CONDUCTIMETRIC PROPERTIES OF SOME SOLID TRACK DETECTORS AND HYPOTHESIS ON THE TRACK FORMATION MECHANISM IN THESE IRRADIATED AND ETCHED DETECTORS

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Abstrat

The purpose of this work is to study the conductivity variations of solid track detectors with ester function after etching and irradiation. The different conductimetric behaviour of these detectors allows to assume the chemical etching mechanism. This hypothesis seems to be confirmed by IR and RMN studies.

All the papers about latent track formation in solid track detectors point out the following condition : detectors must have electrical resistivity above 2 000 Ω/cm to record any track (1). So it is interesting to study the conductimetric properties of these insulators and especially the variation of their resistivity as a function of irradiation dose, etching time and concentration of etching reagent. For this purpose, we have studied cellulosic esters and polycarbonate films.

## CONDUCTIMETRIC MEASUREMENTS

Experimental procedure

First of all, we studied a 40 µm thick film of cellulose dinitrate. Analysis gave a nitrogen quantity of 12 % and a camphre quantity (plasticizer) of about .0 %. This material had been pro-·ided by Kodak Pathé Society (France).

Cellulose dinitrate (R=OH or ONO$_2$)
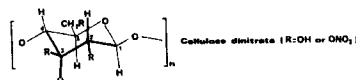
Then, we used a 40 µm thick film of cellulose triacetate without any plasticizer, purchased from Bayer chimie (France) (Triafol TN).

Cellulose triacetate
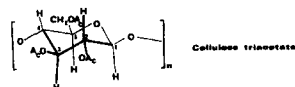
At last, Makrofol film (44' dioxydiphenyl 22 propane polycarbonate) was chosen.
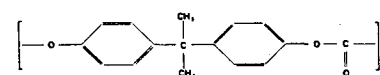
44' dioxy diphenyl 22 propane polycarbonate

These samples were irradiated with the fission fragments from ^{252}Cf (10^6 fissions/cm^2/hours). α particles from ^{241}Am were also used after being reduced to an energy in the range 0 to 2.27 Mev for a better recording.

Etching reagents were aqueous sodium hydroxyde solutions of 5N, 6,5N and 8N in a constant temperature bath (60° C).

Then etched samples were carefully washed by distillated water. At last they were kept in vacuum. No detectable variation in conductivity measurement of a particular sample was observed after a sufficient drying time (about 10 days). The electrical conductivity was measured with Wayne Kerr impedance bridge.

The measurement cell (fig. n°1) had been made in our laboratory. The electrodes were held by a insulating material in coaxial position inside two brass tubes, one of which was free of movement. This device was mounted in a rigid frame. The movable electrode was connected with the other by the mean of a screw. A torque wrench enabled a constant pression (45 Kg/cm^2) on the electrodes.
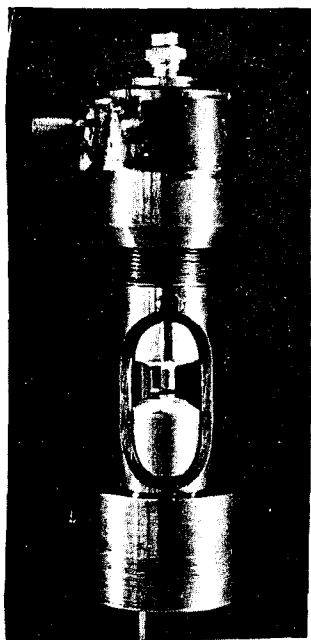
1470

fig. 1

fig. 2

RESULTS AND INTERPRETATION

It is well known that ionizing particles produce breaking points in the macromolecular chain of organic polymer detectors.

The experiments were initiated in an effort to display clearly the existence of these defects by a conductimetric method. No conductimetric difference appeared when samples were irradiated but not etched even for large irradiation doses.

The etching process of tracks, making channels more or less wide, more or less deep and so substituting bulk material by air should have decreased the conductivity of the film (because air is a better insulator than cellulosic esters).

Besides, samples measured in vacuum showed a conductivity lower than in atmospheric conditions.

In fact, we observed that conductivity was increasing more or less with irradiating time, this leads to the idea that an another phenomenon may be invoked, this phenomenon would increase the heterogeneity of material and consequently its conductivity. Fig. n° 2 summarises the results obtained with three detectors etched with sodium hydroxyde 6,5 N up to one hour. First of all we notice the different conductivity of these three esters etched but non irradiated.
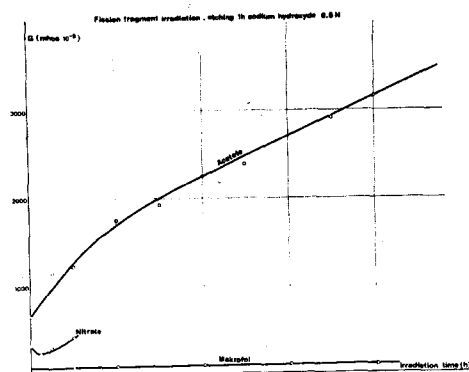
The following values were found :
- cellulose acetate : 700 mhos 10^{-9}
- cellulose nitrate : 310 mhos "
- Polycarbonate   : 60 mhos 10^{-9}

It also appears on fig. n°2 that cellulose acetate and Makrofol show a conductivity augmentation represented by a monotonous increasing function , but this variation is very different according to the detector. In the case of Makrofol indeed, it is nearly negligible.

For cellulose nitrate, the sample destruction etched one hour after 45 minutes irradiation constrained us to reduce the etching time to 35 minutes (fig. n° 3) ; so we obtained for this compound a linear increasing function of the irradiation time (for irradiation times longer than 30 minutes).
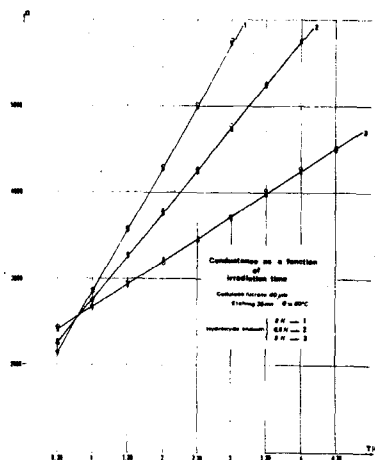

fig. 3

These conductivity augmentations can be naturraly used to know the irradiation dose ; in a recent work, (2, 3) we perfected a method based on this observation in order to evaluate the track density. It is of interest to compare the behaviour of the three compounds (i.e. cellulose acetate, cellulose nitrate and polycarbonate) at short irradiation times (below 30 minutes) , the conductivity of cellulose nitrate (and only this polymer) is decreasing with irradiation dose. It is assumed that a different etching mechanism may be invoked for this detector ; this mechanism will be drawn later. Fig. n° 3 also shows the conductivity for a same irradiation time and a same etching time as a function of etching agent concentration. Of course, the augmentation of conductivity with concentration is greater, the irradiation dose is more important. In the case of irradiation by α particules, similar results have been obtained but the conductivity variations observed are not so important.

We tried to explain these conductivity variations.

It is very important to notice that conductivity increase is not due to sodium hydroxyde itself remaining in tracks because the samples were washed up as long as necessary to have no more change in conductivity measurement. Of course, the thickness of the film fell off after etching but the chemical attack was lasting the same time for a line of samples so that the thickness could be modified in the same manner at the etching step.

However, if track density is very important it is possible the chanels become edge to edge ; so, the decrease of thickness would be a function of the irradiation dose. It seems likely this effect would take a part in the conductimetric decrease. But that is not enough to explain the results ; computation show indeed that the observed variations would be correlated with a thickness decrease greater than the undammaged film thickness itself. So, in all probability, another phenomenon would take place.

To be precise, we used a chemical reagent and we assume the conductimetric variation is the result of a chemical dammage in polymer. It is therefore possible to invoque a saponification reaction. In the case of non irradiated etched samples, the above reaction is limited to a thin layer at the surface of material. When irradiated, the chemical attack would occur deeply along the latent tracks that allow sodium hydroxyde diffusion. Then chemical change, especially formation of new hydroxyl groups should induce a conductivity enhancement.

It would seem this saponification reaction would be slightly efficient in the case of Makrofol. For cellulose nitrate, (4) sodium hydroxyde reacts in two ways : on one hand saponification (with a low rate), on the other hand oxydation degradation (with a fast rate) which would enlarge the tracks. So in case of short irradiation times, oxydation degradation would play a leading part. Perhaps that would explain the specific conductivity decreasing above mentionned for this polymer, because the presence of air, a better insulator, in tracks. When track density was important, reagent diffusion in bulk material became easier, so that hydroxyl group number would be sufficient to increase conductivity.

Furthermore oxydation degradation would be liable for nitrate sample destruction by 45 minutes etching whereas acetate film can suffer that etching time without being broken up.

CHEMICAL TRACK FORMATION MECHANISM AFTER ETCHING

The purpose of the following section is to test the above mentionned hypothesis, drawn from observations of conductimetric properties of samples exposed to different irradiation doses and then etched.

First, in order to prove the existence of oxydative degradation reaction, we changed etching condition. For cellulose nitrate we used a sodium hydroxyde solution in reducing condition (saturated by sodium nitrate). As a result (fig. n° 4) a general conductivity decrease was observed for each irradiation dose. This fact could be explain because hydroxyde sodium diffusion was more difficult, oxydative degradation reaction would not be so important, so film thickness is not so

reduced. The inverse phenomenon that is to say general conductivity increase was observed for an nitrate sodium oxydative bath.
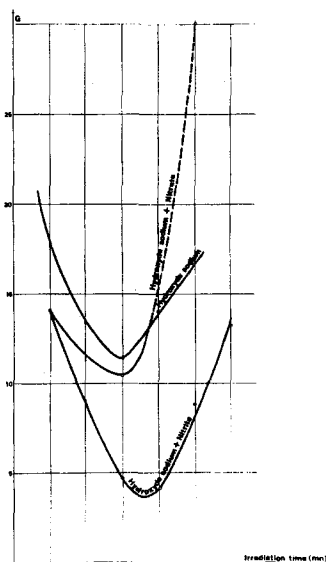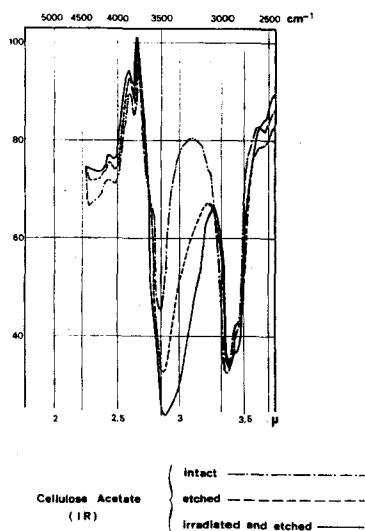

fig. 4

A similar behaviour is observed for cellulose nitrate. In the case of Makrofol fig. n° 6) this peak is very small and practically does not increase with etching and irradiation. Methyl groups and carbonates groups absorb at about 3 000 cm^{-1} and 1800 cm^{-1} respectively. The absence of OH groups is related first with the chemical formula of this polymer and secondly with the fact that a chain breaking is necessary for this reaction.
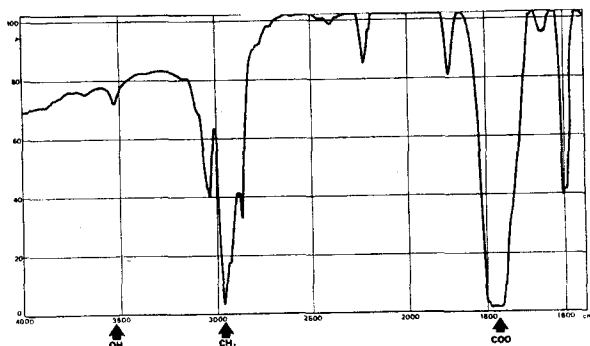

fig. 6

On the other hand, we tried to point out the important enhancement of saponification reaction with the irradiation dose and for a constant etching time. Two powerful tools, i.e. NMR and IR spectroscopies were used for such investigations.

First IR spectra of cellulose acetate are shown on fig. n° 5. It can be seen that the peak corresponding to OH groups (3500 cm^{-1}) is clearly increased.

fig. 5

NMR studies confirmed the above observations : unfortunately, solubility problems appeared in the case of cellulose acetate samples. If intact films are soluble in chloroform and methylene chloride (NMR study of this polymer has been done by Gagnaire and Vincendon (5, 6) etched especially when irradiated films are only partly soluble in any solvent. This is an additional argument to support the hypothesis of the important chemical change due to irradiation and etching. One could suggest the following explanation : the result of the saponification is, in fact, to decrease the degree of acetylation. This reaction is only effective in irradiation damaged zones; consequently polymer solubility is affected.

Cellulose nitrate, probably due to the oxydation degradation process, is always soluble in acetone. NMR spectra of various cellulose nitrate films in deuterated acetone were recorded with a Varian HA 100 Spectrometer. On fig. 7, 8, 9, we can see spectra of intact film, of 35 minutes etched with 6,5N sodium hydroxyde film and 35 minutes etched film after irradiation. The

peak corresponding to oxydrile groups appears at δ = 3 ppm (from TMS internal Standard) it must be noticed that any water trace would give a contribution to this peak. However it is possible to compare different film spectra because all the samples were dryed in the same conditions. The area of this peak is slightly increased when the polymer film is etched but a considerable area enhancement is observed when irradiated and etched. At hight field, it can be observed camphre peaks (plasticizer). Broad absorption lines in the range 3,5 to 6 p.p.m are connected with the seven cyclic protons.
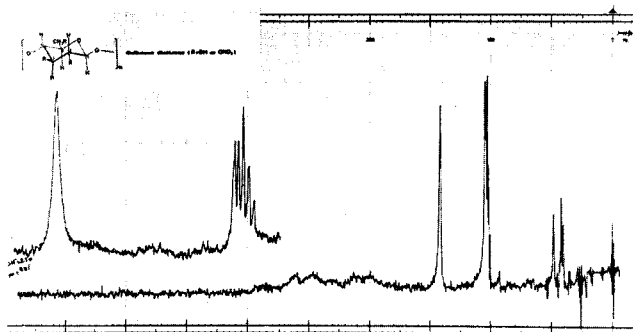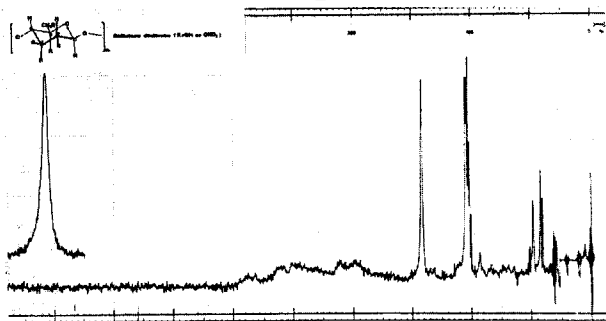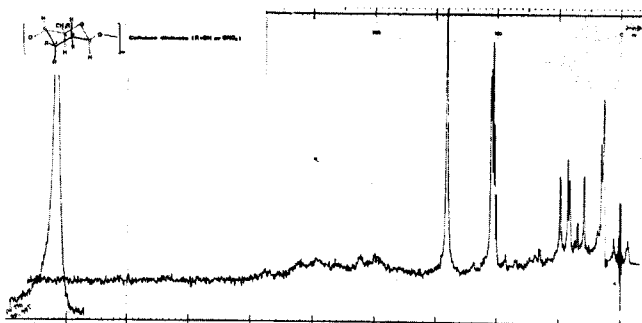

fig. 7

fig. 8

fig. 9

NMR Spectra of Makrofol films in deuterated chloroform were recorded with a 250 MHz Spectrometer from Cameca (Thomp-

son C.S.F.) This high field Spectrometer was needed in order to detect any slight variation that could have occured. On fig. n° 10, a Makrofol film spectrum is shown. A typical para substitued aromatic signal is founded at about 7 p.p.m (8 phenyl protons). The methyl groups (6 protons) appear at δ = 1,35 p.p.m. A small peak at δ = 1,25 p.p.m is attributed to hydroxyl groups (probably the ends of macromolecular chains). This observation fit with the conclusions drawn from IR Spectra. The irradiation and etching effect is not clear because it is difficult to evaluate the hydroxyl peak importance at δ=1,25 ppm which is closed by methyl group peak. Nevertheless, in order to obtain a better information we used TFA (trifluoracetic acid) to shift out the OH group. We calculated the ratio of peak areas at 7 p.p.m and 1,3 p.p.m with and without TFA for each film (intact, etched, and irradiated etched). For instance, for the intact film the above ratio is 1,45 before TFA addition and 1,45 after.
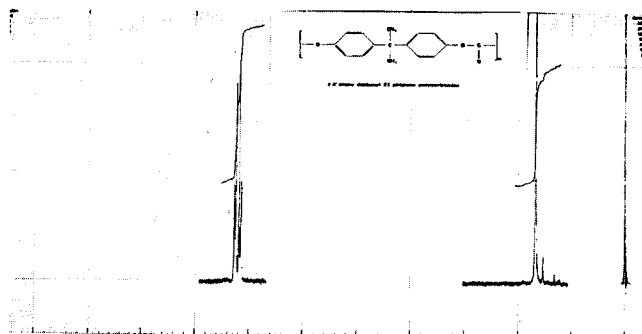

fig. 10

In the case of etched sample as irradiated etched samples the ratio is equal to 1,25 before TFA addition and 1,45 after TFA addition (fig. 11 and 12) (it can be observed on fig. 12 the shifted OH TFA peak at about δ = 10 p.p.m) So it appears there is a weak augmentation of hydroxyl peak area for an etched sample compared with an intact film ; increase is no more important in the case of an irradiated etched sample. That is in good agreement with IR Spectra for Makrofol. In fact, it would seem likely that reagent diffusion is allowed even in non irradiated sample by flexibility of molecules, so that irradiation would not matter a good deal for saponification reaction.
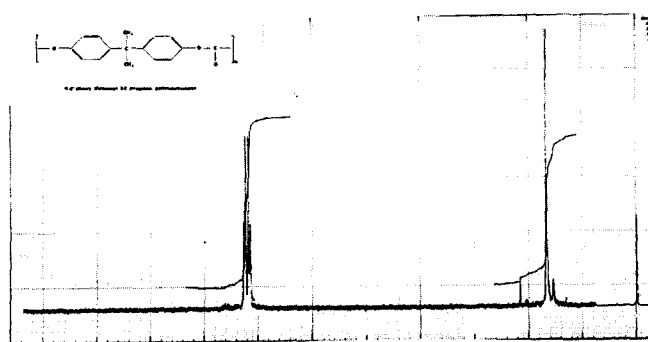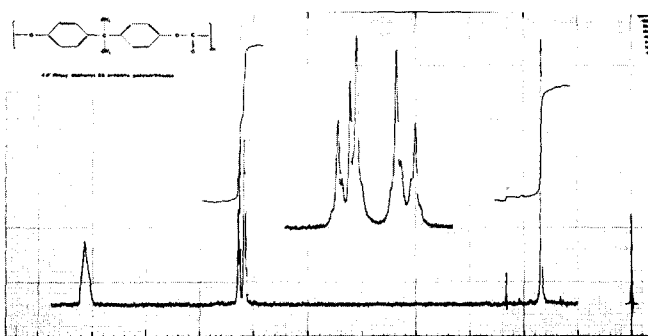
fig. 11

fig. 12

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In conclusion, we have noticed corre-
lation between conductimetric properties
and saponification reaction for all stu-
died detectors. That reaction is easier
for cellulosic esters ; in the case of
polycarbonate, it is more difficult.

At last it can be note that the sen-
sitiveness of these detectors, charac-
terized by the critical rate of energy
loss $(\frac{dE}{dx})_c$, for the lightest recorded
particle, rate which is 0,86 and 1,41
for nitrate and acetate (in the case of
α particles) and which is 5,5 for poly-
carbonate (in the case of ^{16}O), was also
correlated.

Thus we have been able to approach
chemical track etching process by the
mean of conductivity study i.e. by the
mean of physical property study.

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