing composite materials. Methyl methacrylate (MMA), the most widely used methacrylate, 2-hydroxyethyl methacrylate (HEMA), and 2-dimethylaminoethyl acrylate (DMAEMA) have been considered in this study (Scheme 1).

Electroreduction of MMA has been first studied in ACN, and only one diffusion peak has been observed, indicating that the solvent is preferably adsorbed onto the cathode within a monomer concentration range of 0.1 M to 3 M.

In reference to Scheme 2, DMF, i.e. a solvent of a higher donicity than ACN (Table 2) was substituted for ACN, in order to increase the probability for the monomer to be preferably adsorbed on the cathode. At MMA concentrations smaller than 2 M, only one reduction peak (diffusion peak) is observed. Beyond 2 M, this unique peak splits into two steadily resolved components. Figure 6 shows the voltammogram when the MMA concentration is 3 M. Undoubtedly when MMA concentration is increased, the intensity of the less cathodic peak rapidly decreases (Table 4) and the resolution between the two peaks increases. This behavior is typical of the inhibition peak observed in experiments conducted with AN and EA. The main difference with respect to these monomers, has to be found in the high concentration required to evidence the MMA electrografting. This observation indicates that MMA can only successfully compete for adsorption onto the cathode when its relative abundance with respect to DMF is high enough. The same experimental observations have been reported for methacrylonitrile[11], which is a poorer acceptor than acrylonitrile due to the electron donating effect of the α-methyl substituent.

Figure 7 shows the cathodic response of a 2 M MMA solution in DMF when the cathodic scan of the potential

Figure 6. Voltammetry of MMA on nickel in a 0.05 M TEAP solution in DMF, [MMA] = 3 M; v = 20 mVs^{-1}

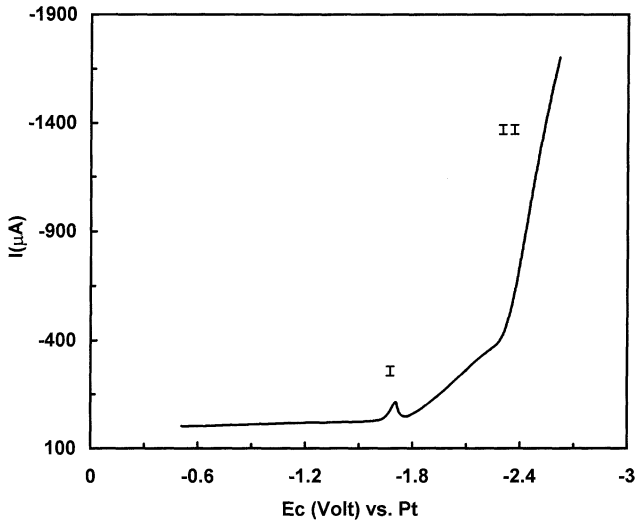


Table 4. Intensity of peak I (ip1) for various MMA concentrations in DMF; v = 20 mVs^{-1}

[MMA] = 0.5 M	[MMA] = 1 M	[MMA] = 2 M	[MMA] = 3 M
[a]	[a]	160 μA	90 μA

[a] Peak I superimposed to peak II.

range of peak I followed by a 20-s voltage hold is repeated. In contrast to what happens when this experiment is conducted with acrylic monomers such as AN or EA, the cathode is not fully passivated after one scan. Indeed, ip1 decreases slowly upon repeated cathodic scans. A film is clearly seen by the naked eye on the cathode when it is withdrawn from the electrochemical cell after one scan. When the number of scans is increased, the PMMA coating is seen as a thick gel-like layer poorly adhering to the metal. This result is quite surprising and in contrast with previously published data for PAN. Indeed the PAN film thickness measured ex situ by ellipsometry does not change when the cathodic scans are repeated in the potential range of peak I[34]. The IR spectrum of the polymer coating (dried in vacuo but not rinsed with solvent) (Figure 8a) confirms the PMMA deposition, the main absorption bands at 3006, 1739, and 1151 cm^{-1} being assigned to $\nu_{as}(CH_2)$, $\nu C{=}O$), and $\nu C{-}O$), respectively. However, the intensity of the absorption bands decreases if the electrode is previously washed with THF, i.e. a good solvent for PMMA, (comparison of Figures 8a and 8b). Since only the polymer chains strongly bound to the electrode remain on it after the washing step, one may suppose that unbound polymer chains are produced simultaneously to grafted ones, which may lead to unreliable film thickness. Consistently, PMMA is formed in solution as demonstrated by PMMA precipitation from the electrochemical bath in methanol (nonsolvent for PMMA, solvent for Et_4NClO_4). This observation is very similar to that one reported by Tanguy et al. for the electrografting of methacrylonitrile (MAN)[11]. Measurements performed with a quartz crystal microbalance[12] have shown that unbound polymethacrylonitrile chains are embedded in a thin layer of grafted ones. On the basis of that observation valid for one monomer (MAN), the authors have proposed a mechanism of "oligomer grafting" instead of the "monomer grafting" they claimed until now[15]. This revision of the grafting mechanism, which is not essential for the purpose of this paper, might, however, be hasty, since unbound polymers in the potential range of peak I (at which the grafting occurs) have never been observed in case of acrylic monomers (such as AN or EA). This observation is actually confined to the electrografting of methacrylates, i.e. methacrylonitrile and MMA, and is certainly not a general behavior. Although the high concentration of methacrylonitrile and MMA which is required for electrografting is in a qualitative agreement with the competitive solvent/monomer adsorption concept, it is not clear yet why unbound methacrylate chains are observed in

Figure 7. Voltammetry of MMA on nickel in a 0.05 M TEAP solution in DMF carried out in the potential range of peak I, [MMA] = 2 M; v = 20 mVs^{-1}: a) first scan; b) second scan

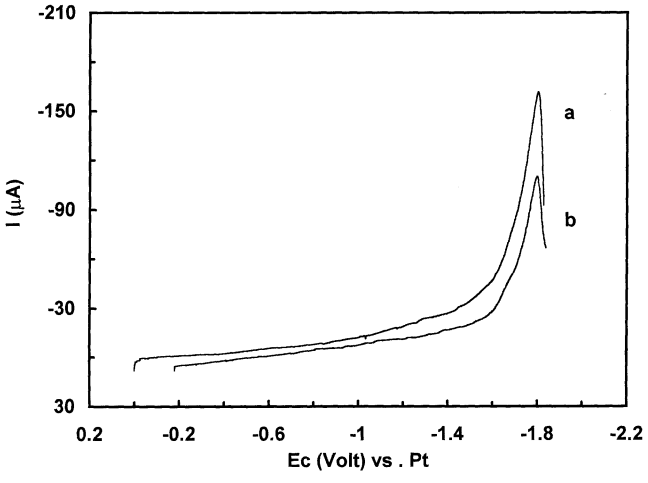
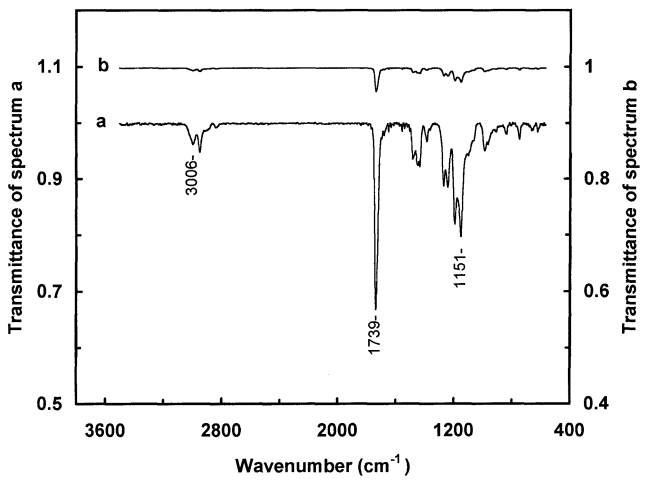


Figure 8. Infrared spectrum of a PMMA film deposited on Ni from a solution of [MMA] = 3 M in DMF at potential of peak I: a) before rinsing with THF; b) after rinsing with THF



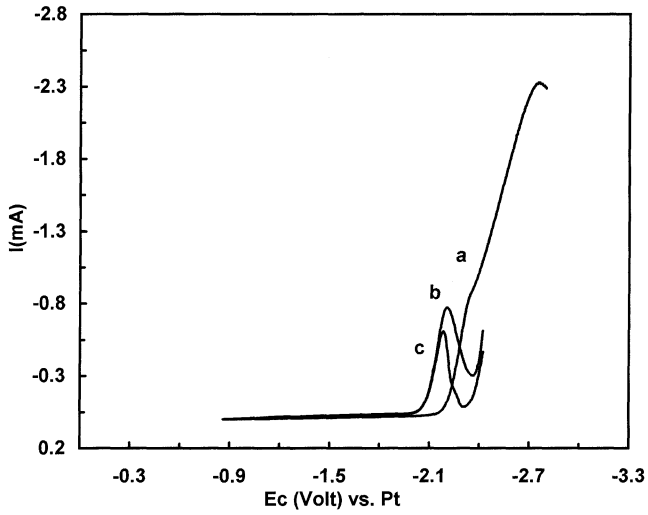
the potential range of peak I. This problem will be discussed in a forthcoming paper.

TMSOEMA and DMAEMA Reduction in ACN and DMF

Nowadays an increasing interest is paid to 2-hydroxyethyl methacrylate (HEMA)[35] and the parent poly(HEMA), which are suitable biomaterials for implants because of their lack of toxicity and their high resistance to degradation[36]. Furthermore, hydroxy groups are reactive towards various topcoats (paint, varnish) that could be used for imparting specific properties to the metal substrate. HEMA may, however, not be used as such, because of the interference of the hydroxy proton reduction. It is the reason why HEMA has to be protected by a trimethylsilyl group, which is easily removed after polymerization. Electrochemical experiments have been conducted with the protected monomer (TMSOEMA) in ACN. Within the 0.1 M to 2 M concentration range, only a diffusion peak is observed. Nevertheless, the classical grafting "signature" has been observed in DMF (poorer acceptor and better donor than ACN) beyond a 0.1 M concentration (Figure 9). It must be noted that in agreement with what happens for MMA and MAN, unbound PTMSOEMA is also embedded in the thin layer of grafted chains when the electropolymerization is conducted in the potential range of peak I.

Finally, the grafting of the third methacrylate, DMAEMA, remained impossible in ACN and in DMF, suggesting so that this monomer cannot compete with these solvents for adsorption onto the cathode.

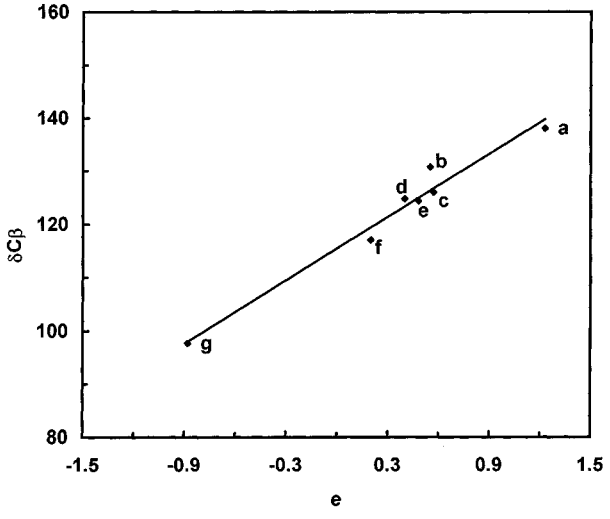
Figure 9. Voltammetry of TMSOEMA on nickel in a 0.05 M TEAP solution in DMF: a) [TMSOEMA] = 0.1 M; b) [TMSOEMA] = 0.2 M; c) [TMSOEMA] = 0.5 M; v = 20 mVs^{-1}



Tentative Prediction of the Cathodic Monomer Grafting

From the experimental results reported in this paper, it appears that the ability of vinyl monomers to be electrografted onto a metal, strongly depends on the electron deficiency of the β-carbon atom double bond. In case of radical copolymerization, the monomer reactivity can be predicted by the Alfrey-Price Q−e scheme[37]. According to these authors, the electrostatic factor e is representative of the monomer polarity and thus of the electron-donor (or -acceptor) character of the vinyl substituent. A linear relationship[38] has been found between the ^{13}C-NMR chemical shifts of the β-carbon atom of the double bond [δ(C-β)] and the corresponding e values[39][40]. By analogy the ^{13}C-NMR spectra of the monomers considered in this paper have been recorded in mixed DMF/$CDCl_3$ solutions. The experimental δ(C-β) values agree with the previously reported data when plotted against e (Figure 10) and they are consistent with an electrografting propensity that decreases when the vinyl β-carbon atom is more shielded, thus less inclined to accept electrons. AN has clearly the less shielded β-carbon atom and is thus the best competitor towards the solvents, since vinyl chloride and vinyl acetate have the more shielded β-carbon atom and have no chance to be adsorbed onto the cathode and to be electrografted as confirmed experimentally. According to the electrochemical experiments reported in this paper, EA is more competitive than MMA towards DMF in agreement with the inductive effect of the α-methyl group in MMA that counterbalances the electron-withdrawing effect of the ester group so that the electron delocalization of the MMA double bond is less pronounced than in EA. This conclusion agrees with the relation of δ(C-β) shown in Figure 10 for EA and MMA. This qualitative consistency is, however, no longer observed when TMSOEMA and DMAEMA are concerned. In a similar way, Figure 10 cannot explain why DMAEMA is not electrografted in DMF. This behavior also remains unexplained when inductive or mesomeric effects are considered. It could, however, be explained by the presence of the silicon group in TMSOEMA and of amino group in DMAEMA. The silicon atom (electron acceptor) can contribute to the monomer adsorption and thus to the electro-

Figure 10. ^{13}C-NMR chemical shifts [δ(C-β)] of monomers vs the corresponding e values: a) AN; b) EA; c) TMSOEMA; d) MMA; e) DMAEMA; f) vinyl chloride; g) vinyl acetate



grafting, whereas the amino group (electron donor) can prevent this adsorption from occurring. These assumptions will be supported by theoretical calculations in a forthcoming paper.

Concluding Remarks

The important potentiality of grafting monomers other than AN has been demonstrated in this paper. We have indeed observed that under suitable conditions, ethyl acrylate (EA), and some methacrylates can be electrografted on e.g. nickel, thus with creation of a stable polymer−metal interface, although the reaction is carried out in a good solvent for the polymer. It is now clear that the choice of the solvent for the cathodic grafting of vinyl monomers has a decisive effect on the issue of the electrochemical reaction by deciding whether a strong chemisorption of the electropolymerized material occurs or not.

The explanation for this solvent effect has to be found in a competition between the solvent and the monomer for the localization at the electrode. The issue of this competition strongly depends on the relative donor-acceptor properties and polarity of the solvent with respect to the monomer as confirmed by a great effect on the potential and intensity of the inhibition peak. The polarity of the solvent is more important as this solvent is a better electron-acceptor (and a poorer donor) than the monomer and has thus higher probability to be adsorbed onto the cathode. Conversely, the effect of the solvent polarity decreases when the solvent is a poor acceptor (and a good donor), thus when this solvent has less chance to be in the electrical double layer. If solvent and monomer have a comparable liability to be adsorbed at the cathode, then the monomer concentration has a decisive effect on the grafting issue.

One important criterion for the cathodic electrografting of a monomer is the choice of a solvent with a weaker acceptor character and higher donicity than the monomer, provided that this solvent is not electroactive in the potential range of interest. As a consequence of this rule, the more the substituent of the polymerizable double bond decreases the acceptor capacity of the monomer, the smaller the ability of this monomer to be electrografted. The measurement of the ^{13}C-NMR chemical shifts for the β-carbon atom of the vinyl double bond could accordingly serve as a preliminary semiquantitative tool for predicting the grafting ability of new monomers. However, some problems can arise when the monomer substituent contains atoms or groups of atoms that do not influence too much the β-carbon atom although they can contribute to the cathode adsorption by their electron acceptor or donor capacity.

A theoretical model accounting for the competitive adsorption of monomer/solvent pairs is currently studied and will be the topic of a forthcoming paper.

The authors are grateful to the *Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles* in the frame of the *"Pôles d'Attraction Interuniversitaires: Chimie and Catalyse Supramoléculaire"*. They thank the *R & D groupe Cockerill Sambre* for continuous interest and *M. Micheels* for her technical assistance.

Experimental Section

Acrylonitrile (AN: Aldrich, > 99%), ethyl acrylate (EA: Acros, 99.5%), methyl methacrylate (MMA: Acros, 99%), 2-(dimethylamino)ethyl methacrylate (DMAEMA: Acros, 98%), and acetonitrile (ACN: Acros, p.a.) were dried over calcium hydride (Acros: 93%) and distilled under reduced pressure. Dimethylformamide (DMF: Acros, p.a.) was dried over phosphorus pentoxide (Acros 98%) and distilled at 70°C under reduced pressure. Propylene carbonate (PC: Acros, 99%) and 2-hydroxyethyl methacrylate (HEMA: Acros, 96%) were dried over molecular sieves 4 Å for 24 h and distilled at 85°C and 50°C, respectively, under reduced pressure. Pyridine (PY: Acros, 99.5%) was dried over potassium hydroxide (Acros: 98%) for 2 h at 120°C and distilled at 40°C under reduced pressure. Hexamethylphosphoramide (HMPA: Aldrich 99%) was dried over calcium hydride for 24 h and distilled at 80°C under reduced pressure. Tetraethylammonium perchlorate (TEAP: Fluka, > 99%) was heated in vacuum at 80°C for 12 h prior to use.

2-Trimethylsilyloxyethyl methacrylate (TMSOEMA) was synthesized by adding dropwise chlorotrimethylsilane (ClTMS: Acros, 98%) to a mixture of previously dried HEMA and triethylamine (Acros, 99%) in tetrahydrofuran (THF: Acros, p.a.)[31]. The reaction was carried out in THF at 0°C, under an inert and dry atmosphere and stirring for 12 h. Triethylamine hydrochloride was filtered off, and THF distilled off under reduced pressure. The residue was purified just before use by distillation under reduced pressure at 50°C. The product was then identified as TMSOEMA by ^{1}H-NMR spectroscopy [i. e. presence of the trimethylsilyl $-Si(CH_3)_3$ resonance at $\delta = 0.1$ and absence of the hydroxy $-OH$ resonance at $\delta = 3.3$]. The purity was ascertained to be higher than 99.5% by gas chromatography.

Voltammetry (CV) experiments were carried out with each monomer (10^{-2} to 2 M), dissolved in an appropriate solvent containing tetraethylammonium perchlorate (TEAP) as a conducting salt ($5 \cdot 10^{-2}$ M).

The water content was measured by the Karl-Fischer method (Tacussel aqua processor) and ascertained to be lower than 5 ppm. All the experiments were carried out in a glove-box at room temperature under an inert (lower than 10 ppm in oxygen) and dry atmosphere.

The potentiostat used for the voltammetry experiments was a PAR-E. G&G model 273A. The electrochemical cells are described elsewhere[5]. Potentials were measured against a Pt pseudo-reference electrode. The nickel working electrodes of 2 cm^2 area, were mechanically polished with an alumina suspension in water, washed with heptane and acetone, and finally treated overnight in vacuum at 150°C. The residual nickel oxide on the electrode surface was then electrochemically reduced in an ACN/TEAP solution in the glove-box just prior to electropolymerization. The oxide layer was completely removed as assessed by a reduction current dropping down to zero after several potential scans. The rapid transfer of the cathode from one solution to the other within the glove box ensures the absence of oxide at the metal substrate, which is a prerequisite for polymer grafting[32].

A reference poly(ethyl acrylate) sample (PEA) was prepared by free radical polymerization of EA in DMF (0.5 M solution) initiated by 2,2′-azobis(2-methylpropionitrile) (AIBN: Acros, 98%) at 60°C for 6 h. The polymer was precipitated in methanol, washed several times with methanol in order to remove the unreacted monomer and AIBN, and dried in vacuo at 40°C for 24 h. A PEA film was solvent-casted (DMF) onto nickel plates, such that infrared spectra could be recorded by the same technique as for the electrografted films.

Except for specific treatment mentioned in the discussion all the electrografted films were carefully rinsed with a good solvent for the polymer in order to remove any ungrafted chains and conducting salt, and dried in vacuo for 2 h before characterization.

IR spectra were recorded ex situ with a BRUKER (Equinox IFS 66) FTIR spectrometer equipped with a grazing angle accessory (83°) and a polarizer (Specac KRS-5). – ^{13}C-NMR data were recorded in a mixed DMF/$CDCl_3$ medium with a BRUKER AM 400 apparatus operating at 100 MHz.

[1] B. Yurttas, L. Toppare, V. Akbulut, *J. Macromol. Sci.* **1988**, *A25*, 219.
[2] S. N. Bhadani, Q. Ansari, S. K. S. Gupta, *J. Appl. Polym. Sci.* **1992**, *44*, 121.
[3] G. Lécayon, C Le Gressus, A. Le Moel, Eur. Patent no. 0038244, **1981**; *Chem. Abstr.* **1982**, *96*, 21350m.
[4] C. Boiziau, G. Lécayon, *Recherche* **1988**, *19*, 888.
[5] M. Mertens, C. Calberg, L. Martinot, R. Jérôme, *Macromolecules* **1996**, *29*, 4910−4918.
[6] P. Jonnard, F. Vergand, P. F. Staub, C. Bonnelle, G. Deniau, C. Bureau, G. Lécayon, *Surf. Interface Anal.* **1996**, *24*, 339.
[8] M. Mertens, C. Calberg, N. Baute, R. Jérôme, L. Martinot, *J. Electroanal. Chem.* **1998**, *441*, 237−244.
[8] V. Geskin, R. Lazzaroni, M. Mertens, R. Jérôme, J. L. Brédas, *J .Chem. Phys.* **1996**, *105*, 3278.
[9] G. Deniau, G. Lécayon, P. Viel, G. Zalczer, C. Boiziau, G. Hennico, J. Delhalle, *J. Chem. Soc., Perkin Trans. 2* **1990**, 1433.
[10] J. Levisalles, B. Castro, M. Jozefowicz, *Chimie Organique, Flammarion Sciences* **1973**, *2*, 92.
[11] J. Tanguy , G. Deniau, C. Auge, G. Zalczer, G. Lécayon, *J. Electroanal. Chem.* **1994**, *337*, 114.
[12] J. Tanguy, G. Deniau, G. Zalczer, G. Lécayon, *J. Electroanal. Chem.* **1996**, *417*, 175−184.
[13] F. M. Fowkes, in *Physicochem. Aspects Polym. Surf.* (K. L. Mittal, Ed.), Plenum Press, New York, **1983**, vol 2, 583−603.
[14] D. L. Allara, F. M. Fowkes, J. Noolandi, G. W. Rubloff, M. V. Tirrel, *Mater. Sci. and Eng.* **1986**, *83*, 213−226.
[15] G. Lécayon, Y. Bouizem, C. Le Gressus, C. Reynaud, C. Boiziau, C. Juret, *Chem. Phys. Lett.* **1982**, *91*, 506.
[16] B. H. Loo, T. Kato, *Surf. Sci.* **1993**, *284*, 167.
[17] A. Bewick, C. Gibilaro, M. Razaq, J. W. Russel, *J. Electron Spectrosc. Relat. Phenom.* **1983**, *30*, 191.
[18] P. Parent, G. Laffon, G. Tourillon, A. Cassuto, *J. Phys. Chem.* **1995**, *99*, 5058.
[19] G. Xue, J. Dong, J. Zhang, Y. Sun, *Polymer* **1994**, *35*, 723.
[20] J. Perreau, C. Reynaud, C. Boiziau, *Surf. Sci.* **1985**, *162*, 776.
[21] X. Crispin, V. Geskin, R. Jérôme, R. Lazzaroni, J. L. Brédas, *Proceeding of the international Conference on Polymer-Solid Interfaces*, Namur, Belgium, **1996**, in press.
[22] C. Fredrikson, R. Lazzaroni, J. L. Brédas, M. Mertens, R. Jérôme, *Chem. Phys. Lett.* **1996**, *258*, 356.
[23] M. O. Bernard, C. Bureau, J. M. Soudan, G. Lécayon, *J. Electroanal. Chem.* **1997**, *431*, 153−162
[24] J. Lawrence, R. Parsons, *J. Phys. Chem.* **1969**, *73*, 3577.
[25] J. O′M. Bockris, M. A. V. Devanathan, K. Müller, *Proc. R. Soc.* **1963**, *274A*, 55.
[26] B. Roelfs, C. Schroeter, T. Solomun, *Ber. Bunsenges. Phys.* **1997**, *101*, 1105.
[27] V. Gutmann, *Coordination Chemistry in Non-Aqueous Solutions*, Springer-Verlag, New-York, **1968**.
[28] V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*, Plenum Press, New York, **1978**.
[29] V. V. Kuznetsov, V. P. Grigor′ev, L. G. Bozhenko, *Elektrokhimiya* **1980**, *16*, 495.
[30] M. Munakata, S. Kitagawa, M. Miyazima, *Inorg. Chem.* **1985**, *24*, 1638−1643.
[31] B. Ivan, J. P. Kennedy, P. W. Mackey, *Polymeric Drugs and Drugs Delivery System* (Eds.: L. Dunn, R. M. Ottenbrite), *ACS Symp. Book Ser.*, vol. 469, Am. Chem. Soc., Washington, D. C., **1991**, p. 203−212.
[32] Y. Bouizem, F. Chao, M. Costa, A. Tadjeddine, G. Lécayon, *J. Electroanal. Chem.* **1984**, *172*, 101−121.
[33] V. Gutmann, A. Steininger, E. Wychera, *Monatsh. Chem.* **1966**, *97*, 460.
[34] C. Calberg, M. Mertens, R. Jérôme, X. Arys, A. M. Jonas, R. Legras, *Thin Solid Films* **1997**, *310*, 148−155.
[35] J. P. Montheard, M. Chatzopoulos, D. Chappard, *J. Macromol. Sci. – Rev. Macromol. Chem. Phys.* **1992**, *C32*, 1−34.
[36] J. Kalal, *Makromol. Chem., Suppl.* **1984**, *7*, 31.
[37] T. Alfrey, C. Price, *J. Polym. Sci.* **1947**, *2*, 101.
[38] J. J. Herman, P. Teyssié, *Macromolecules* **1978**, *11*, 839.
[39] R. E. Greenley, *J. Macromol. Sci. Chem.* **1980**, *14*, 427.
[40] E. C. Leonard, *High Polymers*, vol. 24(1), Wiley Interscience, New York, (*Vinyl and Diene Monomers*), part 1, Wiley Interscience, **1970**.

[I98105]