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INTERACTION OF ENERGETIC HEAVY IONS WITH POLYMERS

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Abstract

The effects of electronic excitations due to irradiation of electrons or energetic heavy ion (>1 MeV/amu) irradiations on linear polymers of general formula $-(CR_1R_2-CR_3R_4)_n-$ are reviewed and compared with previous results obtained with δ and electron irradiation. The polymer modification are discussed accounting for the nature and the position of the R_1 , R_2 , R_3 and R_4 substituents on the main chain. It is suggested that linear polymers can evolve according to the "R" nature ($R=R_1, R_2, R_3, R_4$). This paper includes the physical and chemical processes of electronic excitation and the mechanisms which lead to modification of the macromolecules.

An attempt is made to relate the macromolecular structure of polymers and their structural modifications under irradiation.

Introduction

Radiation effects induced by ionizing particles like electrons, ions, photons, have been largely used recently to modify the chemical and physical properties of organic compounds. Unfortunately, these modifications are not yet totally controlled as the result is often a superposition of several mechanisms including the interaction of the incident particle with matter and the different secondary reactions initiated. The most important modifications observed in irradiated polymers (crosslinking, grafting, and degradation) can be closely understood by studying crosslinking and scission reactions produced by irradiations of monomers or low molecular weight compounds. Other effects like stimulated desorption, double bond or multiple bond creation can also be observed. It is interesting to note that drastic changes in the polymer properties correspond to only minor chemical modifications and can lead to very specific effects (conductivity, piezoelectricity, pyroelectricity or optical properties...).

One of the major difficulties encountered during the study of the radiation modifications lies in the fact that one is faced with reactions generally occurring in a solid medium. Little is known about the mechanism of such processes and no classical methods permit the study of the complicated reactions which may be involved. Work has been done both on the changes in the physical properties of polymers under irradiation and on the chemical modifications underlying the changes in the physical properties.

The study of radiation chemistry of polymers by electronic excitation induced by the interaction of energetic heavy ions (>1 MeV/amu) appears to be an interesting way because of the control of the modified area of the irradiated compound. This new chemistry is now in full development using large heavy-ion accelerators like GANIL in France.

Key Words : Energetic ions, polymers, electronic excitation.

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Physical process of electronic excitation under irradiation of ions

The energy loss of particles which pass through a material is strongly dependent on their velocity. The intensity of this energy loss per unit length of path, which is also called stopping power, dE/dX , is represented in Fig. 1 as a function of energy. This curve reflects the large difference between low energy and high energy incident ions. At low energy (first part of the curve) the ions lose energy through collisions with nuclei of the target (nuclear stopping power). At high energies (> 1 MeV), the ion velocity is comparable to that of the valence electrons of the solid. The energy is lost through collisions with these electrons. Because of the great size and mass difference between electrons and ions, the energy loss to the electron during a collision is small, though there are a large number of collisions. Polymer modifications under electronic excitation can be described as a three step process, according to the time constants involved. In the first step ($t > 10^{-14}$ sec), part of the energy of the incident ion is absorbed by the polymer through electron i.e. excitations. In this first step, δ rays (secondary electrons) are emitted along the excitation path. Owing to the high level of energy deposited by the particle, the second step (thermal equilibrium) is reached in times ranging from 10^{-12} sec to 10^{-9} sec. The absorbed energy is released in three processes: radiative decay (ultra violet photons are reabsorbed by the polymer), production of new reactive species (radicals, gas desorption) and thermal energy which is the most important process which triggers a significant atomic reorganization. The third step is the achievement of the chemical equilibrium for times greater than 10^{-8} sec. Indeed, free radicals, ions, excited molecules and electrons still exist in the polymer. All these mechanisms are summarized in Table 1. The second step of the process of electronic excitation is essential for the polymer modifications because of the creation of species (radicals, ions, radical ions, excited molecules) which initiate all the further modifications in the polymer.

The ion track is then comprised of a highly damaged zone, nearly cylindrical with a radius of about 30 Å and a length comparable to the ion range (eg. $R \approx 3$ mm for 50 MeV/amu, 0¹⁶).

Chemical processes induced by energetic heavy ions

Recent publications show an increasing interest in the use of energetic ions to selectively modify the original structure of polymers by inducing crosslinking, grafting or multiple bonds creation.

These modified polymers find very interesting applications because of their new chemical and physical properties. Venkatesan <36> studied the effects of high energy Ar ions (2 MeV) in films of polymethylmethacrylate (PMMA) and classified the modifications as a function of the dose (Table 2). At low doses, scission and crosslinking take place. For increasing doses dissociation of the polymer, loss of integrity is observed. For higher doses, graphitisation, carbonisation can lead to the creation of inorganic substances. It must be noted that these modifications are often difficult to produce by conventional ways, owing to the solid state of the polymers.

The chemical changes induced by ion irradiation involve: creation of free radicals which initiate the modifications; formation of chemical bonds between different molecules (intermolecular crosslinking); irreversible cleavage of bonds (scission) in the main chain which results in the fragmentation of molecules; formation of unsaturation, unsaturated groups with stimulated desorption of gas; irreversible degradation of the organic compound.

The crosslinking increases the weight of the compound whereas irreversible degradation with mass loss decreases it.

In the past much work has been devoted to radiation induced degradation of polymers (36, 8, 37, 20). Schnabel <30> studied the specific aspects of radiation induced changes in polymers related to the molecular weight. The number of scissions observed per molecule decreases by a factor 100 when the molecular weight of a given compound increases by a factor 10^4 . This behavior strongly outlines the attachment of the molecules in the high weight macromolecular compound.

One of the most striking observations in the study of the radiation effects in linear polymers is the fact that polymers either crosslink or degrade depending on their chemical structure <6, 13, 15, 22, 5>. This is confirmed by using heavy ions to achieve controlled changes in the polymeric structure of bulk materials. Several theories have been advanced to explain the ability of some polymers to crosslink rather than to degrade. Nevertheless none of them appears entirely satisfactory. For vinyl polymers, Chapiro <5> suggests that the crosslinking can be related to the binding of each carbon atom of the main chain to a carbon atom, whereas degradation would be the result of the existence of a tetrasubstituted carbon in the monomer unit. That theory can be supported by the existence of steric repulsions of these carbon atoms which induce degradation under ionizing radiations.

Interaction of energetic heavy ions with polymers

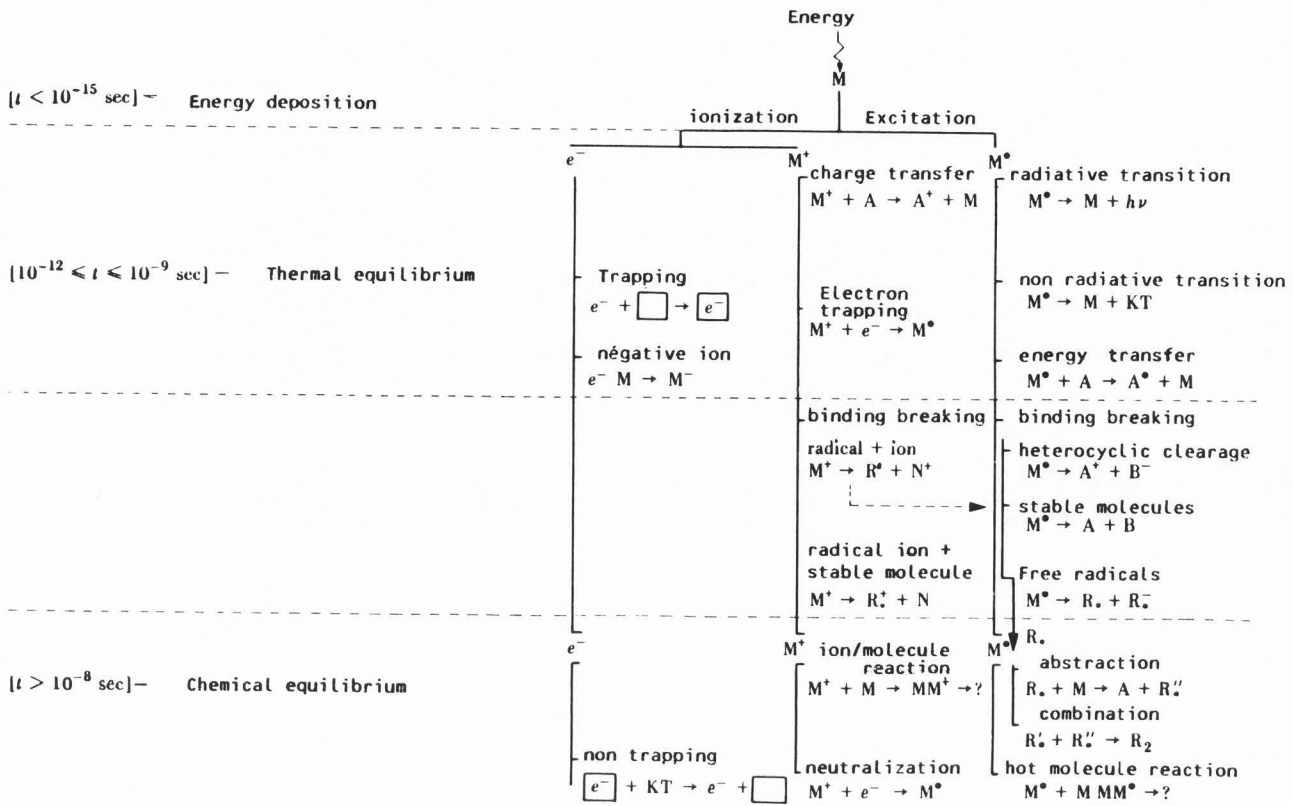


Table 1: Fundamental process of the latent track creation in polymeric materials. (From: E.V. Benton (1970) On latent track formation in organic nuclear charged particle track detectors, Radiation Effects 2(4), 273-280)

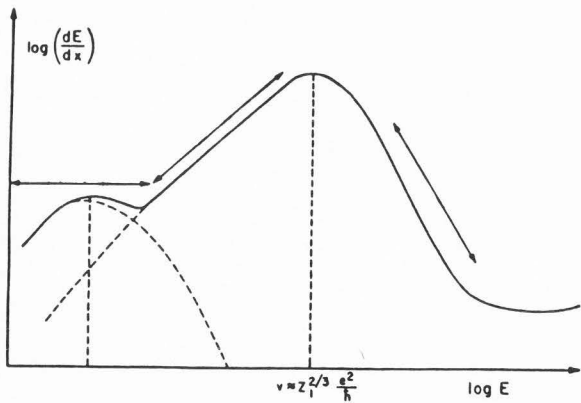
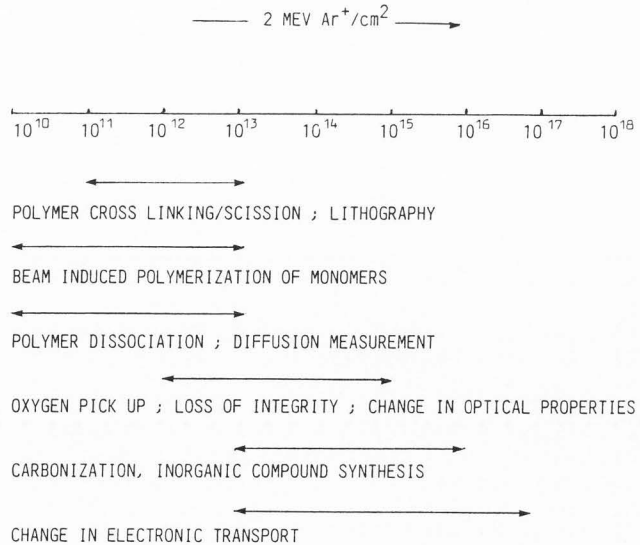


Fig. 1 - Stopping power dE/dx of an ion versus energy E (from 34) - At the low energies, corresponding to the shoulder of the curve, the ion energy is lost in a collision with the atoms of the solid \Rightarrow nuclear stopping power. At the higher energies corresponding to the peak, the loss of energy is in collision with electrons \Rightarrow electronic stopping power. The maximum of the electronic stopping power occurs when the ion has a velocity $v \sim Z_1^{2/3} \frac{e^2}{h}$ comparable to that of a valence electron of the solid. Z_1 is the atomic number of the atom target.

Table 2 - Ion polymer interaction phenomena observed as a function of dose for Ar^+ ions at 2 MeV/amu (from 36).



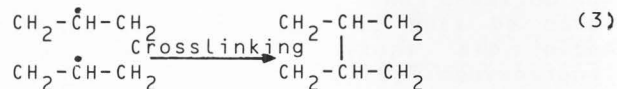
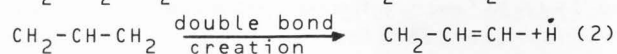
The advantage of high energy radiation to promote reproducible changes has been put forth by Charlesby <7>. This technique allows one to avoid the use of chemical reagents and a complete control of temperature, environment and additives, the most important aspect being to carry out the radiation process usually in the solid state, so that the chemical modifications can be induced in a fabricated object. According to this author the main factors which direct polymer modifications towards crosslinking mechanisms are: the dose of irradiation; the kind of radiation, sparsely ionizing (electrons, X-rays, γ -rays) or highly ionizing (fast protons, α -particles, heavy ions...); the requirement of unsaturated or other reactive groupings; the chemical structure.

It was also suggested that the alternative reaction to cross linking was degradation. However, these reactions are not necessarily exclusive, and both may and do occur in the same polymer. This is confirmed by recent results <35>. From these general phenomena, it is possible to propose a classification of the modifications of linear polymers accounting for the structural organization of the main backbone. It is important to outline that it relies on experiments realized in vacuo and under controlled atmosphere. Air or oxygen pressure considerably modifies the evolution of the polymers. This aspect will be examined in the next section.

Taking into account a linear polymer of general formula $(CR_1R_2-CR_3R_4)_n$ submitted to electronic excitations, we will successively examine, according to the nature of the substituents R_1, R_2, R_3, R_4 , the behavior of these polymers under irradiation. It is quite reasonable to separate these polymers in four classes: symmetrical polymers with $R_1=R_2=R_3=R_4$; alternating polymers with $R_1=R_2$ and $R_3=R_4$; polymers with $R_1=R_2=R_3 \neq R_4$; complex polymers with $R_1 \neq R_2 \neq R_3 \neq R_4$.

Symmetrical polymers - These polymers correspond to the general formula $-(CRR-CRR)-_n$ with $R = H, F, \dots$. It is in particular the case of polyethylene (PE) and polytetrafluoroethylene (PTFE). Recently, Ungar <35> reviewed the effects of high energy radiations on polyethylene and n-alkanes. The author shows that a four step mechanism accounts for the modification of this polymer: i) formation, spatial distribution and decay of free radical migration; and ii) formation of crosslinking and other stable by products; iii) effects of crystallinity, crystalline modifications and morphology on radiation crosslinking; iv) radiation induced changes in the crystal lattice and the destruction of crystallinity at high irradiation doses.

The exposure of PE and n-alkanes to high energy radiation results in the following chemical changes after the creation of free radicals by dehydrogenation: crosslinking, main-chain unsaturation, i.e. transvinylene $(-CH=CH-)$, diene $(-CH=CH-CH=CH-)$ and polyene groups. Cross linking generally occurs mainly by recombination of two free radicals:



Similar results were obtained by the authors <9,16> on PTFE compounds. They studied the modifications of this polymer under 10 keV electron irradiation, in vacuo, by photoelectron spectroscopy. They suggest that the first step of the modification of PTFE was the progressive creation of multiple double bonds evolved with increasing dose into bulk cross links. These modifications would perhaps be on the basis of the explanation of the aging process.

Fig. 2 shows the evolution of the PTFE vs dose as observed by photoemission. For PTFE the reactional mechanism is similar to that of PE, with the substitution of protons by fluorine atoms. Desorption of fluorine molecules was studied by mass spectroscopy. Fig. 3 represents the mass spectrum of species desorbed from PTFE under irradiation. Previously, PTFE was considered as a degrading polymer; our study shows that this polymer is first a crosslinking polymer. We never found "premises" of degradation effects under electronic excitation.

Alternating polymers with $R_1=R_2, R_3=R_4$ - The most current polymers which belong to this second class are built with $R_1=R_2=H$ and with $R_3=R_4$ which are halogenic atoms: polyvinylidene fluoride (PVDF), polyvinylidene chloride (PVC) or groupings like polyisobutylene ($R_3=R_4=CH_3$). In a recent work, we studied by XPS the modifications induced in PVDF samples by energetic heavy ions ($Kr^{26+} 10MeV/amu$) and low energy electrons. In both cases the first step of modifications is the desorption of hydrogen fluoride molecules and the creation of allenic compounds <17>. These mechanisms are confirmed by the C_{1s} line evolution (Fig. 4). In the case of Kr ions irradiation (Fig. 4b) a line located at ~ 285 eV indicates that energetic heavy ions induce first in saturations but also a beginning of crosslinkings which are supposed to be the reevolution of allenic compounds when the appropriate dose is increased.

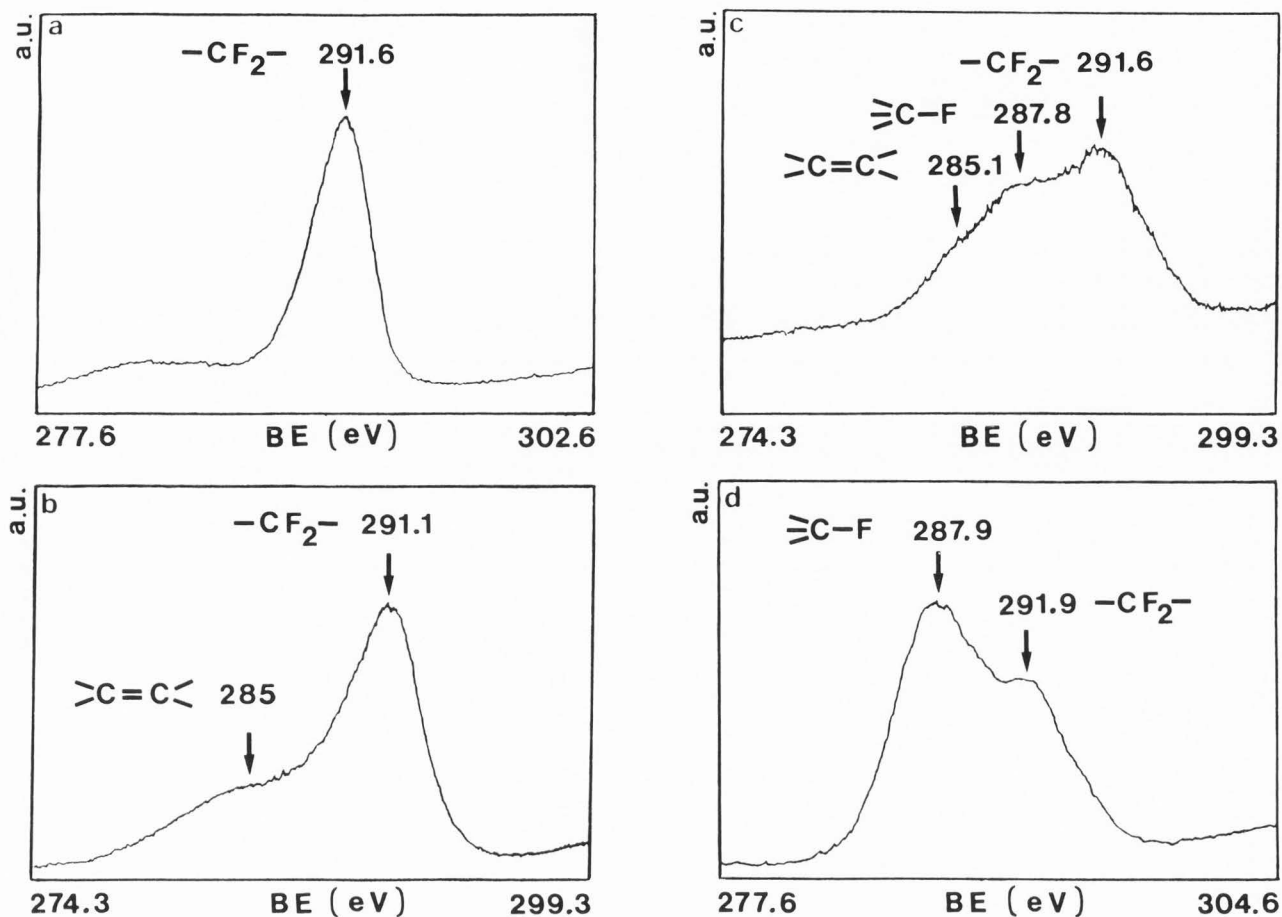


Fig. 2 - Evolution under electron bombardment of PTFE sample as a function of the irradiation dose.

- a) unirradiated PTFE
- b) under electrons (10 kV - 8.10^{13} \bar{e} cm^{-2} - 15 min)
- c) under electrons (10 kV - 2.10^{14} \bar{e} cm^{-2} - 6 h)
- d) aged two weeks in ultra high vacuum

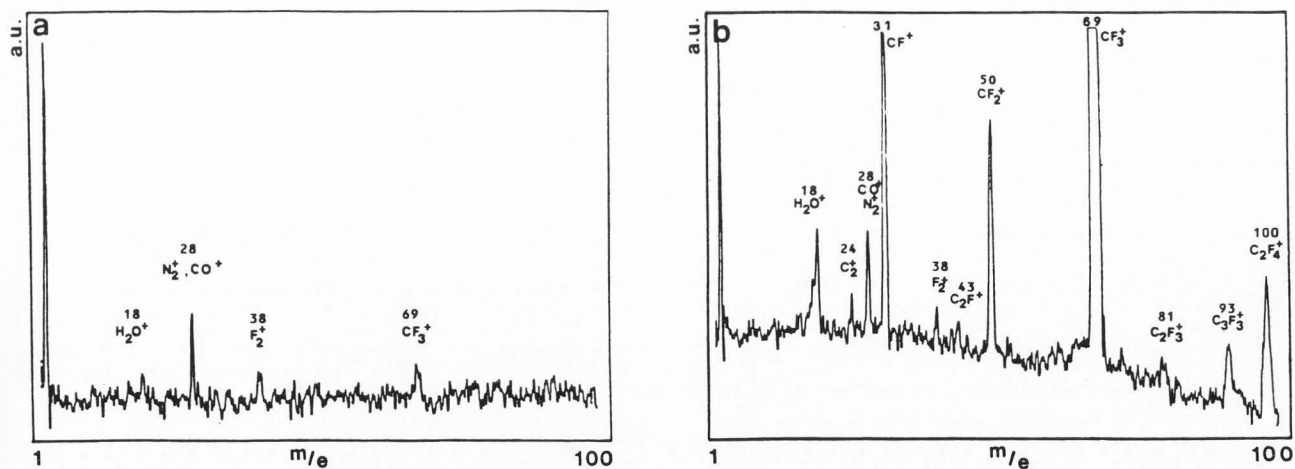


Fig. 3 - Analysis of gas desorbed from PTFE under irradiation

- a) residual gas analysis
- b) under electron bombardment

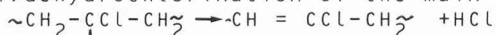
Hydrogen fluoride molecule desorption and creation of allenic compounds are confirmed by gas analysis spectra (Fig. 5). Other authors <21,10> studied the changes induced in the higher polar β -crystalline form of PVDF by irradiation with high energy ions.

The initial structural modifications are the creation of unsaturations. Then a large decreasing of the crystalline properties (alteration of the piezo and pyroelectric activities) is observed. ESR experiments have been used to detect the free radicals generated under irradiation in vacuo <39,33,31>. Powders of PVDF were irradiated with γ -rays <32> and the subsequent ESR measurements revealed the following radicals :

$\sim\text{CF}_2-\dot{\text{C}}\text{H}-\text{CF}_2$ (I); $\sim\text{CH}_2-\dot{\text{C}}\text{F}-\text{CH}_2$ (II) and two radicals initiated by the main chain scission : $\sim\text{CH}_2-\dot{\text{C}}\text{F}_2$ (III) and $\sim\text{CF}_2-\dot{\text{C}}\text{H}_2$ (IV).

The radicals (I) and (II) are responsible for the creation of unsaturations and crosslinkings. These results are confirmed by very recent unpublished results obtained on non polar PVDF thin films (25 and 50 μm) irradiated with heavy ions at GANIL. Similar results are described elsewhere for PVC. The only difference under irradiation comes from the steric effects induced by the presence of chlorine atoms and the ease of producing HCL molecules. The loss of Cl_2 is a two step mechanism :

i) dehydrochlorination of the main polymer



ii) dehydrochlorination of the polyene formed by the first dehydrochlorination



These two steps don't appear simultaneously as in PVDF polymers.

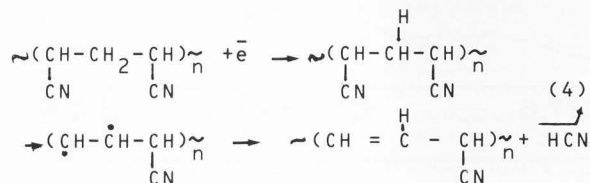


which can be considered as an alternating polymer with $\text{R}_1=\text{R}_2=\text{H}$ and $\text{R}_3=\text{R}_4=\text{CH}_3$, a fast degradation has been observed under irradiation <13,5,2>. Resulting in a steady decrease of the molecular weight until a viscous liquid of low molecular weight is reached. A gas analysis indicated that almost exclusively hydrogen and methane are desorbed from the modified polymer.

Polymers with $\text{R}_1=\text{R}_2=\text{R}_3\neq\text{R}_4$ - The general formula of these compounds is $-(\text{CRR}'-\text{CRR}')_n-$. The most common polymers which belong to this group are :

Polyvinylfluoride ($\text{R}'=\text{F}$) polyvinylchloride ($\text{R}'=\text{Cl}$), polypropylene ($\text{R}'=\text{CH}_3$), polyacrylonitrile ($\text{R}'=\text{C}\equiv\text{N}$) and polystyrene ($\text{R}'=\text{C}_6\text{H}_5$). Under energetic electron irradiation, desorption of HCL has been demonstrated <19> for polyvinylchloride.

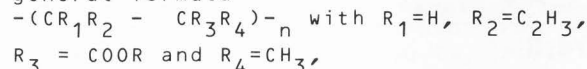
For polyacrylonitrile (PAN), it can be considered that the group $-\text{C}\equiv\text{N}$ (pseudo-halogen) has the same behavior as that of halogen atoms. The only difference is the ability to create cyclisation by opening of the $-\text{C}\equiv\text{N}$ triple bond. The modifications of PAN thin films, electrodeposited by an electro-chemical way under electronic excitation have been investigated <27,18>. These studies showed that the first step of the modifications of PAN was the outgassing of HCN molecules and the creation of unsaturation



The modifications of polystyrene under electronic excitation are still not very well understood. The first changes are very likely creation of crosslinkings with a participation of the aromatic groups in this complex process.

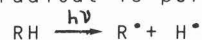
Complex polymers with $\text{R}_1\neq\text{R}_2\neq\text{R}_3\neq\text{R}_4$

- It is reasonable to think that more complex the polymer structure is, the more difficult will be the comprehension of the mechanisms leading to modifications. For example, a polymer of general formula



could evolve towards main chain scission, crosslinking, creation of unsaturations with CH_2 departive cyclization.

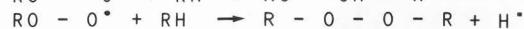
If all the experiments described above are performed under air or oxygen pressure, the first step of the modification is the creation of the radical formed as the electronic excitation takes place. Very rapidly this free radical is peroxidized



Production of free radicals



Propagation



we obtain, in the polymer bulk, a mixing of peroxy radicals $\text{R}-\text{O}-\text{O}^\bullet$, hydroperoxide $\text{R}-\text{O}-\text{O}-\text{H}$ and other compounds which evolve by different ways (oxygen desorption, dimerisation, crosslinking, etc...). It is very difficult to predict in this case which compound one will obtain after the irradiation experiments. No one polymer has the same behavior and the same evolutions when irradiated under air or oxygen.

Interaction of energetic heavy ions with polymers

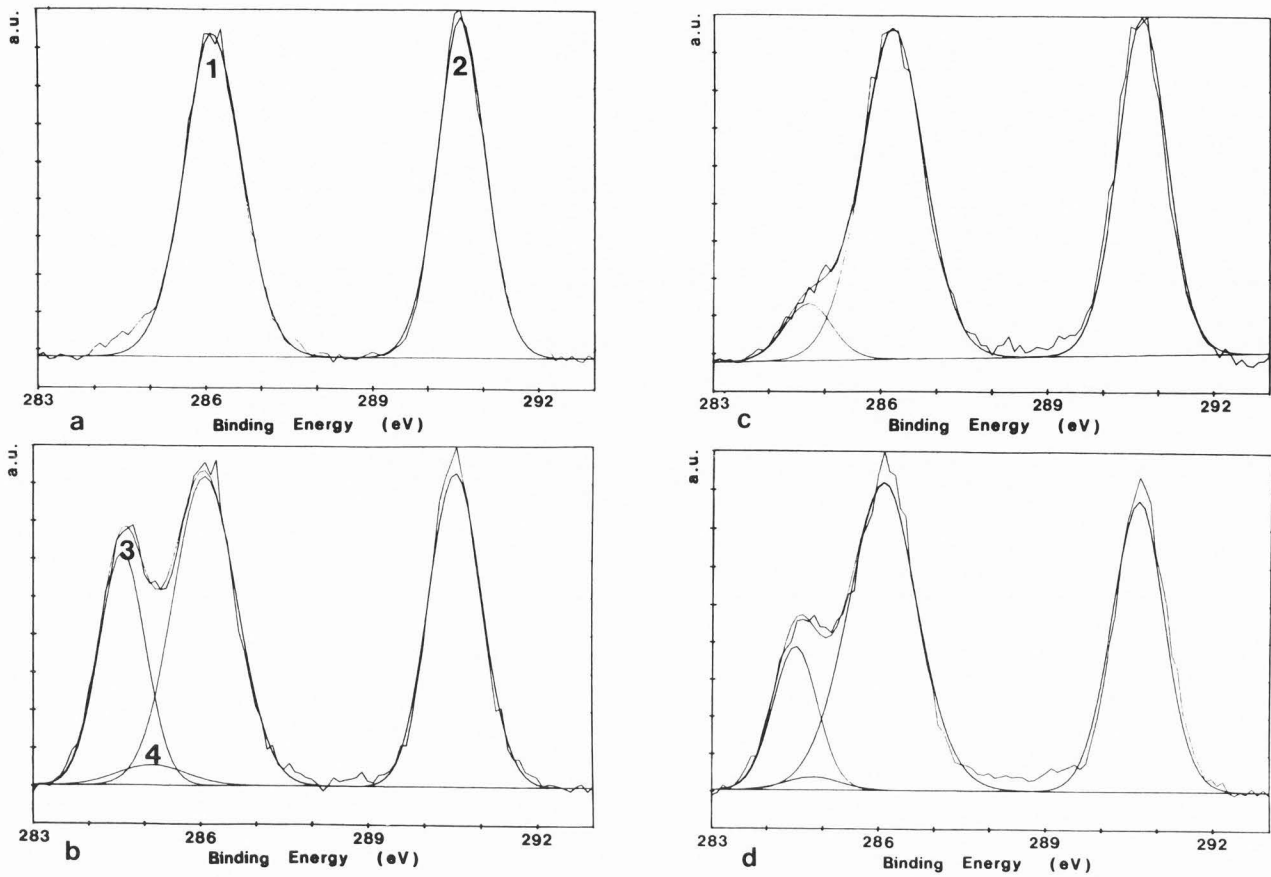


Fig. 4 - Evolution of the C_{1s} photoemission line of PVDF under different kinds of irradiation
 a) untreated sample
 b) under Kr ions ($10 \text{ MeV/amu} - 10^9 \text{ ions/cm}^{-2}$)
 c) under electrons ($10 \text{ kV} - 10^{14} \text{ e}^- \text{ cm}^{-2} - 6 \text{ h}$)
 d) under electrons ($10 \text{ kV} - 2 \cdot 10^{14} \text{ e}^- \text{ cm}^{-2} - 12 \text{ h}$)

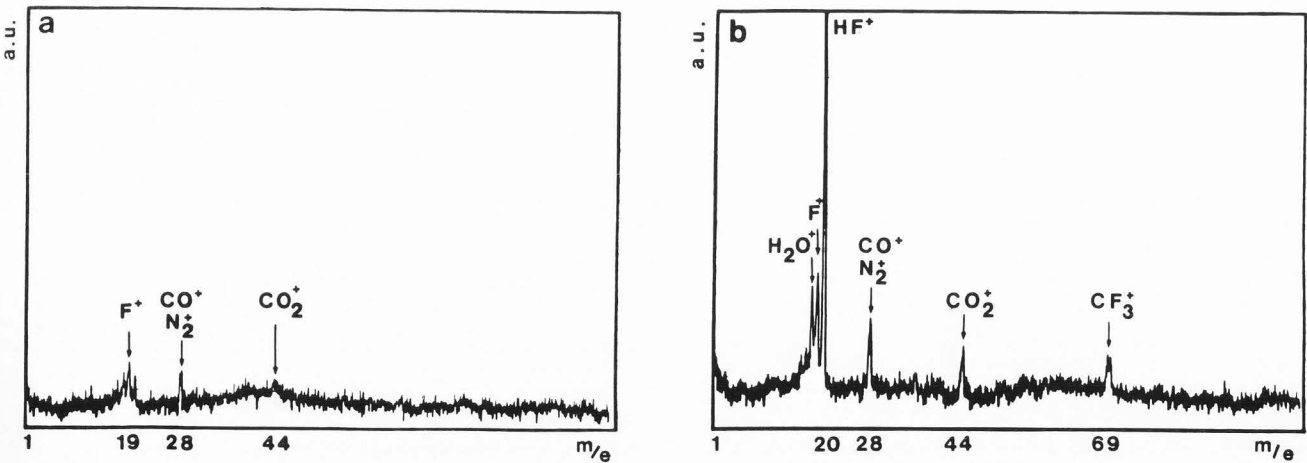


Fig. 5 - Analysis of gas desorbed from PVDF under irradiation
 a) residual gas analysis
 b) under electron bombardment

Physical properties induced by irradiation

The modifications of the physical properties of polymers have potential impact in technology : microlithography, hardening, coatings, adhesion, ion implantation change in the electrical and optical properties, grafting, etc.... These modifications appear with the main chain scission, the crosslinking, the degradation (partial or complete), the creation of unsaturations. Many authors <11,3,29,24,28,23,26,1,4,14,25,34,38,12> studied the modified polymers and established a direct correlation between the modifications and the new physical properties. It is for example quite evident that the initiation of free radicals may enhance the adherence of a polymer coated on a metallic substrate, as the crosslinking will produce a hardening of the polymer and the creation of multiple bond or cyclization, and will modify the electrical properties of another one.

Conclusions

The chemical and physical modifications of linear polymers induced by energetic heavy ions have been compared to those obtained with other electronic excitations.

The observed final chemical states are quantitatively the same as those obtained with X-rays, γ -rays, though a better control of the evolution of the structure of the polymer seems to be achieved by adjusting the experimental conditions (Z, dE/dX, dose rate ...).

For a given polymer, it is still difficult to predict which modifications will result from the heavy ion irradiation, because of the complex interaction between ions, δ -rays and polymers.

The desorption of a polar and asymmetric molecule triggers the reorganization of the modified polymer by giving multiple conjugated bonds (allenes, dienes, cycles). On the other hand, the stimulated desorption of a symmetric gase molecule (H_2 , F_2 , Cl_2 ...) will generally lead to non conjugated compounds.

Moreover, the nature of the irradiation atmosphere may change the evolution of the irradiated polymers.

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Editor's Note: All of the reviewers' concerns were appropriately addressed by text changes, hence there is no Discussion with Reviewers.

