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**TRACK STRUCTURE  
IN SOME HEAVY-ION IRRADIATED  
PLASTIC FILMS**

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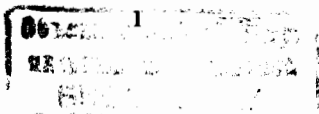
## INTRODUCTION

The application of polymeric track detectors in the analysis of ionizing particles (e.g. fission fragments, alpha particles) is mainly based on the development of the latent tracks produced by ions by means of chemical etching (Fleischer, Price & Walker, 1975). The formation of etchable tracks in polymers is associated with physical and chemical changes (Katz and Kobetich, 1968; Chambaudet, Bernas and Roncin, 1977; Monnin, 1970; Chambaudet and Roncin, 1982; Albrecht, 1983). It has been shown that there is no (or small) difference in the nature of the chemical transformations induced by radiation with high and low linear energy transfer (LET). However it seems of interest to study the effects caused by differences in the spatial distribution of energy absorbed and radiation-induced reactions in tracks.

## EXPERIMENTAL

Three kinds of commercial polymer films have been examined. They are: 1) Polyethyleneterephthalate (Iavsan and Hostaphan RE5) with the nominal thickness  $l_0$  of 10 and 5  $\mu\text{m}$ , respectively. 2) Polycarbonate (Makrofol KG),  $l_0 = 8 \mu\text{m}$ . 3) Polypropylene,  $l_0 = 10 \mu\text{m}$ .

The samples were irradiated in a vacuum with accelerated heavy ions from the cyclotron U-300 at the Laboratory of Nuclear Reactions, JINR, Dubna. The beams of  $^{132}\text{Xe}$  (121 MeV),  $^{129}\text{Xe}$  (124 MeV),  $^{84}\text{Kr}$  (74 MeV) and  $^{59}\text{Co}$  (68 MeV) were used. The ion fluence ranged from  $6 \cdot 10^5$  to  $1 \cdot 10^{11} \text{ cm}^{-2}$ . Additionally, some specimens were irradiated by single ions passing through a narrow diaphragm. The track density in the range of up to  $10^{10} \text{ cm}^{-2}$  was determined using a JSM-840 scanning electron microscope. The etching process was carried out in a conductance cell by simultaneous measurements of the electric conductivity of the foil investigated (Apel, 1982; Apel and Pretzsch, 1986). 0.1N NaOH, 1.0M  $\text{K}_2\text{CO}_3$  and 2.5M  $\text{K}_2\text{CO}_3$  solutions were used as etchants in the case of PETP and PC. The PP film was etched in a solution composed of 16N  $\text{H}_2\text{SO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  (50 g/l) at  $80^\circ\text{C}$ . Absorption spectroscopy measurements were performed in the I.R. and U.V. spectral region with a Specord M80 and Specord M40, respectively. The solubility of the irradiated films was determined gravimetrically using the appropriate solvents. Viscosity measurements were performed in a capillar viscometer.



## RESULTS

PETP. The effective pore diameter  $d_{\text{eff}}$  of the investigated specimens, as a function of time  $t$ , was calculated from the electrical conductivity. If measurements had been performed in 0.1N NaOH, before calculating  $d_{\text{eff}}$  the surface conductivity conditioned by the surface charge (Apel and Pretzsch, 1986) was subtracted from the measured conductivity. In the cases where the ratio  $V_t/V_0$  is high ( $>10^3$ ) after the break-through time the phase of the fast pore diameter enlargement begins and continues for up to about 10 nm. Further, the radial etching rate decreases to a minimum and then rises again tending with increasing diameter to a constant value  $V_0$  (Fig.1). The pore radius  $r$  depending on the etching time in the range of  $r > 7$  nm is describable approximately by the relation

$$V_r = dr/dt = V_0 \exp(-a/r).$$

The parameter  $a$  depends on the type of bombarding particle and its energy. Consequently, the decreasing etching rate in the "penumbra" of a track is caused by the effect of the passing ion and may be conditioned by the cross linking of the polymer. One can suppose that the formation of the cross links results in the increasing rigidity of polymer and, therefore, in the increasing activation energy of the chemical etching.

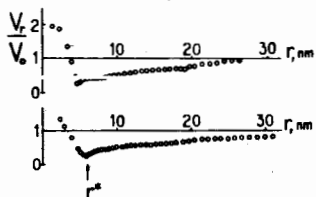


Fig.1. The  $V_r/V_0$  vs  $r$  function for the tracks of  $^{132}\text{Xe}$  with an energy of 0.5 MeV/nucleon (upper curve) and 0.9 MeV/nucleon (lower curve) in Hostaphan RE5.

The parameters  $a$  and  $r^*$  (see fig.1) tend to increase with increasing particle energy (in the range from  $\sim 1$  MeV/nucleon to 0.1 MeV/nucleon). The values of  $a$  for the tracks of xenon, krypton and cobalt are equal to 6-9, 4-7 and  $\sim 3$  nm, respectively.

I.R. spectra showed that the accumulation of the carboxyl end-groups ( $3256 \text{ cm}^{-1}$ ) takes place under heavy-ion irradiation. A general increase in the absorption background in the  $1400\text{-}700 \text{ cm}^{-1}$  region was observed. This effect is usually related to the cross linking of PETP, particularly to the formation of polyphenyl systems (Slovokhotova et al, 1962). The shift of the continuous absorption boundary in U.V. spectrum to the long wave region also indicates that irradiation produces systems of conjugated phenyl rings or double bonds. Cross linking of PETP under ion bombardment is evident from the fact that polymer irradiated with a xenon fluence of  $10^{11} \text{ cm}^{-2}$  (a dose of 1.1 MGy) only partly dissolves in a mixture of dichloroethane and phenol at  $80^\circ\text{C}$ .

PC. The change of the radial pore etching rate with increasing radius is similar to that observed in PETP. We have also found the existence in track "penumbra" of a zone where the etching rate is lower than  $V_0$  although this tendency is weaker (Apel et al, 1987). This result is in accordance with the data obtained by Mazzei et al. (1985) and partly with the results of Schnoor et al. (1982) but contradicts to the reports of Guillot and Rondelez (1981) and DeSorbo (1979). One can suppose that the competition between the chain scission and cross linking of PC macromolecules in the track penumbra can lead both to the increasing and decreasing etching rate.

The  $r^*$  values measured for the xenon and krypton tracks in PC coincide within the experimental error with those obtained in the case of PETP. The viscosity of polymer solutions rises starting from the fluence of xenon ions of  $5 \cdot 10^9 \text{ cm}^{-2}$ . The gel formation was observed at a fluence of ca.  $2 \cdot 10^{10} \text{ cm}^{-2}$  (solvent: chloroform).

PP. The etching ratio  $V_t/V_0$  for xenon tracks in PP amounted to 20-30. This value is too low to provide the possibility of studying track structure by means of the conductometric technique. In this case a monotonically increasing  $d_{\text{eff}}$  vs  $t$  curve with the smeared initial stage was registered. In the U.V. spectrum of the irradiated PP well resolved bands with maxima at 240 and 295 nm appear which correspond to the formation of dienes and trienes with conjugated double bonds. The maximum lying at 210 nm was also observed and tentatively assigned to the accumulating products of the structure  $-\text{C}=\text{C}-\text{C}=\text{O}$ . These products could be formed due to the post-radiation oxidation. After the xenon ion fluence of  $1 \cdot 10^{10} \text{ cm}^{-2}$  the PP film is partly insoluble in tetralyne at  $140^\circ\text{C}$ , the gel fraction has been found equal to 5%. Since the dose of gel formation is to be related to the size of cross linked zones in the tracks one can believe that in the case of PP the radius of "penumbra" is also large.

## CONCLUSION

We assume that around the highly destroyed track core which can undergo selective etching a halo exists where the cross linking may predominate over the chain scission. The intensive damage in the core may be due to the well-known mechanism of an ion explosion spike. The cross linking process takes place at radii of up to (30-50) nm. It is an unexpected result because the local dose at such large distances is relatively low ( $< 10 \text{ kGy}$ ), as known from the literature. The gel formation in PETP, PC and PP under ion irradiation occurs at the fluences which correspond to the dose

values of 100 kGy - 1 MGy, i.e. 10-20 times lower than the doses of  $\gamma$ -radiation required for network formation in these polymers. This indicates that the efficiency of the cross linking process in heavy-particle tracks is very high. Probably, this could be explained by the high concentration of radicals formed in the "penumbra" of tracks due to the eliminating hydrogen atoms from polymer chain. It is not clear whether the radicals are formed only under the influence of delta electrons or according to a certain special mechanism. In principle, one can admit that within the short time of the existence of ion explosion only the most mobile hydrogen ions can be displaced by electrostatic forces from the ionized molecules located not in the nearest vicinity of an ion path. In any case it seems obvious that the formation of tracks in polymers is a more complicated process than it is described by the model of delta rays proposed for plastic detectors.

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Апель П.Ю. и др.  
Структура треков в некоторых пластиковых пленках,  
облученных тяжелыми ионами

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Исследованы изменения, происходящие в полиэтилентерефталатных /ПЭТФ/, поликарбонатных /ПК/ и полипропиленовых /ПП/ тонких пленках при облучении тяжелыми ионами. Особенности травления треков исследованы в субмикроскопическом диапазоне диаметров /1-60 нм/ при помощи кондуктометрического метода. Для исследования радиационно-химических процессов в названных полимерах использованы методы абсорбционной спектроскопии в ультрафиолетовой /УФ/ и инфракрасной /ИК/ области, вискозиметрия растворов полимеров и золь-гель анализ. Обнаружено, что во всех трех полимерах одновременно происходят процессы деструкции и сшивания молекулярных цепей. В сердцевине трека диаметром в несколько нанометров преобладает деструкция полимера. Процесс образования поперечных связей локализован в окрестности сердцевины трека на расстояниях до 30-50 нм и выражен наиболее сильно в случае ПЭТФ, в котором сшивание макроцепей преобладает над деструкцией на больших расстояниях от траектории иона.

Работа выполнена в Лаборатории ядерных реакций ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1988

Apel P.Yu. et al.  
Track Structure In Some Heavy-Ion Irradiated Plastic Films

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The changes occurring in thin polyethylene terephthalate /PETP/, polycarbonate /PC/ and polypropylene (PP) films irradiated with heavy ions have been investigated. The track etching properties were studied in the submicroscopic diameter range of 1-60 nm. The method of absorption spectroscopy in ultraviolet /U.V./ and Infrared /I.R./ regions, viscosimetry of polymer solution and sol-gel analysis were used to investigate radiation chemical processes in the polymers. It has been found that in all the three polymers both the chain rupture and cross linking processes occur simultaneously. The chain ruptures predominate in the track core with a diameter of several nanometers. The cross linking process takes place in the vicinity of the track core at radii of up to 30-50 nm and appears most clearly in PETP where cross linking events prevail over the destruction at large distances from the ion path.

The investigation has been performed at the Laboratory of Nuclear Reactions, JINR.

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