Etching of tracks of accelerated heavy ions in poly(ethylene terephthalate) and some physicochemical properties of track membranes

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The features of etching of latent tracks of heavy ions in poly(ethylene terephthalate) up to pore formation were investigated. It was found that the etching process includes the following stages: (1) electrolyte penetration into the pores due to capillary forces and removal of monomeric radiolysis products; (2) swelling of the cross-linked (due to secondary electrons) polymer areas around the tracks to give the gel layer; (3) removal of the gel layer and the formation of track membranes with a pore radius of 40—50 Å. The radiation-chemical processes in polymers influence the physicochemical properties of the obtained membranes. The microrelief of the membrane surface was studied by atomic-force microscopy.

Key words: membrane, heavy ions, tracks, lavsan.

Previously,[1,2] etching of latent tracks of heavy ions and the formation of pores have been studied by conductometry. In later studies,[3] it has been found that hydrolysis of poly(ethylene terephthalate) (PETP) macromolecules is accompanied by the formation of an electrically conductive[3] polymer gel. For this reason, the characteristics of etching of latent tracks, found by conductometry (especially those for initial stages of etching), can be inaccurate.

A layer-by-layer etching study showed[4] that the most pronounced changes in the polymer are observed in the area around the track axis with a radius of up to 150 Å, and the total area of changed polymer has a radius of ~500 Å.

Therefore, it would be of particular interest to study the regularities of etching of latent tracks up to pore formation by alternative methods.

In this work, we studied characteristic features of etching of the latent tracks of heavy ions and the properties of the resulting track membranes (TM) by layer-by-layer etching and atomic force microscopy.

Experimental

Studies were carried out using a 10-μm thick biaxially oriented PETP film irradiated by Xe ions with an energy of 1 MeV amu^{-1} and a density of $2 \cdot 10^9$ ion cm^{-2}. UV sensitization was performed using an LE-30 mercury lamp with the emission maximum at 310—340 nm. The time of UV sensitization was 1 *h*.

Samples were etched in an aqueous solution of KOH (0.25 mol L^{-1}) at 75 °C. The etching rate was determined based on both the weight loss of the sample and the optical density of the solution in the UV region (240 nm). To elucidate the characteristic features of track etching, the size of samples was increased until reproducible kinetic curves that compared to those for reference samples with the same area (0.15—0.20 m^2) were obtained. The contents of terephthalic acid (TPA) and ethylene glycol (EG) in the solution were calculated using the extinction coefficient found preliminarily, which is equal to $1.06 \cdot 10^4$ L mol^{-1} cm^{-1}. The change in the sample weight during etching was determined with an accuracy of 0.1 mg. The loss of material and accumulation of TPA and EG in the solution due to the etching of tracks were determined as the difference of the corresponding values for an irradiated material and a reference sample with the same area. The membrane permeability was determined under a pressure of 10 MPa using a reverse osmosis setup. The hydrodynamic radius (R_h) was calculated according to Hagen—Puaseul.

The surface microrelief and the size of tracks were studied by AFM. Three-dimensional images of the sample surface were obtained in air at room temperature using a Solver P4-SPM-MDT scanning probe microscope (NT-MDT, Moscow) with a maximum scanning area of 3×3 μm. Standard Si_3N_4 cantilevers (Park Scientific Instruments) with a length of 85 μm and an elasticity constant of 0.03—0.08 N m^{-1} were used. The probe was a 3-μm high tetrahedral pyramid with a tip curvature radius of 500 Å. The surface was studied by the conventional contact method of scanning of the cantilever in the constant-force and side-force modes.

Results and Discussion

The curves for the time variation of the optical density of the solution (D/D_{total}) used for etching (the area of samples was 0.07—0.15 m^2) (Fig. 1) indicate that during the first 15—20 min, the presence of tracks in the samples does not influence the rate of hydrolysis. After 60 min, the rate of hydrolysis of the polymer subjected

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to UV sensitization markedly increases in the region of tracks. We determined the average rates of etching of PETP irradiated by Xe ions (v) and PETP sensitized by UV radiation (v')

R/Å	50—120	120—400
v/kg m^{-2} min	1.1	5.0
$v' \cdot 10^5$/kg m^{-2} min	1.9	5.3

These data demonstrate that when the track radii are 50—120 Å, UV irradiation increases the average rate of etching ~2-fold, whereas for radii of 120—380 Å, the rate increases insignificantly. When the track size is >400 Å, the etching rate does not change.

Figure 2 shows curves for the variation of the weight of the polymer film irradiated by Xe ions and for the accumulation of the hydrolysis products (TPA and EG) due to tracks as functions of time. The difference between the weight loss and accumulation of TPA+EG (these values are equivalent for a nonirradiated film) in an early period of etching (15—20 min) is due to the transfer of monomeric products of radiolysis from the irradiated film into the solution. In the case of UV-irradiated samples, this difference is slightly greater, and the amount of TPA and EG remains the same. It also follows from Fig. 2 that for 40—50 min, no changes in the sample weight caused by the track etching are observed. This is due to the fact that the amount of water absorbed during swelling and not removed during the vacuum drying of samples increases as the weight of the samples decreases due to etching, *i.e.*, a gel-like layer is formed. It is only after 40—50 min that the etching rate starts to prevail over the swelling rate. It was found that UV sensitization does not lead to substantial changes in the obtained correlations for the first 60 min of etching; after that, the rate of etching of sensitized samples increases.

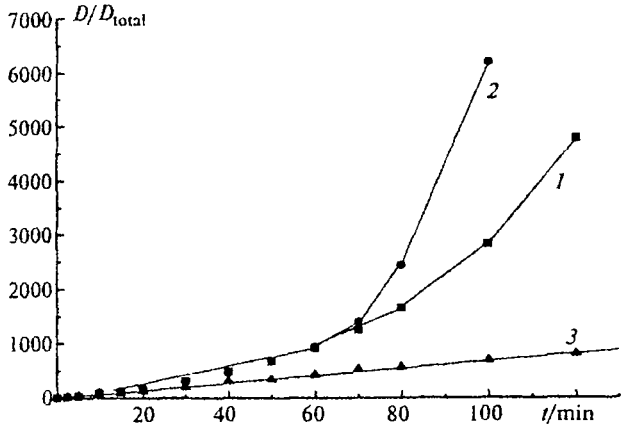

Fig. 1. Kinetics of the variation of the optical density of an etching solution: (*1*) PETP irradiated by Xe ions with a density of 10^9 cm^{-2}; (*2*) the same sample sensitized by UV radiation; (*3*) etching of a nonirradiated PETP.

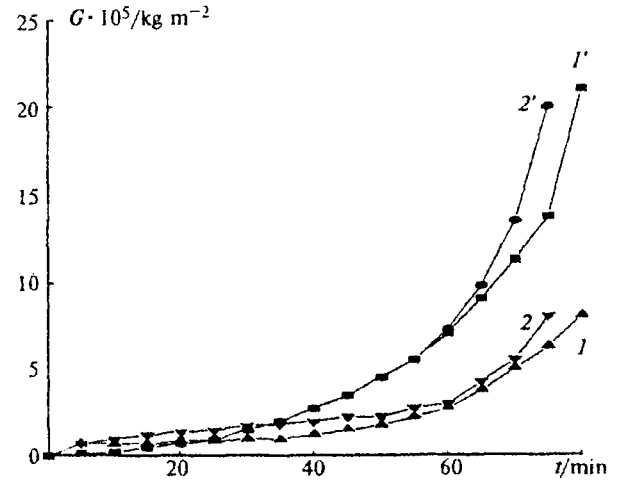

Fig. 2. Kinetics of the weight variation (*1*, *2*) and accumulation of the products of hydrolysis (*1'*, *2'*) of PETP samples due to etching of tracks: (*1*, *1'*) irradiated by Xe ions with a density of 10^9 cm^{-2}; (*2*, *2'*) the same sample sensitized by UV radiation.

The dependence of D/D_{tot} on R_h is shown in Fig. 3. The R_h value is known to depend on the shape of the pores, microrelief of the surface, and the polymer structure. It follows from Fig. 3 that the most intense accumulation of the hydrolysis products in the solution occurs at $R_h \cong 50—120$ Å (curve *1*). This distance is comparable with the range of the δ-electron path.[5] It is in this region that the most pronounced changes in the polymer structure occur and the effect of UV radiation on this structure is manifested.[4] After UV irradiation of PETP, accumulation of TPA and EG occurs less intensey at $R_h \cong 50—120$ Å (curve *2*). This result can be explained by assuming that on exposure to UV radiation, the cross-linked structure of the polymer around the tracks is partially destroyed. Upon contact with the etching agent, a gel-like layer with a less developed specific surface is formed. When R_h = 50—120 Å, cylindrical

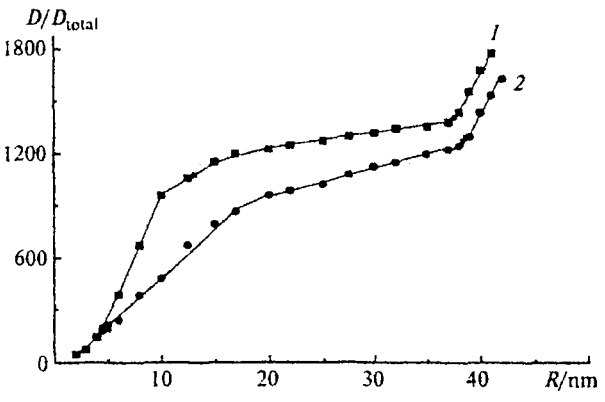

Fig. 3. Optical density of an etching solution *vs* the radius of the etched tracks: (*1*) PETP irradiated by Xe ions with a density of 10^9 cm^{-2}; (*2*) the same sample sensitized by UV radiation.

pores are apparently formed. This is indicated by a sharp change in the curve shape, which is difficult to explain by a change in the polymer structure or the surface microrelief. The data of Table 1 also confirm the fact that the etching of pores with $R_h \cong 100$ to 400 Å does not depend on the mass of the ion, and, hence, it depends on the polymer structure and the surface microrelief. An increase in the rate of TM etching at $R_h \geq 400$ Å (see Fig. 3, curves *1* and *2*) is due to etching of cylindrical pores.

Table 1. Average rates of etching of PETP irradiated by ions with different masses

Irradiation of PETP	Etching rate /nm h^{-1} at R/Å		
/cm^{-2}	~30—120	~120—400	~400—600
Xe (10^9)	5.5—6.0	24	—
Xe (10^8)	6.0	24	28
Kr (10^8)	3.0	25	28
The reference PETP sample	29	29	29

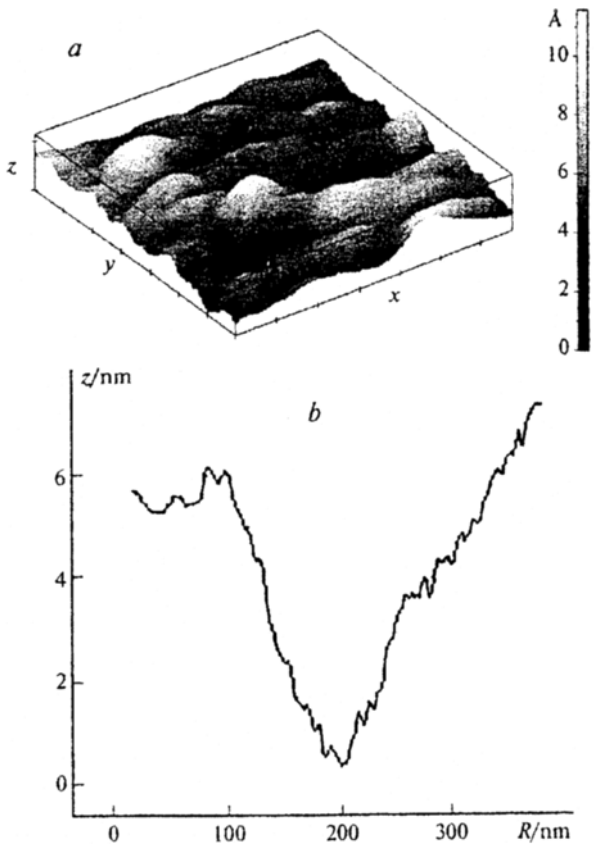

Fig. 4. (*a*) AFM image of the surface of PETP irradiated by Xe ions and etched in a solution of KOH (0.25 mol L^{-1}, 75 °C) for 40 min; (*b*) profile of the pore surface. The scale factor along the *x*,*y*,*z* axes was 100 Å.

Study of the filterability showed that after 10—15 min of etching, the film becomes permeable ($R_h \cong 30$ Å). As shown by AFM study, these samples contain cavities with a density of ~10^8 pore cm^{-2}. The initial density of irradiation is 10^9; therefore, the majority of tracks are opened over this period. On further etching, the film becomes impermeable, *i.e.*, for this period, the pores are closed and cannot be detected on the AFM images of the surface. After 40 min, the samples again become permeable. Pores with $R_h \cong 40$ Å can be clearly seen on the photographs of these samples (Fig. 4, *a*). Study of the surface in the topography mode demonstrates that the film possesses an extensive microrelief, the range of heights ΔZ is ~270 Å ($\Delta Z = Z_{max} - Z_{min}$), and the pores can be seen against the background of relief cavities (see Fig. 4, *a*). Examination of a pore profile showed that near the surface it is shaped like a cone (see Fig. 4, *b*). Since an image obtained in AFM is in essence a convolution of the surface microrelief and the probe,[6] quantitative estimates of nano-sized surface details and, as applied to TM, of the true pore shape and depth can be made only after reconstruction of the surface, *i.e.*, after the deconvolution problem has been solved.

The process of pore formation in sensitized PETP films displays a somewhat different pattern. In this case, samples become transparent after 15—20 min. On further etching, the pore size slowly increases to $R_h \cong 50$ Å.

The performed studies allow one to represent the following picture of etching of heavy ion tracks and the formation of TM. During 10—15 min of etching of a film, the electrolyte penetrates into a porous structure of tracks due to capillary forces and the monomeric products of radiolysis are removed to give through pores with $R_h \approx 30$ Å. This is followed by hydrolysis of linear macromolecules, whereas macromolecules cross-linked to form a three-dimensional structure remain unchanged. As a result, a gel-like layer starts to appear on the inner surface of pores; as etching goes on, the gel fills the pores. For some period, the pores become impermeable to water but remain permeable to ions. As hydrolysis accelerates, the gel-like layer separates from the walls and leaves the pores. This gel, obtained after etching of polycarbonate and irradiated by Kr ions, had already been isolated and its properties had been studied.[3] The gel consisted of a cross-linked polymer saturated with monomeric products with hydroxy, carbonyl, and carboxy groups. In the present work, it proved impossible to isolate the hydrogel in a pure state, because the PETP contained up to 0.1% of a filler, which passed into a total precipitate on etching. Study of its IR spectra showed that it contained a large amount of bound water and several oxygen-containing functional groups.

The removal of the gel gives TM with the minimum possible pore size ($R_h \cong 40$ Å). Only after that, does the further radial etching of pores start, due to the simultaneous formation and removal of a gel-like layer. After the surface moves away from the track axis, the density

of cross-links and, hence, the density of the gel-like layer decrease. Therefore, the rate of pore etching should increase, which is really observed in the experiment. When $R_h \cong 120$ to 150 Å, a pore can be represented as two symmetrical cones sharing the vertex[7]; during etching to $R_h \cong 400$ Å, a cylinder is formed.

After etching, the surface of pores becomes coated by a hydrogel layer, whose density decreases as the distance from the track axis increases. After the gel has been dried, a polymer layer with an enhanced porosity is formed around the pores of these membranes. Therefore, the specific surface area of these membranes should decrease as the radius increases to 400—500 Å and then should remain constant. Adsorption studies[8] confirm these conclusions.

The acceleration of the etching of tracks upon other types of treatment of an irradiated film (chemical sensitization, an increase in the ionic strength of the etching agent, *etc.*) is also due most likely to the change in the structure of the gel-like layer.

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