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"Bonding" Electropolymerization: A New Electron-Transfer Strategy for the Tailoring of Performant Polymer-Based Composites

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Summary : Careful control of experimental conditions in the cathodic electropolymerization of acrylonitrile allows the grafting of thin polymer films, on conducting surfaces offering electrons easily mobilized at a relatively low potential. Matching relative polarity and donicity of solvent and monomer expands the applicability of this methodology to the whole class of (meth)acrylic monomers, paving the way to many new and useful multiphase materials

INTRODUCTION

During the last decades, increasing attention was paid to electrochemistry as an interesting technique to polymerize different monomers (Ref. 1-5), the obvious motivation being of course to combine the potentialities of electrochemical methods and the attractive features of polymer materials science. That time-honored approach was however suffering from a double drawback, i.e. weakness of both interfaces, substrate-polymer and polymer-outside medium (the later being either air or another polymer matrix, a biological medium, etc...). Those problems were somewhat alleviated by using physical treatments (plasma, etching,...), however raising other difficulties : delicate processing, high cost,...

More recently, Lécayon *et al.* arouse great excitement by claiming (Refs. 6,7) that polyacrylonitrile (PAN) could be grafted onto a number of usual metals (e.g., Ni) by controlled cathodic electropolymerization of AN monomer. That result markedly differed

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from previous studies pointing to acrylonitrile dimerization (Ref. 8) and polymerization in solution (Refs. 9-10). The observation of two reduction steps for AN reaction was also reported for the first time, corresponding to a passivation peak (less cathodic potential) and to a diffusion one (second potential). Finally, the polymer grafting was claimed to occur onto Ni at a non-defined potential between these two peaks. A single anionic mechanism was proposed for explaining these phenomena, an unclear situation further complicated by the intrinsic insolubility of PAN in acetonitrile (AC), the only medium used up to then for "electrografting".

Considering these pending questions, and the huge interest of that type of polymerization for composite materials molecular and morphological tailoring, we decided to revisit first the cathodic reaction of AN, and if possible to expand it to other monomers and substrates.

I. PHENOMENOLOGICAL ASPECTS OF AN POLYMERIZATION

A voltammogram of the AN reaction on a clean Ni plate (room T., 0,05 M TEAP electrolyte in AC) clearly shows indeed (Ref. 11) the existence of 2 peaks (see Fig. 1), a weak one around -1.8 V (P.I) and a much more intense one beyond ca. -2.2 V (P.II):

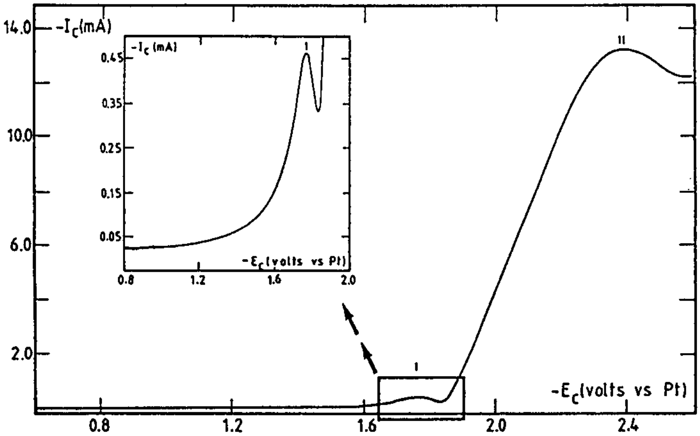


Fig. 1. Typical voltammogram for AN cathodic polymerization (polished Ni electrode v.s. Pt, [AN] = 0.2 M in AC, $[Et_4N^+CCl_4^-] = 5.10^{-2}$, v = 20 $mV.s^{-1}$)

For a minimum monomer concentration, P.I appears to be a typical "passivation" peak, i.e. its intensity decreases upon increasing monomer concentration (while Ep also slightly decreases). P.II exhibits the opposite behaviour, and can be considered as a "diffusion-like" peak. It is essential to note that working in a good PAN solvent such as dimethylformamide (DMF) demonstrates that grafting occurs at P.I yielding an insoluble film with very good abrasion resistance, but not anymore at P.II (where the film formed in AC easily dissolves afterwards in DMF). It is also significant that the film obtained in DMF at P.I exhibits a much smoother surface on AFM micrographs than the corresponding one electrografted in AC.

The existence of these 2 steps has also been confirmed by chronopotentiometric and chronoamperometric measurements. The later experiments suggest a "nucleation" reaction from a constant number of active sites beyond P.I, as also illustrated by SEM micrographs.

Besides adhesion (or not), there are other striking differences between the films obtained at these different potentials. Film at P.I is thin (typically from 50 to 750 Å), transparent and colorless, while at P.II it is thicker, opaque and often yellowish, but offering a good protection against corrosion thanks to its thickness. A similar protection can however be obtained at peak I by running several scans, since the phenomenon is irreversible.

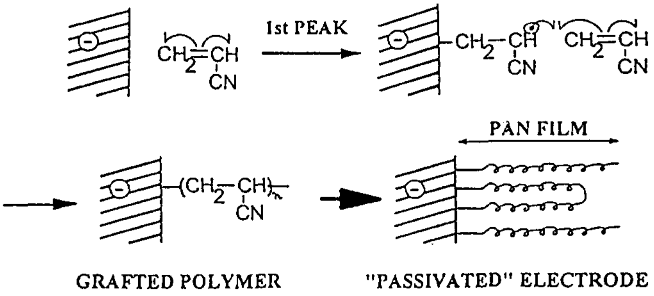
Infrared spectroscopy (reflexion-absorption FTIR) has brought some interesting additional information. Thin films obtained (at P.I) with lower [AN] exhibit indeed (ratio of absorptions at 1230 and 1250 cm^{-1}) an isotactic-rich microstructure (amorphous material), while the thicker ones (high [AN]) are essentially atactic and paracrystalline. Increasing the potential up to P.II promotes "degrafting", or a free PAN exhibiting a high degree of cyclization (bands at 3300-3600 cm^{-1}, =NH, and 1636 cm^{-1}, $>$C=N). These findings have been confirmed by NMR, DSC and TGA experiments, together with dual-cantilever DMTA on Cu plates spectacularly illustrating the difference between an electrografted PAN film and a commercial PAN one cast from DMF (Ref. 12).

It is of course difficult to admit a stereocontrol giving predominantly iso-enchainment, as due to a surface double-layer (i.e. a few Å) influence on the overall propagation. This phenomenon is probably better explained as an initial polymerization of surface-adsorbed monomer (see section III) into "pancakes", which are later converting into "mushrooms" and finally "brushes", possibly entangling "free" chains (Ref. 13).

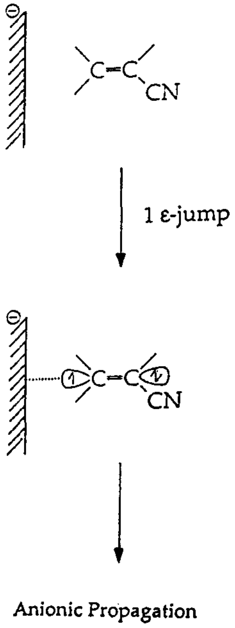
II. MECHANISTIC CONSIDERATIONS

In order to somewhat clarify the nature and course of these obviously complicated reactions, the influence of a number of structural factors and additives has been further studied. It was also hoped that these attempts might help to support one or the other mechanism sketched in Fig. 2a-c. The main resulting conclusions can be summarized as follows.

(a) RADICAL GRAFTING POLYMERIZATION AT -1.8V



(b) OR (AT PEAK I)



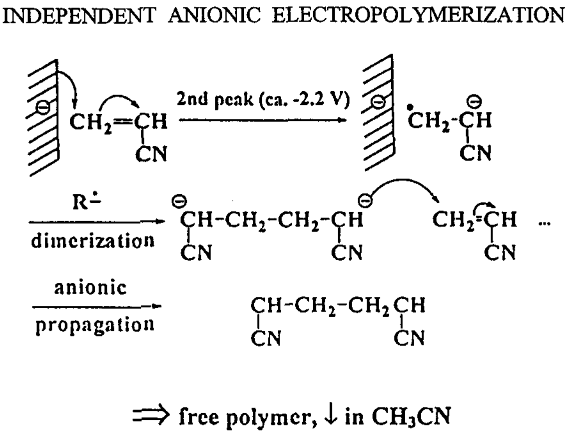

(c) INDEPENDENT ANIONIC ELECTROPOLYMERIZATION

Fig. 2. Proposed mechanisms for the cathodic electropolymerization of AN

(a) "Radical-type" rearrangement mechanisms (at P.I)

(b) "End-on bonded" anion-radical mechanism (at P.I)

(c) "Free" anionic polymerization (at P.II)

1. Typical radical traps such as DPPH (deep-violet diphenylpicrylhydrazyl), and to a lesser extent CCl_4 and $CDCl_3$, have a definite and rather selective influence on the electrochemical process. At peak I, DPPH discolours very rapidly in the vicinity of the electrode, and substantially decreases the thickness of the resulting film (while P.I intensity increases). Typical fragments of both types of additive are witnessed in TOF-SIMS surface spectra of these films, even after thorough washing with good solvents. DPPH discoloration occurs only slowly at higher potential, due to its electroreduction.
2. ε-Caprolactone (CL), a typical monomer for nucleophilic polymerization mechanisms, does not homo- nor copolymerize at all at P.I., and has no influence on AN polymerization. However, copolymers with AN are obtained at P.II, which expectedly are soluble in DMF.
3. The reaction at P.I is very fast (in the order of 1 sec.), i.e. definitely more so than typical solution anionic polymerization. It also promotes a quite strong bonding (high mechanical resistance, insolubility in hot DMF, ...). All that might be in agreement with the formation of a C-M bond of moderate stability, protected by the covering polymer layer (Fig. 2a). As a qualitative confirmation, it has been shown that the film could be "degrafted", under hydrolytic conditions but only in a good solvent like DMF.

4. The most interesting mechanistic feature is certainly the fact that only transition metals, i.e. those with easily mobilized non-bonding electrons from d-orbitals, are efficient in promoting "bonding" polymerization. Remarkably, "saturated" metals, e.g. Zn, ... do not allow polymerization at a potential (ca. -1.8 V) typical of P.I, which indeed does not appear on the voltammogram. On those metals, polymerization still takes place at higher E, i.e. beyond -2 V, but only to yield a soluble polymer (in DMF f.i.).

A striking confirmation of that fundamental difference has been obtained by using another type of conducting substrate, i.e. carbon, the implication being that easily extracted d electrons could be replaced by equally "easy" π electrons such as those engaged in large electron clouds of polyconjugated structures. It was rewarding to observe (Ref. 14), on vitreous carbon plaques, exactly the same type of voltammogram as on transition metals. P.I is witnessed again (as well as P.II), and displays a typical "passivation" behaviour. Furthermore, the bond formed between the substrate and the polymer is now still stronger, and cannot even be broken under hydrolytic conditions.

In conclusion, those results strongly suggest the existence of two different processes, which are difficult to explain by a unique type of mechanism. It seems of course obvious that P.II is representative of the classically accepted anionic mechanism (Fig. 2c), taking place through a one-electron jump to the monomer and a dimerization of the so-formed radical-anion, followed by an usual propagation in solution of that bis-anion P.I however, rather presents the characteristics of a "radical-type" process, induced by an electronic rearrangement between substrate and monomer (Fig. 2a). The question is of course to know if such a rearrangement is able to promote a reduction peak. On the other hand, the alternative explanation (fig. 2b) of the end-on binding of a radical-anion, followed by an anionic propagation (similar to the one at P2 potential) faces a number of contradictions in terms of polymerization rates, influence of additives and reactivity of monomers. The exact nature of the mechanism thus remains somewhat of an open question, and not only an academic one, since an in-depth knowledge of it might give better clues for a selective termination or continuation of the chains, i.e. for functionalization of the film surface.

III. INVESTIGATION AND USE OF MONOMER AND SOLVENT STRUCTURAL INFLUENCE

Until recently, only AN monomer allowed a selective and well-characterized electrografting of a clean polymer (similar to pure PAN obtained by radical initiation). In an effort to understand that limitation, the influence of the reaction medium has been investigated, first by changing the nature of the solvent.

It had already been observed (Ref. 11) that P.I decreased when AN monomer concentration ([M]) increased, indicating a better efficiency of the grafting process ("passivation"). The intensity at P.I has thus been observed in different solvents (Ref. 15), as a probe of that efficiency. The results are gathered in Table 1

Tab. 1. Intensity of P.I for 2 AN concentrations in different solvents (v = 20 mV.s^{-1})

SOLVENT	ε	DN	[AN] = 0.1 M	[AN] = 0.5 M
Propylene Carbonate (PC)	65	15.1	650 μA	90 μA
Acetonitrile (AC)	38	14.1	370 μA	30 μA
DMF	36.1	26.6	95 μA	25 μA
Pyridine (Py)	12.3	33.1	ca. 18 μA	(a)
HMPA	30.0	38.8	ca. 16 μA	(a)

(a) Too weak to be measured

As such, they can be interpreted by a competition between the monomer and the solvent for the cathode surface : the higher their electron donating ability, the lesser they will be efficient in that competition. That electron-donating character is rather well expressed by the donicity number (DN) of the Gutmann's relative scale (Ref. 16). It results from the data gathered up to now that :

- no electrografting will occur if the donicity of the monomer is too high versus that of the solvent;
- when both donicities are low, a high dielectric constant (ε) will favor competition (PC decreases AN grafting efficiency);

- when donicities are high, even a large difference in ε will not promote a significant difference in efficiency (compare Py and HMPA), and grafting may be favored by higher donicity for a similar ε (compare AC and DMF).

On these bases, it was inferred that the main reason for the failure in polymerizing other monomers was a too strong competition from the solvent for the cathode double layer. That working hypothesis has now been successfully substantiated by polymerizing acrylic esters in higher DN solvents, such as DMF (Ref. 17). Among different monomers, the efficiency decreases in the range ethylacrylate > methyl methacrylate > hydroxyethyl methacrylate (the OH of which has been protected by an easily removable $-Si(CH_3)_3$ group in order to prevent interference from the proton reduction). This is again the scale of decreasing electron-withdrawing character, i.e. increasing donicity here also decreases grafting efficiency. In all cases, the same 2-peaks typical voltammogram is recorded, and an adhering film is formed on the cathode.

IV. POTENTIAL APPLICATIONS

Thanks to the good electroreaction control described above, and specially to its extension to other conducting substrates (e.g. carbon) and to a very broad and versatile class of polymers (i.e. those from (meth)acrylic esters), a wealth of exciting applications can be envisioned (some of which have already been implemented) in 3 main areas.

- *Surface coating for corrosion protection.* These reactions are very fast and happen in a solution wherein the structure to be protected can be immersed as the electrode (as far as it contains a transition metal, the dominant type of metals). Those are very favorable conditions for a convenient and efficient protective coating, even of objects displaying complicated shapes (art pieces f.i.).
- *Tailoring of multiphase composites.* Simultaneous reduction of an inorganic derivative in the E-range of monomer polymerization may lead to electroinsertion of very fine and homogeneous dispersions of an inorganic reduced species in a rather thin polymer film deposited on the conducting substrate. A particularly interesting application is the reduction of uranium salts, leading to thin α-emitter devices which enjoy an unusually well-resolved α-spectrum (Ref. 18).

Tailoring of interfaces and interphases. It has already been shown above that chain termination by particular additives might be a strategy for surface functionalization. However, the most substantial progress in that prospect comes from the new possibility of polymerizing (meth)acrylic esters. That type of monomer may indeed carry a number of interesting functional groups, able to strongly interact with the surrounding medium. After eventual deprotection, one is so, in principle, able to promote compatibility and even bonding of the substrate with another phase (polymer matrix, biological medium,...), through groups such as epoxyde, hydroxyl, carboxylic, etc... Needless to say, potential applications in the field of multiphase materials are countless here.

CONCLUSIONS AND PROSPECTS

Practical experimental conditions allowing to electrochemically graft a thin polymer film on a cathode with available electrons at a rather low potential are now pretty well defined. Moreover, that methodology is becoming increasingly versatile in terms of monomer structure and nature of conducting substrate. Accordingly, many interesting applications can already be implemented or foreseen.

Obviously, a lot of work remains to be done in terms of mechanistic understanding of the process, as well as for exploring new areas where these concepts and results can be further developed.

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