

Molecular engineering of the polymer-metal bond

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Abstract

An electrochemical technique is developed for the metal surfaces to be modified by a polymer coating. Using quantum chemistry calculations, it is now possible to predict if a monomer molecule is able to be grafted onto the metal surface, and if this grafting will be followed by the formation of a polymer film, the elementary properties of which being also a priori calculated.

The bond of a polymer on a metal surface is one of the main problems encountered in material science. In the fundamental point of view, it involves the understanding of the Lewis acid-base mechanisms; in terms of applications, it is implied for the adhesive bonding, the behaviour of coatings used ever for decoration or against the corrosion, the deposition of self-lubricating layers, the building of composite materials in polymer matrix, etc...

A lot a new application field will become imaginable as soon as a technique will be mastered and will allow coatings with controlled structure and properties to be designed.

THE ACRYLONITRILE–NICKEL SYSTEM

In order to bring a solution to this problem, we constituted a pluridisciplinary team, in association with laboratories having complementary competences ever in fundamental research or in the pre-industrial field. In effect, during the 80's, we demonstrated that the use of an electrochemical technique is a suitable way for an adherent, structured and passivating polyacrylonitrile film to be built on the surface of an usual metal /1, 2, 3, 4/.

A systematic study of the acrylonitrile-nickel system (the nickel sample being the negatively polarized electrode) showed that the process of surface modification can be described according to the figure 1.

- i) The oxide layer is reduced; the metal surface is nude; the valence electronic orbitals point towards the solution.
- ii) The electrochemical double layer field orients the polar molecule; its acid end is in front of the metal surface which has a basic character, due to the negative polarization.
- iii) A Lewis acid-base reaction occurs, leading, according to a donor-acceptor mechanism, to the formation of a chemisorbed anion radical.
- iv) A second monomer molecule, following the same reactional process, interacts with the chemisorbed anion radical, and, from place to place, the polymer chain is built.

As suggested by this figure, each metal surface site can be involved in such a process: the grafting rate is thus exclusively limited by the steric characteristics of the molecules. Moreover, the monomer orientation in the electric field leads to the formation of a well structured film, which is experimentally verified by XANES measurements. /5/.

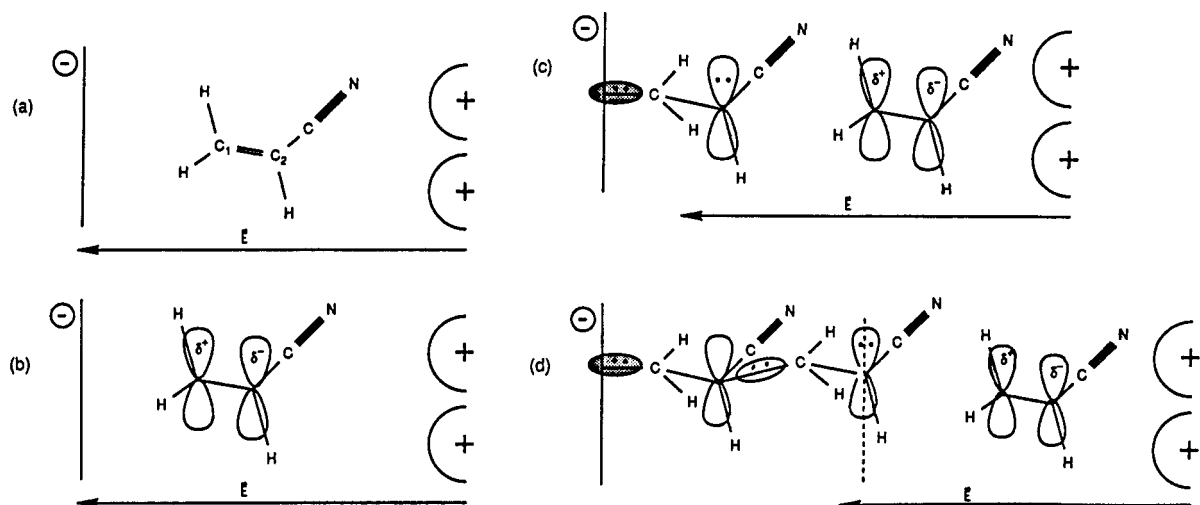


Fig. 1 Molecular model of the acrylonitrile-metal interaction in the double layer field
 a - the molecule is oriented; b - the molecule is polarized; c - a chemisorbed radical anion is formed, which can interact with another molecule; c - from place to place, the polymer chain grows.

a: acrylonitrile;
 b: crotonitrile (trans);
 c: crotonitrile (cis);
 d: methacrylonitrile;
 e: 3 butene nitrile.

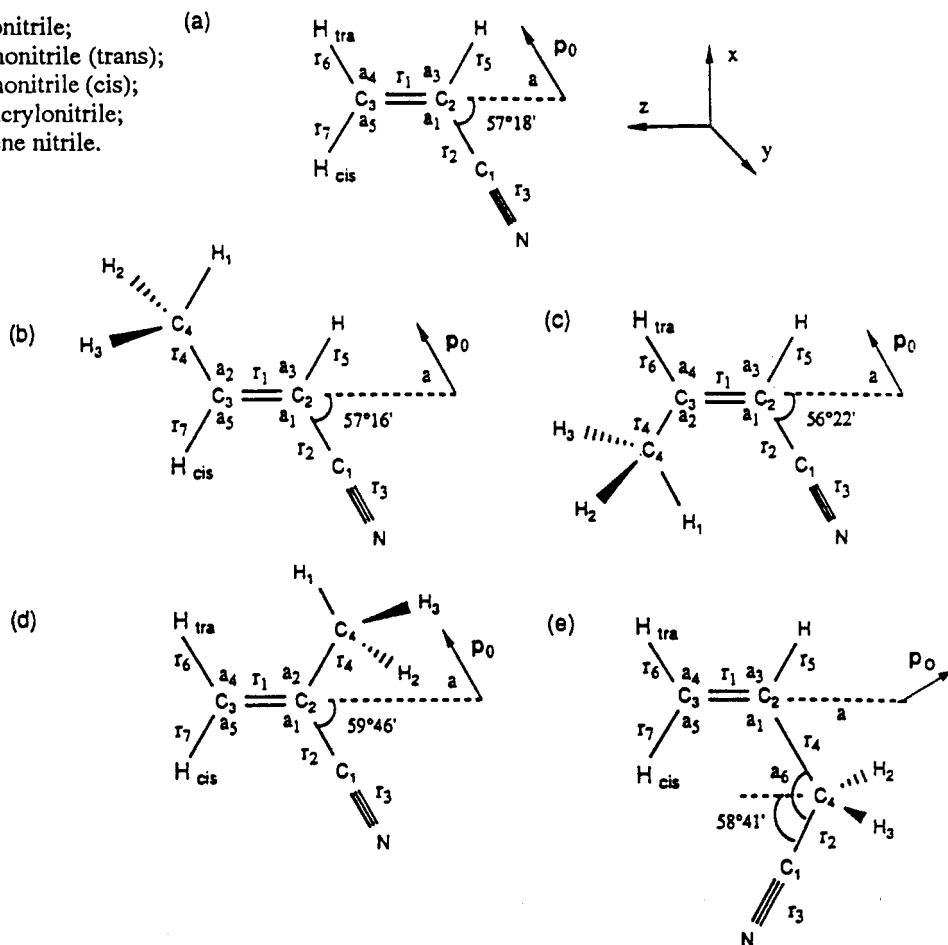


Fig.2 Vinyllic molecules we chose for comparison between experimental results and theoretical calculations .

GENERALIZATION OF THIS MODEL

In a second step, we studied the ability of this model, which has been elaborated to explain the results obtained with the acrylonitrile-nickel system, to be generalized. In this purpose, we started experimental /6/ and theoretical researches /7/ with a series of vinylic molecules (fig.2).

The largest behaviour differences are observed, experimentally, between the acrylonitrile and 3 butene-nitrile molecules : the first one allows a fast growth of a dense and well structured polymer film (see above), while the second one remains completely inactive. The theoretical results explain this difference.

ROLE PLAYED BY THE FRONTIER ORBITALS IN THE GRAFTING REACTION

The Lewis acid-base reactions are the result of an exchange of an electron pair between an occupied orbital (base) and an empty orbital (acid). We chose thus a molecule representation showing the electronic isodensity curves of the HOMO (highest occupied molecular orbital) and of the LUMO (lowest unoccupied molecular orbital) when the monomer is submitted to an electric field, the order of magnitude of which being comparable to the one of the double layer field ($E=2.10^{10} \text{ V.m}^{-1}$).

In the case of the fig.3, the metal surface is situated on the left side of the molecules, and behaves as a base.

The acid-base reaction is thus highly probable between nickel and acrylonitrile : resulting on a donor-acceptor mechanism, a strong covalent bonding can be obtained, with a large coverage rate. This is not the case with 3 butene-nitrile : under electric field, the overlapping of the monomer LUMO is impossible with the valence orbitals of the metal; the grafting probability is negligible.

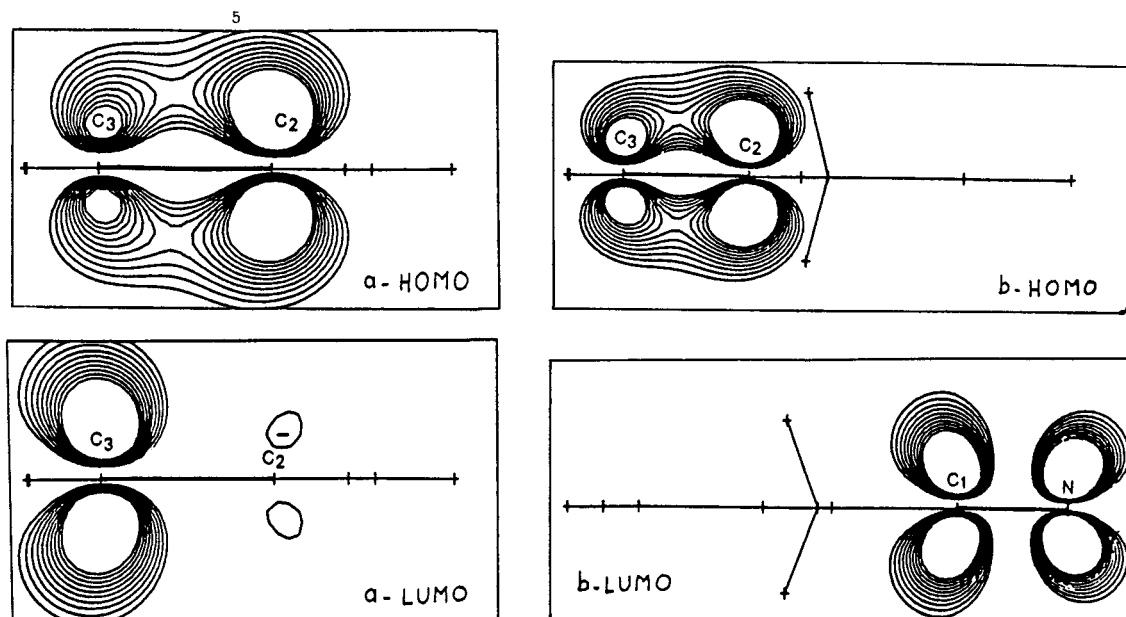


Fig.3 HOMO and LUMO of acrylonitrile (a) and 3-butene nitrile (b) under electric field. The metal surface is on the left side of the molecules.

ROLE PLAYED BY THE FRONTIER ORBITALS IN THE SUBSEQUENT POLYMERIZATION PROCESS

According to the monomer we use, we have a complete monolayer of acrylonitrile anions and, perhaps, some 3 butene-nitrile-anions chemisorbed on the surface. The problem is now to know if a polymerization process is possible, and in what manner. In order to simulate the cathod, we chose the simplest Lewis base : H^- . The chemisorbed anion radical is thus, with acrylonitrile : $\text{H}-(\text{CH}_2-\text{CH}-\text{CN})^-$ and, with 3 butene-nitrile : $\text{H}-(\text{CH}_2-\text{CH}-\text{CH}_2-\text{CN})^-$.

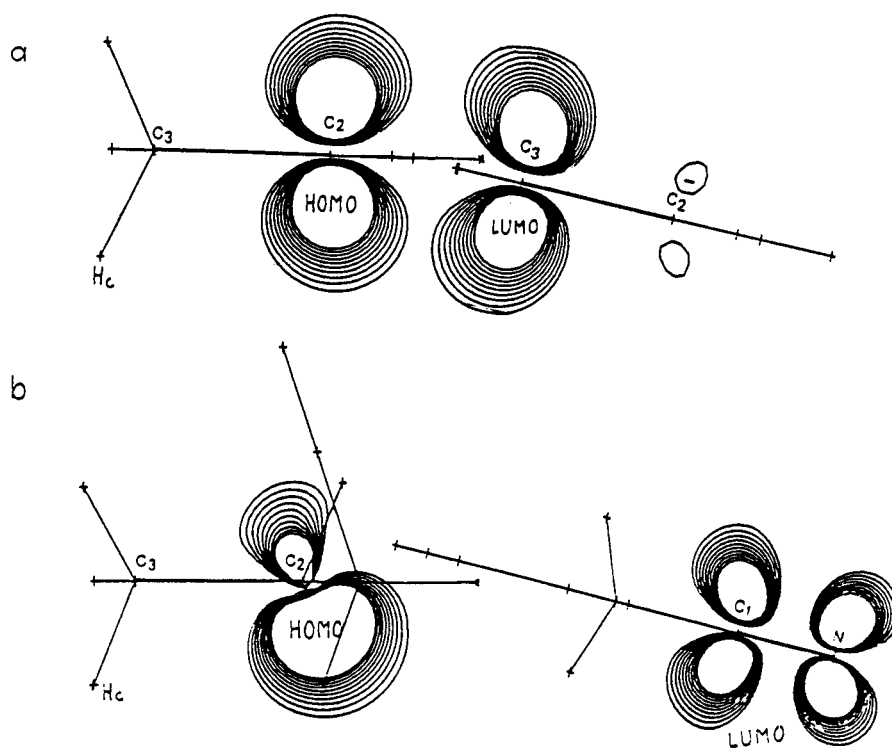


Fig.4 Interaction of an activated molecule with the chemisorbed anion radical. The cathode is simulated by H_c .

-a; acrylonitrile : a LUMO-HOMO overlapping is possible.

-b; 3-butene nitrile : a LUMO-HOMO overlapping is impossible.

The figure 4 shows, for both molecules, the HOMO of the chemisorbed anion and the LUMO of a second monomer molecule activated in the electric field.

In the case of acrylonitrile (fig.4a), a perfect HOMO-LUMO is possible, favourable to a donor-acceptor reaction : the polymerization is highly probable. This is not at all the case with 3 butene-nitrile : a negligible polymerization probability will follow a negligible grafting probability ! the experimental behaviour differences are now completely explained.

Naturally, the simulation of the cathod surface has to be improved; this is the aim of a theoretical work we started in the perspective of the generalization of the acid-base reaction concept. Nevertheless, this simulation, easy to calculate, is now currently used to predict, with a satisfactory approximation, the behaviour of monomer molecules we want to test experimentally.

THEORETICAL STUDIES OF THE ELEMENTARY PROPERTIES OF THE POLYMER FILM

For a molecular engineering to be designed, it is also necessary to be able to predict the main elementary properties of the polymer which will be built on the metal surface. In this way, we already demonstrated it is possible to calculate, a priori, the electronic density of states /8/ and the infra-red optical properties /9/ of the polymer. Moreover, it must be emphasized that the comparison of the theoretical calculations and the experimental measurements is also a fruitful tool to determine the molecular properties of the actual polymer film, such as tacticity, conformation, and to characterize the structural defects which can appear during its formation.

CONCLUSION

This fundamental research is naturally completed by a lot of studies concerning the behaviour laws of the modified metal surface, and particularly the effects of heat treatments or intense irradiations, the resistance to corrosive environments (ever chemical or biological ones), and the friction properties. The aim we pursue is the determination of the correlation between the properties we are able to calculate at a molecular scale and the macroscopic behaviour of the bi-material we will elaborate.

Acknowledgements

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REFERENCES

- 1- G.Lécayon, Y.Bouizem, C.Le Gressus, C.Reynaud, C.Boiziau, C.Juret
Chem.Phys.Letters 91, 506 (1982).
- 2- C.Boiziau, G.Lécayon, Int.J.Adhesion and Adhesives, 6, 207 (1986).
- 3- C.Boiziau, G.Lécayon, La Recherche 201, 888 (1988).
- 4- C.Boiziau, G.Lécayon, Surf.and Interfaces Analysis, 12, 475 (1988).
- 5- G.Tourillon, R.Garrett, N.Lazarz, M.Raynaud, C.Reynaud, G.Lécayon, P.Viel,
Journal of the Electrochemical Society, 137, 8 (1990).
- 6- G.Deniau, G.Lécayon, P.Viel, G.Hennico, J.Delhalle.
Accepted for publication in Langmuir.
- 7- G.Hennico, J.Delhalle, E.Younang, M.Defranceschi, G.Lécayon, C.Boiziau,
Accepted for publication in Intern. J. of Quantum Chemistry.
- 8- G.Hennico, J.Delhalle, C.Boiziau, G.Lécayon, Faraday Trans.86, 1025 (1990).
- 9- D.Mathieu, M.Defranceschi, J.Delhalle, G.Lécayon (To be published).