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AN ORGANIC REFERENCE SPECIMEN : POLYACRYLONITRILE FILM DEPOSITED ON OXIDIZABLE
METALS BY ELECTRO-POLYMERIZATION

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Abstract

Surface investigations of organic materials require the provision of reference specimens for calibrating experimental equipment.

Because of their specific properties (purity, reproducibility, well-known molecular structure and orderly inter-molecular structure, electronic properties associating conductive and insulating behaviour, quality of the film-to-metal bound), polyacrylonitrile films obtained through electro-polymerization on oxidizable metal cathodes (Fe, Ni, Cu) may be used as a first type of reference sample.

Experimental results, obtained by various surface investigation techniques are presented, and their validity evaluated.

Introduction

A current trend in surface analysis is to progress from the study of simple systems (e.g., metallic single crystals in clean condition, or coated with a known, controlled adsorbate) to that of more complex cases : it becomes one of the essential tools of materials research. As shown earlier /1, 2/ the same technical requirements are applicable to experimental equipment, specimen pollution, and therefore surface alteration during measurements is prevented through the use of ultra-high vacuum. Further, additional analytical techniques lead in most cases to a realistic interpretation of results, provided that one is careful to use an increasing number of approach methods as the system under investigation becomes more complex.

Failing theoretical support, data analysis and interpretation become less reliable. All uncertainties due to instrumentation must be removed; above all, calibration must be perfect. A requirement therefore arises for reference specimens which should be as representative as possible of the material type under investigation, and have comparable overall properties. It will be readily appreciated that the investigation of organic materials requires the provision and specification of reference specimens which differ from those used in metal investigations. Specimens are expected to account for structural (intra- and inter-molecular architecture) as well as electronic aspects of the material, and possibly to overcome the difficulties resulting from radiation damage.

Our first section will thus be devoted to a review of the criteria which we consider relevant to the specification of an organic reference specimen; we will then proceed to show that polyacrylonitrile (PAN) films obtained by electropolymerization meet such criteria. Last, a number of typical spectra recorded by various techniques will be presented and discussed.

Criteria for the specification of
organic reference specimens

Organic materials are characterized above all by the architecture of their constituent molecules, as well as by their relative positions. Although the relevance of the first structural parameter

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to specimen properties is readily understood, the incidence of the second parameter is often disregarded, usually because of the difficulty in controlling it. However, the fact that a material is ordered or not, obviously affects its response to various stimuli. In the latter case, its response to any stimulus has a mean value which generally shows a wide spread from one specimen to the next, due to poor reproducibility.

The first criterion to observe is thus :

Well-known and reproducible { molecular architecture
inter-molecular arrangement

This criterion is met by polymers with ordered structures.

A more detailed consideration of parameters which characterize organic materials shows the existence of the specific "structure alteration criterion", supplementing the conventional "purity" criterion applicable to any material. It is well-known that usual preparation processes result in the introduction of chemical impurities originating either in the process itself (e.g., traces of solvents or catalysts) or in the environment (e.g., atmospheric oxygen, alkaline substances, etc...). In the same way, one may observe departures from the standard molecular structure, due either to the preparation process (e.g., molecular breaks in plasma) or to the presence of impurities (nucleophile substances, e.g., oxygen).

The presence of such impurities affects the response to any external stimulus as in the case of doping effects (p or n doping) with electronic properties, of bridging effects with mechanical properties, and active center effects with chemical properties.

The second relevant criterion is thus the nature and density of known and reproducible impurities (including structural alterations).

Attention should also be given to a third type of consideration, the stability of specimens. They should not be affected by storage in air (i.e., they should not oxidize) or in a vacuum (they should not sublime). Further, the molecular - structure and inter-molecular structure and inter-molecular arrangement of organic polymers are highly sensitive to heat treatment and to irradiation; in the case of reference specimens, the resulting alterations must be accurately known. The third criterion may thus be stated as follows:

- stability in air and in vacuum
- well-known, reproducible effects of heating and irradiation.

Last, organic materials are generally very poor electrical conductors, which justifies the use of the thinnest specimens available. Also, specimens must be connected mechanically and electrically to the specimen carrier, which is usually metallic. The connection should be reliable and introduce no disturbances in measurements, neither as regards electrical conductivity (motion of electric charges resulting from irradiation) nor chemical purity (which excludes adhesives).

The fourth criterion therefore is :

- an organic material-to-metal bond well-defined electrically, and physically reliable.

It will now be shown that all of the above criteria can be met by reference specimens made of thin polyacrylonitrile film prepared by electro-polymerization on metal cathodes.

Summation of properties of electro-polymerized polyacrylonitrile films.

Preparation

The specimen preparation process, described in detail elsewhere /5/ will now be summarized. The polymer film (polyacrylonitrile) is formed by grafting and polymerizing molecules of the monomer (acrylonitrile) on an oxidizable metal cathode (e.g., nickel, iron, copper) in which the superficial oxide layer is reducible by an electrochemical process when the electrical circuit is completed (see : the electro-chemistry of reduction /6/).

The monomer is diluted in a stable organic solvent (acetonitrile), in the presence of a salt (tetraethylammonium perchlorate) which serves as a supporting electrolyte. The entire system is kept under a controlled argon atmosphere, free from impurities (H_2O) : 1 ppm approx.) and oxygen (O_2) : 5 ppm approx.).

For a given monomer content in the solution, polymer film thickness is determined by the value of cathode polarization relative to a reference electrode (Ag/Ag⁺ couple) and by the time during which polarization is applied (Fig.1).

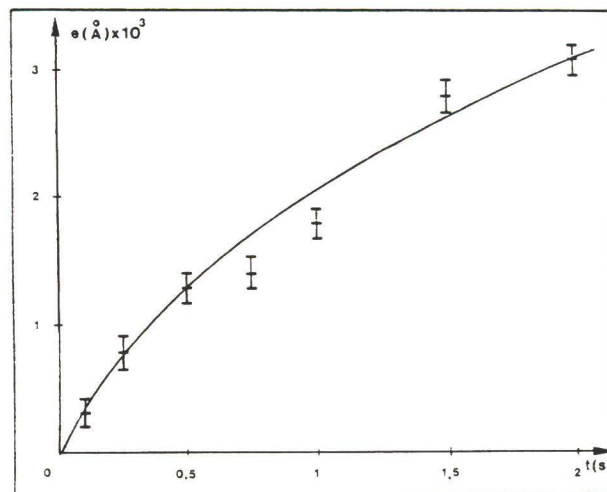


Fig.1 - Plot of film thickness vs. electropolymerisation time for given values of V and concentrations :

$$V_{\text{cath./Ag/Ag}^+} = -2.8 \text{ V}$$

$$[CH_2CHCN] = 5.10^{-1} \text{ M}$$

$$[(C_2H_5)_4N_1^+ ClO_4^-] = 5.10^{-2} \text{ M}$$

$$[H_2O] < 1 \text{ ppm}$$

$$[O_2] < 5 \text{ ppm}$$

The film thickness is measured using an optical interferometer (Tolansky method).

Structure of specimen

When investigated by infra-red absorption spectroscopy, the film molecular structure is as shown by figure 2. The deposit consists of polyacrylonitrile chains (fig.2a) with local segmentation (fig.2b); the density of defects (segmentation, bridging) as compared with the ideal structure increases with film thickness /7/. It should however be noted that the presence of such defects has no influence on the elementary composition of the material, which still consists of three carbon atoms and three hydrogen atoms for one nitrogen atom.

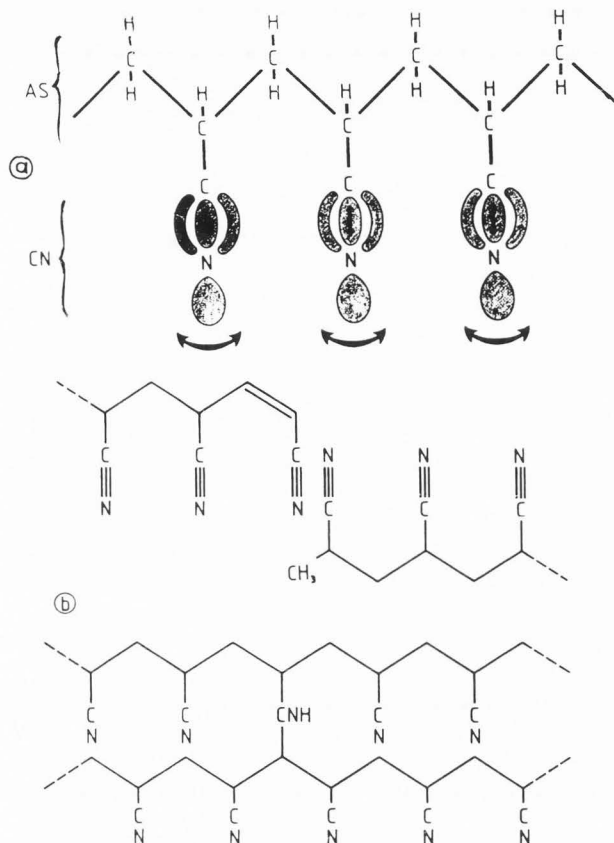


Fig.2 - Schematic molecular structure of the PAN film. (plane representation of a 3 dimensions system).

The main structure consists of polyacrylonitrile chains (a), with two types of alterations (b) : segmentation, the dipole-dipole interaction maintaining the film cohesion, and inter-chain bridges, reinforcing the film cohesion.

As for the intermolecular structure of the PAN chains which make up the film, it may be inferred from analysis of the growth mechanism in an electric field /6/; this analysis is confirmed through metastable de-excitation spectroscopy /3/. PAN chain orientation is perpendicular to the specimen plane. The surfaces of all specimen films thus show identical configurations, with the orbitals linked to CN groups oriented toward the outside /8, 9/.

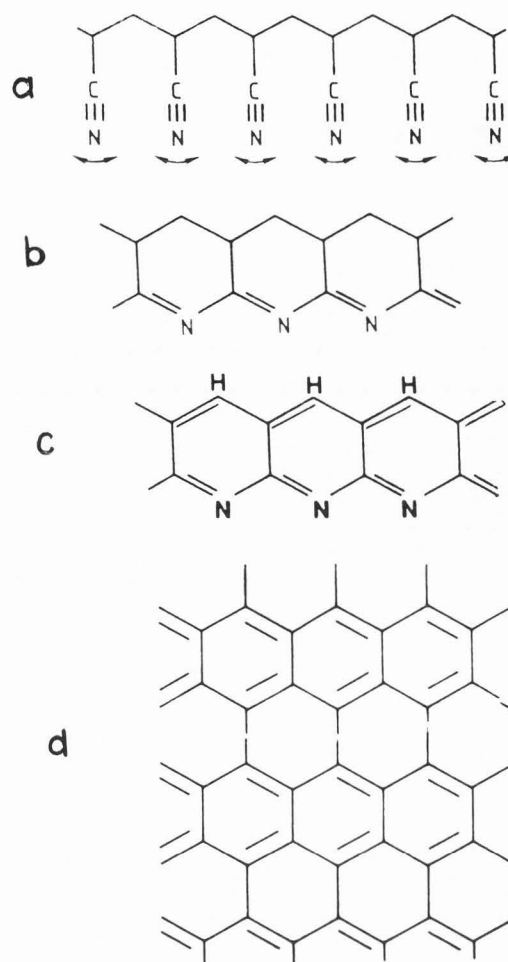


Fig.3 - Pyrolysis of PAN leads to a so-called carbon fiber structure. Several steps can be observed. (b) : cyclisation, (c) : de-hydrogenation, (d) : denitrogenation.

For a given film thickness, the experimental conditions for these transformations are reproducible, under ultra-high vacuum conditions.

Specimen purity

The film preparation process guarantees chemical purity. This is verified by Auger electron spectroscopy and secondary ion mass spectroscopy (elementary purity) and by infra-red absorption spectroscopy (absence of solvent molecules and quaternary ammonium ions). Impurity content was found to be below the detection threshold.

Specimen stability

Like all organic materials, polyacrylonitrile undergoes changes in the course of heat treatment; in particular, it is well known that pyrolysis of PAN leads to a so-called "carbon fiber" structure. This transformation was investigated on the basis of specimen intrinsic properties (i.e., under ultra-high vacuum conditions, therefore in the absence of any contaminant). It is shown by figure 3 /8/.

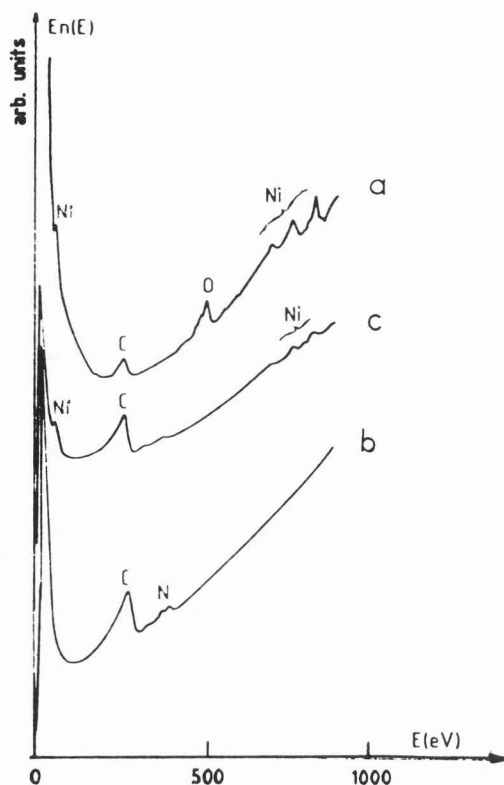


Fig. 4 - Stability of a cyclized PAN film when exposed to the atmosphere, studied by Auger electron spectroscopy ($E_p = 2.5$ keV, $I_p = 5 \cdot 10^{-9}$ Amp., Scanning speed = 1 V.sec $^{-1}$).

a - the sample surface before electrolysis exhibits characteristic lines of Ni substrate and atmosphere contamination: carbon and oxygen.
 b - after deposition of the PAN film, the sample surface is a pure organic material one (carbon and nitrogen lines), even after a long exposure to atmosphere.
 c - after ionic abrasion (Ar^+ , $E = 1$ keV), the Nickel-film interface does not contain oxygen: the oxide layer is removed at the first step of the electrochemical process, and atmosphere oxygen cannot go towards the substrate through the film.

Although the transformation varies according to specimen thickness (the thinner the film, the lower the temperature at which the fiber structure appears), it is fully reproducible for specimens of identical thickness. Structure and elementary composition of specimens can thus be varied in a controlled way.

Let us now consider specimen stability with respect to time. PAN molecular structure is obviously subject to change, even at ambient temperature. This instability can however be reduced to a considerable extent, through cyclization (fig. 3b), as shown by a combination of two tests:

- infra-red absorption spectroscopy is used to verify that the molecular structure of cyclized PAN shows no detectable change even after one year's storage in the laboratory atmosphere.

- Auger electron spectroscopy confirms that the film is inert as regards atmospheric oxygen.

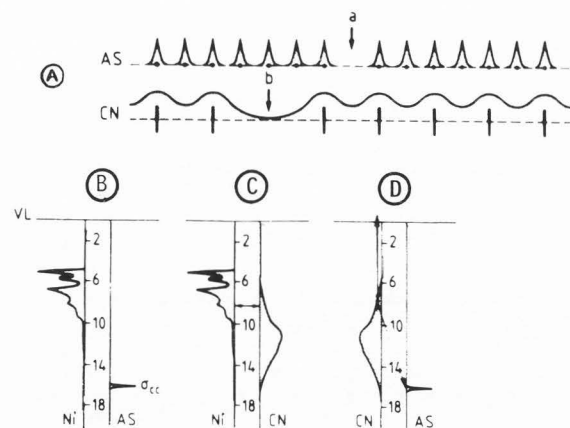


Fig. 5. Electrical properties of the sample.

A - Electron localisation along the polymer chains AS (aliphatic Skeleton): the wave functions are very localised around the carriers. A structural defect (a) is shown by a loss of periodicity. CN (series of nitrile groups): the wave functions of the π bonds are found to establish a level band; a structural defect (b) is shown by a less well filled region.

The holes created on the aliphatic skeleton, localised between two defects, are not at favourable levels and distances to be neutralised by the metal (B), such as that which exists between the metal and CN (C). The holes created on the aliphatic skeleton are exclusively relaxed by vertical transitions (D) involving CN π electrons.

Further, the PAN film is fairly uniform and acts as a passivation barrier which is sufficient to prevent oxide film from forming again on the metal surface (fig. 4).

At ambient temperature, a cyclized PAN specimen may thus be regarded as stable when exposed to the atmosphere.

The same conclusions may be drawn in the case of ultra-high vacuum storage (10^{-8} Pa): no outgassing or sublimation was observed. Under MDS investigation, the specimen surface remains unchanged irrespective of the time of exposure to the ultra-high vacuum (the test covered several thousand hours).

Lastly, the stability of PAN films should be evaluated as regards radiation damage. Results obtained with specimens subjected to various types of irradiation will be given in another publication.

Properties of the metal-to-film bond;

Electrical properties of specimens

As stated earlier, the metal-film interface is chemically stable, especially as regards atmospheric oxygen. However, the validity of a non-metallic material as a reference specimen is subject to two other conditions: the physical and electrical reliability of the connection to the specimen carrier, and the reproducibility of that connection.

The specimen as proposed consists of a polymer film strongly bonded (chemisorption bond) to a metal substrate (solid metal support: 1 mm approximate thickness, usual diameter from 8 to 15

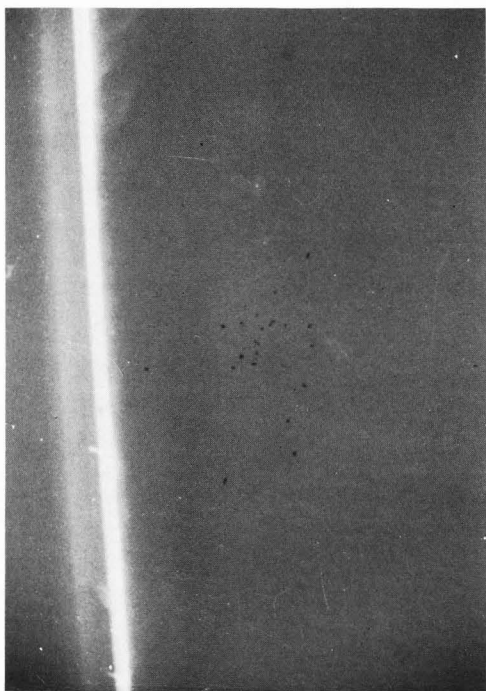


Fig.6 - Scanning electron microscopy image (1cm=10 μ m) of a PAN film. The film surface is perfectly homogeneous. Image contrast is obtained notching the film with a thin cutter.

mm). Quality of the chemisorption bond is verified through heat treatment (the carbon-to-metal bond remains after heating at 1000°C under a vacuum) and by a peeling test. The specimen can thus be adapted to any conventional specimen carrier, in the same way as a metal target. As to specimen electrical properties, they are described in detail elsewhere /4/ and summarized by figure 5.

Charges induced at the film surface as a consequence of electron emission are released through a number of simultaneous processes : hole type conduction along the line of nitrile groups, phonon-assisted site-to-site jump at the location of structural defects, and Auger-type relaxation of induced charges at localized electronic levels. Excellent overlapping of film (line of nitrile groups) and metal-filled bands rules out charge accumulation at the metal-film bond.

No charge phenomenon appears at the specimen surface when the temperature is raised to 100°C; further, this temperature is not sufficient to cause a transformation of the film molecular structure (the chemical transformation threshold is 200°C).

Spectroscopic investigation of specimens

Polyacrylonitrile films, electro-polymerized on oxidizable metal substrates thus exhibit the properties required for use as reference specimens in the organic material field. A systematic investigation of such specimens, pursued over several years, has yielded a set of typical data obtained through a combination of methods: scanning electron microscopy (SEM, figure 6);

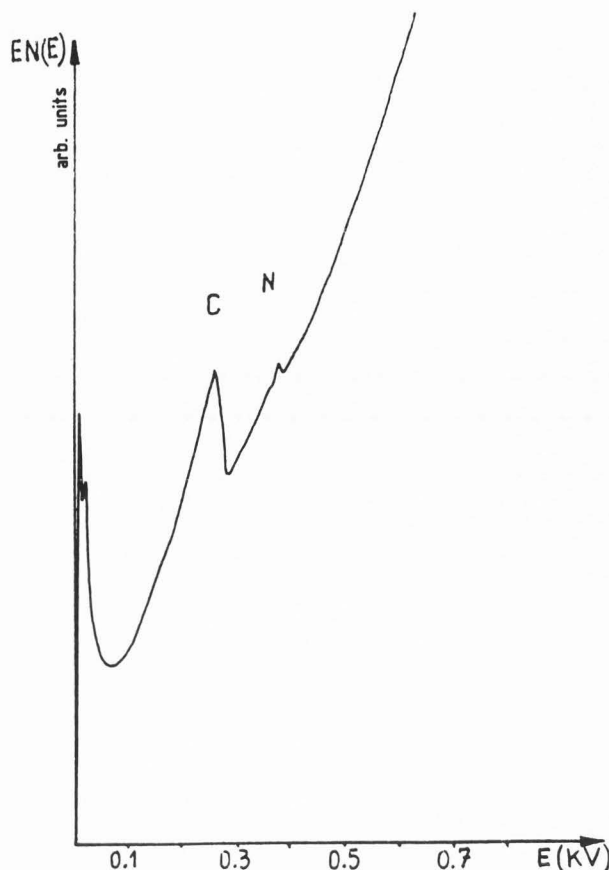


Fig.7 - Auger Electron Spectroscopy on a PAN film. Experimental conditions :

- film thickness = 100 Å
- primary electron energy = 2.5 keV
- primary electron intensity = $5 \cdot 10^{-9}$ Amp.
- scanning speed = 1 V.sec⁻¹.

The film surface contains exclusively carbon and nitrogen atoms (and hydrogen atoms, which are not seen in AES). The secondary emission intensity increases with the structural defects concentration (e.g., the film thickness).

Auger electron spectroscopy (AES, figure 7), secondary ion mass spectroscopy (SIMS, figure 8), infra-red absorption spectroscopy (IRAS, figure 9), UV photo-electron spectroscopy (UPS, figure 10), metastable de-excitation spectroscopy (MDS, figure 11).

Conclusion

After explaining why it is necessary to specify reference specimens in the organic material field, we have shown that polyacrylonitrile films obtained by electro-polymerization on oxidizable metals meet the criteria applicable to such specimens, e.g., purity, stability, known and reproducible molecular and inter-molecular structures, easy electrical and mechanical connection to specimen carrier.

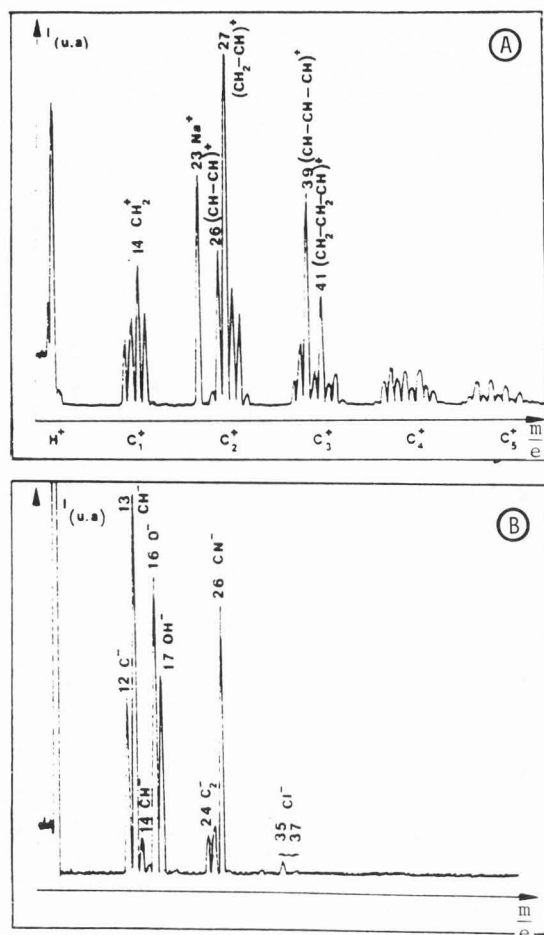


Fig.8 - Secondary Ion Mass Spectroscopy on a PAN film.

Experimental conditions:

- film thickness = 200 Å
- primary ion energy = 1 kV
- primary ion intensity = 10^{-9} A.
- scanning speed = 1 mass unit per second.

The film is a pure organic layer. The high sensitivity of SIMS for Na (positive ions) and for O (negative ions) explains the presence of the peaks characteristic of these atoms which have, in fact, a very small concentration (cf AES spectrum, fig.7).

A set of experimental data, obtained through a combination of various techniques, illustrates the above properties. These results are a first step in the preparation of a document for an organic reference specimen.

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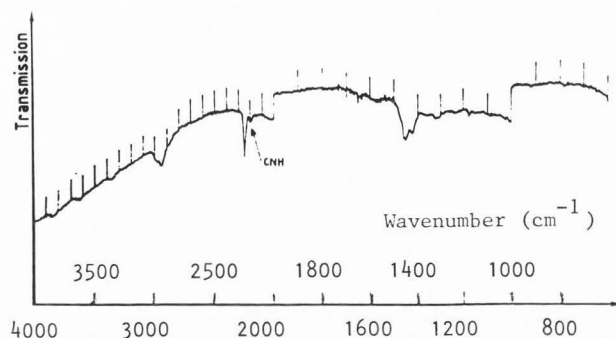


Fig.9 - Infra-red absorption spectroscopy on a PAN film. Experimental conditions :

- film thickness = 1000 Å
- scanning speed = 4 cm^{-1} per second

This spectrum is characteristic of the polyacrylonitrile molecular structure. The intensity of the CNH peak is in relation with the bridging alteration concentrations.

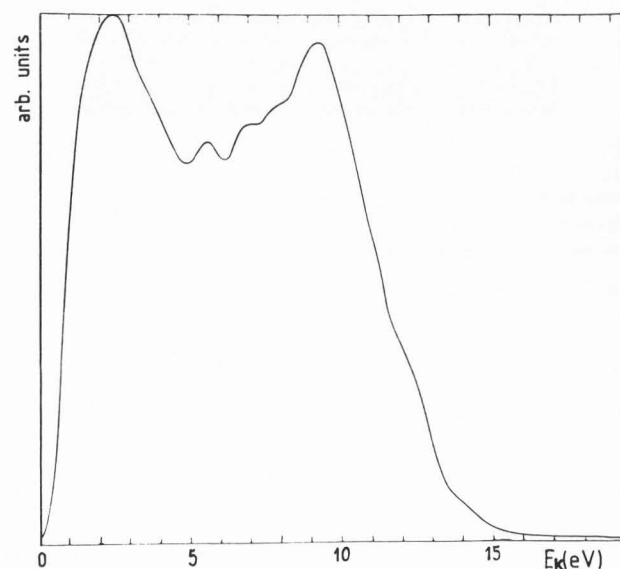


Fig.10 - Ultraviolet photo-electron spectroscopy on a PAN film. Experimental conditions:

- film thickness = 100 Å
- photon energy = 21.2 eV
- scanning speed = $0.5 \text{ V} \cdot \text{sec}^{-1}$

The density of occupied states of the film is the one of a semi-conductor having a large gap (3eV). The valence band is constituted with the electrons of the CN series.

The secondary electron emission increases with the structural defect concentration.

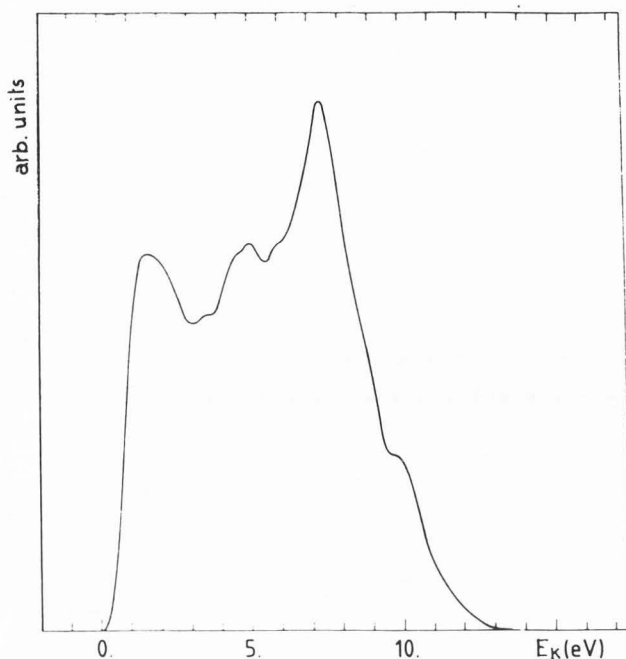


Fig. 11 - Metastable De-excitation Spectroscopy on a PAN film. Experimental conditions :
 - film thickness = 100 Å
 - metastable energy : Potential energy = 19.8 eV;
 Kinetic energy = 60 meV;
 - scanning speed = 0.5 V sec^{-1} .

The orbitals pointing out of the surface are those of the CN groups, essentially the ones of the nitrogen lone pairs.

The relaxation of positive charges (due to the meta-emission process) located on structurally altered aliphatic skeletons is responsible for the secondary electron emission.

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Discussion with Reviewers

J.M. White : Can the authors describe the extent of surface damage inflicted on the sample by the AES and SIMS measurements ? Generally organics are particularly sensitive to beam damage. I think it is important to establish measurement criteria for the use of reference samples.

Authors : We also observed that organics are particularly sensitive to beam damage, and the PAN is not an exception. In fact, the secondary ion mass spectroscopy (SIMS) is based on the progressive destruction of the sample from which the sputtered ions are analyzed. The main problem encountered with SIMS technique is the modification of the surface composition during ion bombardment; it is thus particularly interesting to note that the spectrum shape (thus the surface composition) does not change during the measurement, with a PAN sample.

Unfortunately, this is not the case when using Auger Electron Spectroscopy (AES) : the electron bombardment leads to a molecular transformation of the PAN film which will be described in details in another paper. Schematically, Infrared absorption spectroscopy (IRAS) measurements show a decreasing of the CN group density and an appearance of C=C bonds in the aliphatic skeleton (i.e. a partial de-hydrogenation) which implies a relative diminution of the nitrogen Auger peak, and an evolution of the secondary emission intensity.

In comparison with some other materials, the measured thresholds for irradiation damages when the PAN is bombarded by energetic electrons is given in the following table :

material	pure metal	SiO ₂ *	PAN**
without damage up to :	$10^{20} \text{ e cm}^{-2}$	$10^{17} \text{ e cm}^{-2}$	$10^{14} \text{ e cm}^{-2}$

* oxygen desorption

** graphitization

In this paper, we present Auger electron spectra obtained with low values of the primary energy ($E_p = 2.5 \text{ keV}$) and of the primary intensity ($I_p = 5 \cdot 10^{-9} \text{ A}$), in order to limit the irradiation damages during the measurement.

B.E. Koel : You point out the need for a reference organic material that represents well organic material encountered in materials research. Also, you note that as a reference standard, the sample should be conducting and not damaged by irradiation. Aren't these two criteria usually mutually exclusive since "real" materials are insulating and very sensitive to radiation damage? It seems that much more research on the particular organic material or polymer to be analyzed would be required to make sense of the data, don't you agree ?

Authors : These questions must be answered together. First, it is true that a reference

standard must be "conducting", in order to avoid charge phenomena during the electron spectrometer alignment. Secondly, the irradiation damage threshold must be accurately known (see the discussion with J.M. White) in order to compare the obtained spectra with the referenced one. When the mechanical and electrical alignment procedure is achieved, it becomes at last possible to study the properties of technological materials, such as insulating properties (charge phenomena) and evolution under irradiation (composition and molecular arrangement) as functions of time, intensity and energy of incident beams, etc...

B.E Koel : The molecular-level structure of the metal-polymer interface is a very interesting problem. Do you have any information on the nature of the strong chemical bonds that are formed at the metal-polymer interface ?

Authors : The grafting and the growth of the PAN film on the metal substrate are the results of the strong effects of the double layer electric field in an electrolytic cell : this electric field orients and polarizes the monomer molecules, the electronic level of which is shifted. In particular, the LUMO borne by the acid end of the polarized molecule ($^+CH_2-CH^-CN$) becomes in front of the top of the metal valence band (the metal is used, in the electrolytic cell, as a cathode). An electronic doublet can thus be localized on the metal-carbon bonding. It should be emphasized that this bonding is not destroyed by heat treatment (up to 1300K under vacuum conditions): the pyrolyzed PAN film becomes a carbon film adherent on the metal (see J.Perreau et al, to be published in Surface Science). Mechanical measurements of the adhesion force are now in progress, and the electronic characterization of the bonding are in project.

B.E. Koel : Do you have a good idea of the largest thickness of film that would be suitable as a reference standard, considering your criteria ?

Authors : Generally, we use films the thickness of which are in the range 50-1000 Å.

R.W. Vook : How stable are your films under low (25-200 eV) and high (1000-20,000 eV) electron irradiation ? How would Fig.7 change with time of electron irradiation ? Similarly how stable are the films under UV irradiation and how does Fig.10 change with time of UV irradiation ?

Authors : The stability of the PAN films under electron irradiation is evocated through the response to the question of J.M. White. The major effects on the Auger electron spectra are the decreasing (up to the disappearance) of the nitrogen peak ; simultaneously, the number of low energy electrons (secondary electrons) increases. On the contrary, ultra-violet photoelectron spectra do not change with time during a HeI ($E_h = 21.2$ eV) photon irradiation, the largest irradiation time being, in our laboratory, one hundred hours. It must also be noted that the same observation was made during irradiation with helium metastable atoms ($E_{23S} = 19.8$ eV, $E_k = 60$ meV).