

# TRACKS OF HIGH-ENERGY IONS IN POLYIMIDE: III. INVESTIGATION OF ETCHING PROCESS, TRACKS STRUCTURE AND PORES FORMS IN THE TRACK MEMBRANES OF POLYIMIDE

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**Abstract.** The results of investigations of pores formation process in polyimide films after their irradiation by argon, krypton and wolfram high energy ions with the further treatment in concentrated hydrogen peroxide are presented. The size of the destruction zone and the zone of formation of a changed polymer structure as well as chemical resistance increasing are defined. The rate of etching of polymer along tracks and etching selectivity are determinated. A method of preparing the polyimide track membranes with cylindrical or conic forms of pores is shown.

## 1. INTRODUCTION

A method of track membranes making is universal and may be applied for many polymers, including polyimides, with very good radiation resistance and thermostability [1]. Size and forms of membranes pores are being determined both by the high-energy ions track structure and by the means of their development (etching). The characteristic radius of a track depends on ion charge, energy and a little bit less on polymer composition [2]. And vice versa, a polymer composition defines the process of pores formation and development from latent tracks, the choice of etchants and treatment conditions. Only for polyethyleneterephthalate (PETP) the etching mechanism has been studied well enough by now [3-5]. The processes of polypropylene and polycarbonate etching [6,7] were also investigated.

Some compositions of polyimide (PI) etching solutions are suggested in [1,2,8,9]. The solutions contain strong oxidizers such as  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ . Pores formation mechanism for this polymer was not studied yet. So, in works

[8,9] there is only information about the form of pores, obtained by Cu and S ions track development in PI film. It has been established by the authors of [11] that the concentrated solution of hydrogen peroxide (30% solution of  $\text{H}_2\text{O}_2$ ) is the perspective reagent for track etching in PI.

The object of present work, is to investigate the processes of PI etching in this reagent, and tracks structures as well as pores forms and sizes.

## 2. EXPERIMENTAL PROCEDURE

As a research object we used PI films with thickness of 10 and 20  $\mu\text{m}$  as initial ones (with the residual solution content (RSC) of 1.1%) and PI films after thermotreatment (temperature 320°C, 2hours, RSC 0.6%) [10].

The PI film was exposed to radiation by ions of argon (1 MeV/nucleon), krypton (2.6 MeV/nucleon), and wolfram (0.3 MeV/nucleon) [10].

The membranes pores structure investigation was conducted on the scanning electron microscope (SEM) BS-340, TESLA. Conducting layers on the membranes surface (20-40 nm in

thickness) were formed by Au or Cu evaporating in vacuum. To investigate the pores structure the polymer was broken at the temperature of liquid nitrogen. The density of track membranes pores was between  $10^7$ – $10^8$   $\text{cm}^{-2}$ . The pores diameters were determined by a hydrodynamics procedure. The etching rate along track  $V_t$  was determined from the time it took for a through pore formation, the radial rate - from the curve of etching time dependence of pores radius  $r(t)$ . The etching rate of non-irradiated polymer was measured by a weight method and by a thickness change defined by means of SEM.

IR-spectroscopic investigations were carried out on a spectrophotometer Specord M80, in the range of wave number range between 1800 and 700  $\text{cm}^{-1}$ . The surface density of high-energy ions<sub>2</sub> irradiation (fluence) was  $10^8$ – $10^{11}$   $\text{cm}^{-2}$ .

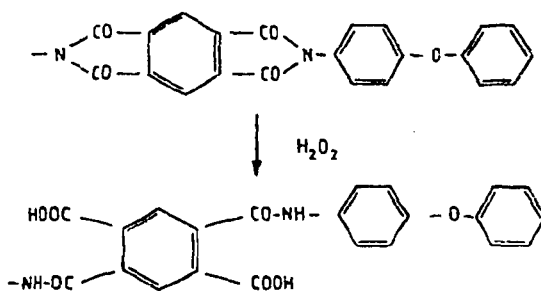
### 3. RESULTS AND DISCUSSION

Previously [10] it was established that as a result of PI exposure to high energy ion radiation the imide rings destruction with amide groups formation takes place. This was well-seen on IR-spectrum, where the optical density of absorption bands  $D_{1776}$  and  $D_{726}$  decreased ( $1776 \text{ cm}^{-1}$  and  $725 \text{ cm}^{-1}$  are the bands of deformable and valence oscillations of  $\text{C}=\text{O}$  groups of imide rings) and new absorption bands have appeared. Those bands were typical for amides  $1680 \text{ cm}^{-1}$  (Amide-1) and  $1550 \text{ cm}^{-1}$  (Amide-2) and intermolecular bond  $160 \text{ cm}^{-1}$  [10,12,13].

On PI film treated by hydrogen peroxide the intensity of these bands were the same. This reagent action on the irradiated PI films causes appearing of  $1680 \text{ cm}^{-1}$  and  $1550 \text{ cm}^{-1}$  absorption bands, appearing and decreasing of the magnitude of the  $D_{1776}$  and  $D_{726}$  bands.

The process of imide rings destruction by hydrogen peroxide is most likely to be proceeded by a alkali hydrolysis mechanism.

Such a process can be described schematically like:

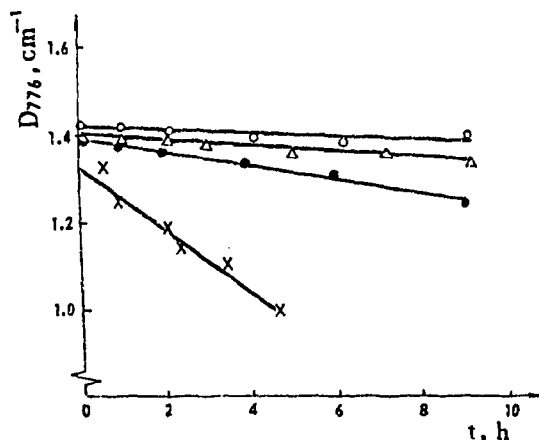


The imide rings are destroyed when act upon by hydrogen peroxide. The forming amidoacid is being removed from the polymer.

Fig.1 shows the  $D_{1776}$  change related to time of etching of PI in  $\text{H}_2\text{O}_2$  for different conditions of irradiation. These dependencies, as well as those of  $D_{726}(t)$ , which behave in the same manner, are correlated with the total area of membranes surface and, therefore, they are defined by the polymer decrease in quantity as it dissolves.

The most intensive decrease of  $D_{1660}(r)$  is characteristic of the  $D_{1660}$  relation to radii of etched pores  $r$  (Fig.2) at pores radii below 5-15 nm [10]. Further the value of optical density of this band changes much slowly. Thus the intermolecular bonds are formed in cylinder around track spaces of 5-15 nm

Fig. 1. The relation of optical density of the absorption band  $1776 \text{ cm}^{-1}$  to time of polyimide film etching (thickness of 10  $\mu\text{m}$ , RSC 0.6%): 1 — initial film; 2 — irradiation by Ar-ions, density-10 ions/ $\text{cm}^2$ ; 3 — irradiation by Kr-ions, density-10 ions/ $\text{cm}^2$ ; 4 — irradiation by Ar-ions, density-10 ions/ $\text{cm}^2$



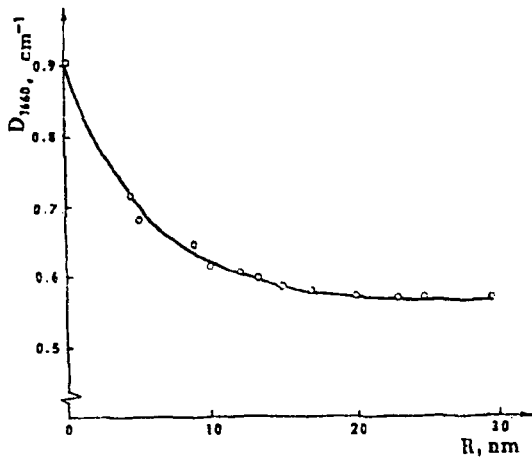


Fig. 2. The relation of optical density value of band 1660  $\text{cm}^{-1}$  which characterizes the number of intermolecular linkages, to radius of etched pores

radius. This is directly confirmed by the kinetics of change of pores radii which were formed as the PI film of  $20 \mu\text{m}$  in thickness, irradiated with surface density of  $10^9 \text{cm}^{-2}$  by Kr-ions, was being etched. The four characteristic stages of etching process are well seen.

At the first one (duration of such conditions approximately 10 min) there is a quick pores etching up to the radius of 5 nm, the polymer etching rate along track constitutes  $V_T$  - 1000 nm/min, the radial etching rate is  $V_r$  - 0.5 nm/min and corresponds to etching rate of non-irradiated PI polymer after the thermotreatment  $V_b$  - 0.5 nm/min [11]. So, the etching selectivity in this state is  $V = V_T/V_r = 2000$ .

At the second state (10-60 min) there is an essential slowing-down of etching process. We suppose this is connected with the polymer resistance increase due to formation of a zone with density abnormally high or due to another possible process of pores diameter decrease as a result of polymer swelling. The swelling influence was valued by a correlation between the results of investigations of kinetics of etching for two different polymer modes of treatment. In one case the polymer film was transferred from one solution into another without drying, that is to say, if the PI polymer swelled, pores diameters would be underestimated. In another case the pores diameters were determined

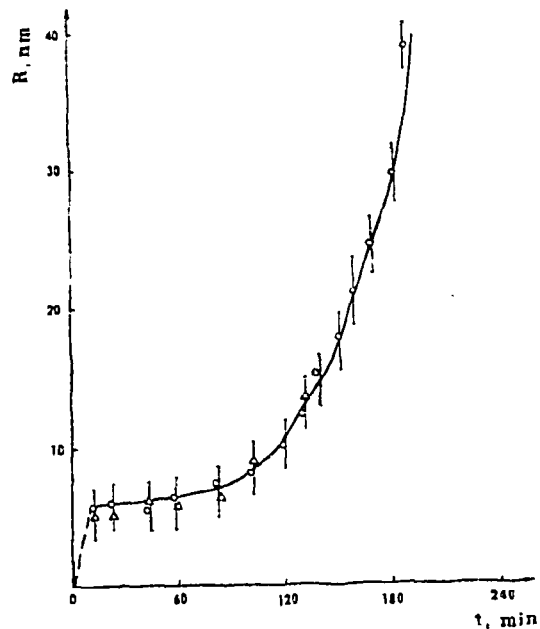


Fig. 3. Kinetics of PI film (thickness of  $20 \mu\text{m}$ , non-thermotreated, irradiated by Kr-ions with energy of 2.6 MeV/nucleon, and surface density of  $10^9 \text{cm}^{-2}$ ) etching in hydrogen peroxide at  $90^\circ\text{C}$ .  $\Delta$  -- the film was transferred from the etching solution into a cell for pores radii determination by means of a hydrodynamic method without drying;  $\circ$  -- after every step of etching polymer was dried

after polymer drying. Considering that the pores diameters practically do not depend on the treatment mode, we can say that the influence of polymer swelling was small. This was also confirmed by the absence of the absorption bands of water in PI films which were etched and then dried on air. By this means, a cylindrical zone around a track of a high-energy ion with PI resistance increased is formed, that may be connected to the intermolecular linkages formation [12,13]. The biggest chemical resistance corresponds to the radius of 5 nm.

At the third stage (pores diameters - between 5 and 35 nm, time of etching - 60-200 min) the intermolecular linkage concentration decreases, the radial etching rate increases.

At the fourth stage (pores diameters - above 35 nm, time of etching above 200 min) the radial etching rate is constant and is equal to the one of non-irradiated, non-thermotreated PI film  $V_r = V_b = 1 \text{ nm/min}$  [11]. This means that the high-energy ion influence on polymer is

Table 1. Form of PI track membranes pores (etching in hydrogen peroxid at temperature 90°C)

No.	Thickness $\mu\text{m}$ ; RSC, %	Ion	Etching time, on both sides hour	Diameters of pores of films, $\mu\text{m}$
1.	10	Ar	5	0.10/0.15
	1.1		10	0.29/0.41
	10	Ar	5	0.10/0.20
	0.6		10	0.20/0.57
2.	10	Kr	5	0.15/0.30
	1.1		10	0.46/0.53
3.	20	Kr	5	0.35/0.40
	1.1		10	0.65/0.65
4.	20	Kr	10	0.38/0.45
	0.6			

limited by the radius of 35 nm.

From the proceeding, the pores forming in PI track membranes can be presented in the following way; polymer completely destroys under irradiation in the space of high-energy ion track (radius below 5 nm) with the formation of low-molecular products which are easily being removed from the track zone. Around the zone there is formed a space up to 15 nm in diameter where polymer structure is changed and where chemical resistance is increased. Further the fraction of polymer with the changed structure is reducing, and beyond 35 nm the material does not differ from non-irradiated polymer.

A formation of space of increased resistance makes it possible to obtain track membranes for ultrafiltration (with pores diameters approximately 10 nm).

It is well known that the track etching rate is connected with the energy losses of ions,  $dE/dx$ . These losses are a non-monotonous function of ion energy  $E$ . Passing through the polymer, the high energy ions loss their energy and slow down. As this takes place, the values of  $dE/dx$  first increase, go across the maximum, then, as the effective charge of

a ion diminishes, decreases. In such a manner the polymer etching rate changes along track what is reflected by the departure of pores shapes from cylindric form. Figure 4 shows the relationship of Ar, Kr and W ions energy losses  $dE/dx$  to ions range  $x$  in polymer (with density of  $\rho$  - 1.4 g/cm<sup>3</sup>), which were calculated on the base of work [14] data for initial energy of ions, used in this study.

The W ions range in polymer is approximately 9  $\mu\text{m}$ ,  $dE/dx$  is a monotonously diminishing function. The Kr ions range is 30  $\mu\text{m}$ . If the irradiated film thickness is 10  $\mu\text{m}$ ,  $dE/dx$  is a monotonously increasing function; if the thickness is 20  $\mu\text{m}$  - the inlet energy losses correspond the outlet one. The Ar ions range reaches 12  $\mu\text{m}$ , the  $dE/dx$  is asymmetric about the film surface. Thus in such conditions the films with thickness of 10  $\mu\text{m}$  are expected to have pores of conic form, with 20  $\mu\text{m}$  thickness and if irradiated by Kr ions - to have pores of surface close to cylindric form.

Table 1 lists values of pores diameters measured on different sides of PI film for different conditions of irradiation and treatment. Figure 5 shows a microphotograph of membranes breaks

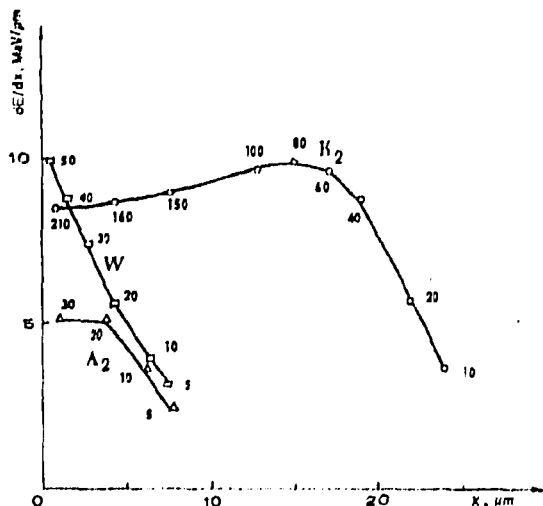


Fig. 4. The relation of energy losses  $dE/dx$  for the Ar, Kr, W ions to range in polymer (density  $\rho = 1.4 \text{ g/cm}^3$ ). The initial ions energy: 40 MeV (Ar), 220 MeV (Kr) and 55 MeV (W). Number on curves are the ions energy values (in MeV) in the corresponding points

with pores of cylindric form (diameter -  $1.2 \mu\text{m}$ ).

For  $10 \mu\text{m}$  thick films, the formed pores are of characteristic conic form. As they are etched, pores diameters on different sides of the film equate, so the cylindric form is characteristic for big pores. The pores form practically does not differ from cylindric if PI film with thickness of  $20 \mu\text{m}$  is irradiated by Kr ions.

#### 4. CONCLUSIONS

Thus, the following picture of pores formed and etched in PI can be imagined. As a result of high-energy ions passing the polymer through they form some latent tracks, which are characterized by inside rings destruction in the central part with radius up to 5 nm and by forming of polymer with changed structure for the remote zone with radius up to 35 nm. The rate of etching of the central part by hydrogen peroxide (concentration 30 %, temperature  $90^\circ\text{C}$ ) is high enough and along the track reaches  $V_t = 1000 \text{ nm/min}$ ; the etching selectivity is  $V = V_t/V_r = 2000$ . The density of polymer peaks at a radius of 5-15 nm causes high chemical resistance of polymer in this zone. This



Fig. 5. A microphotograph of a break of track membrano obtained by PI film irradiation (thickness  $10 \mu\text{m}$ , non-thermotreated, HSC 1.1 %) by Ar-ions with energy of 1 MeV/nucleon and surface density of  $5 \cdot 10^7 \text{ cm}^{-2}$ , treated in hydrogen peroxide at  $90^\circ\text{C}$  during 15 h

makes possible to obtain track membranes with pores diameters of about 10 nm for ultrafiltration. Due to high selectivity of etching in  $\text{H}_2\text{O}_2$  the track structure appears also when they form pores of big diameter. Therefore, changing the energy losses of ions, thickness, PI specification, and conditions of treatment in hydrogen peroxide, one can obtain TM with pores of desired forms (cylindrical or conic).

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