# Study of pore formation during etching of latent tracks of accelerated heavy ions in poly(ethylene terephthalate) by atomic force microscopy

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The process of transformation of latent tacks of accelerated heavy ions of poly(ethylene terephthalate) into pores and the formation of a porous structure of track membranes was studied by atomic force microscopy. It was shown that on initial etching, 10-nm high knolls with an average diameter of 800—1000 Å are formed in place of tracks. Based on the knolls, through channels are formed, which emerge on the surface as conical cavities. It was shown that further etching gives first cylindrical channels of diameter 800—1000 Å, which then undergo radial etching.

**Key words:** membrane, heavy ions, tracks, etching.

Characteristic features of the etching of latent tracks,[1] resulting in the formation of through pores in track membranes (TM), have been studied using small-angle X-ray and neutron scattering,[2,3] conductometry,[4] and scanning electron microscopy.[3,5,6] The appearance of atomic force microscopy (AFM) permitted the surface of polymeric materials to be studied with high resolution both in the vertical and horizontal directions. Atomic force microscopy has been successfully used to obtain information on the size of tracks in mica[7] and on the pore shape and size in polycarbonate TM.[5,6]

Previously, based on the data on layer-by-layer etching of poly(ethylene terephthalate) (PETP) and AFM, we have shown that the development of latent tracks passes through several steps[1]: through etching with the removal of the radiolysis products, swelling of the polymer cross-linked around the tracks, segregation of microgel from tracks into the solution, and the formation of pores. The present work is a continuation of our study of the formation of pores from latent tracks by their etching. Various modes of AFM (contact, side-force, and resonance modulation modes) were used to study the surface of irradiated PETP at different times of its contact with the etching agent.

## Experimental

Studies were carried out using a 10-μm thick biaxially oriented PETP film irradiated with Xe ions with an energy of 1 MeV/amu and a density of $2 \cdot 10^9$ ion $cm^{-2}$. Etching was carried out in a solution of KOH (0.25 mol $L^{-1}$) at 75 °C. The membrane permeability was determined under a pressure of 10 MPa using a reverse osmosis setup. The pore diameters ($D_p$) of TM were calculated according to Hagen—Puaseul.

3D surface images of the samples under study were obtained in air at room temperature using a Solver P4-SPM-MDT scanning probe microscope (NT-MDT, Moscow). The images in the contact and side-force modes were obtained using $Si_3N_4$ cantilevers (Park Scientific Instruments) with a length of 85 μm, a resonance frequency of 120 kHz, and a tip curvature radius of 500 Å; for the modulation resonance mode, Si cantilevers (Nanotechnology-MDT) with a length of 90 μm, a resonance frequency of 310—410 kHz, and a tip curvature radius of 100 Å were used. In the case of the $Si_3N_4$ cantilever, the probe is a 3-μm high tetrahedral pyramid with a tip curvature radius of 500 Å, while in the case of Si, this is a 7-μm high cone with an angle of less than 20° and a tip curvature radius of less than 10 nm. To obtain precise metric data in the *xy*-image plane of the surfaces being studied, the instrument was calibrated against atomic patterns of the HOPG (highly oriented pyrographite) surface (the accuracy of measurements along the *x* and *y* axes is 1%); for those along the *z* axis, the instrument was calibrated against test samples (the accuracy of measurements through the tower is 10%). The size of etched tracks (*D*) was determined from the surface profiles. In addition, parameters of the surface roughness of the sample, namely, the range of heights ($S_y$/Å) and roughness as a two-dimensional root-mean-square value ($S_q$/Å), were estimated.

## Results and Discussion

The image of the surface (the resonance modulation mode) of a non-irradiated PETP film that has been etched for 15 min (Fig. 1) and the roughness parameters (Table 1) indicate that the surface is relatively uniform. After the amorphous component of the polymer has been etched, the film surface has a clear-cut globular structure (100—200-Å large crystallites can be seen).

The exposure of PETP to accelerated heavy ions changes the character of the surface, which becomes

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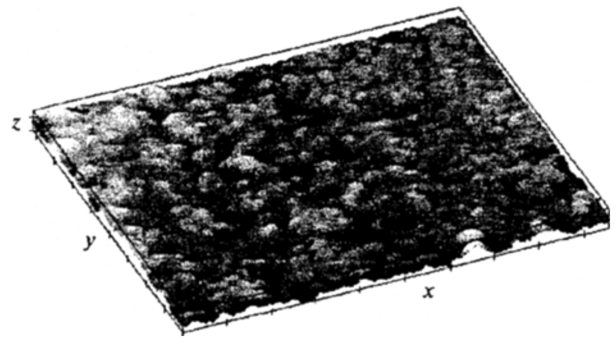


**Fig. 1.** Topographic image of the surface of a PETP film etched for 15 min (the scale factors on the *x* and *y* axes are 500 Å, that on the *z* axis is 100 Å, resonance mode).

irregular (Fig. 2, *a*). The concentration of surface imperfections corresponds to an average density of irradiation of the polymer by heavy ions ($2 \cdot 10^9$ tracks $cm^{-2}$).

**Table 1.** Surface roughness parameters of track membranes

| Etching time /min | UV radiation | $S_y$ | $S_q$ |
|---|---|---|---|
| | | Å | |
| Initial sample | No | 152.3 | 18.9 |
| 15 | No | 338.6 | 28.4 |
| 15 | Yes | 587.9 | 48.2 |
| 80 | No | 459.7 | 37.1 |
| 80 | Yes | 756.3 | 102.8 |
| 120 | No | 1087.2 | 107.1 |

*Note.* The size of the scan area is 3.1×3.1 μm. $S_y$ is the height range, $S_q$ is the root-mean-square roughness.

The surface image obtained in the side-force mode gives a view on the character of these imperfections. When the cantilevers are scanned over the surface in the direction +*x* (see Fig. 2, *b*), they look like hollows,

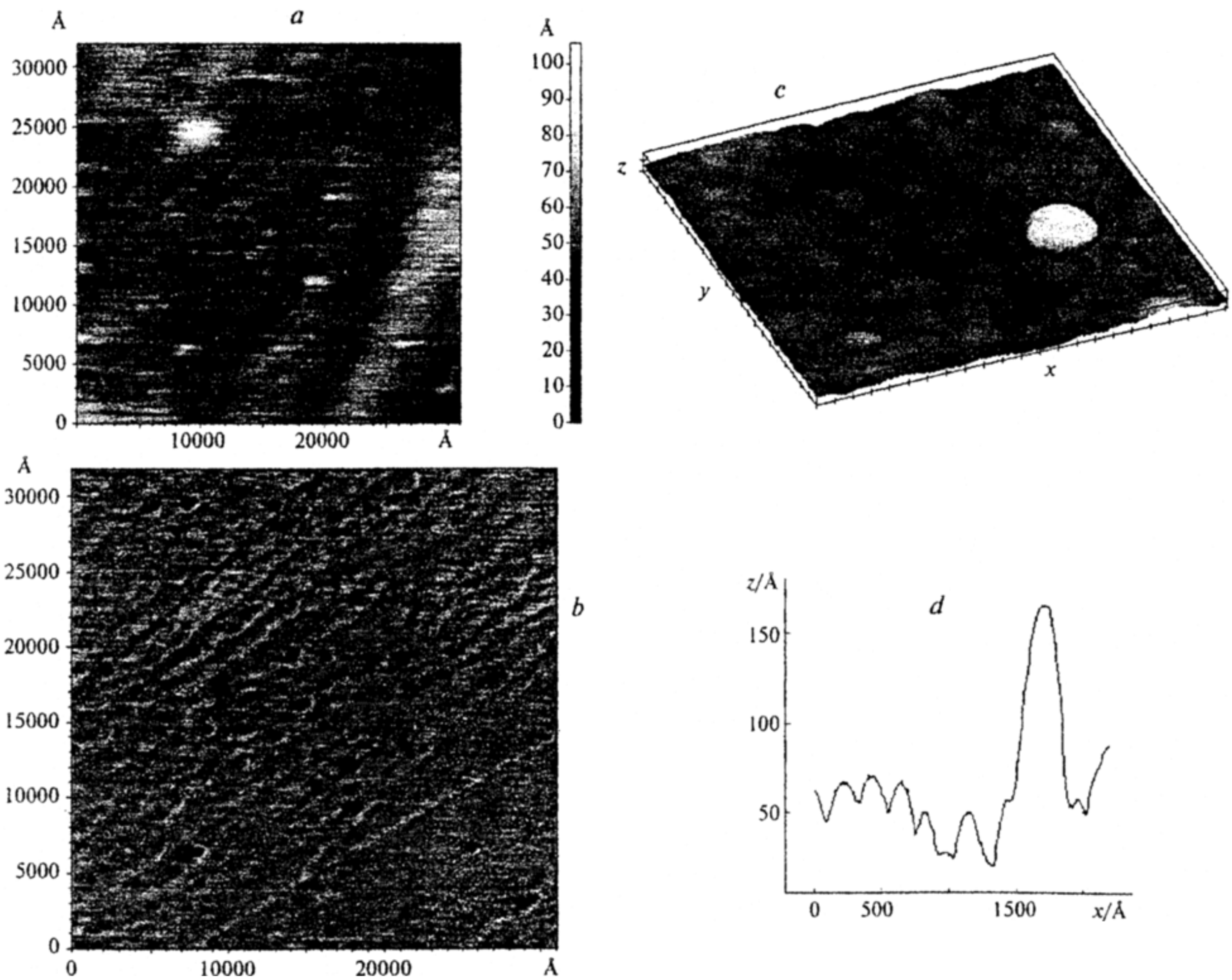


**Fig. 2.** Image of PETP surface irradiated with Xe ions and etched for 15 min: (*a*) contact mode (topography), (*b*) side-force mode, (*c*) the image of a separate knoll (the scale factors on the *x*, *y*, and *z* axes are 100 Å, resonance mode), (*d*) cros-sectional profile of the surface with a knoll.

whereas when scanning is performed in the opposite direction, they are hillocks, *i.e.*, knolls (see Fig. 2, *c*). The size of the knolls can be estimated from the surface profile (see Fig. 2, *d*); they are nearly equal and have a diameter of 800—1000 Å and a height of ~100 Å. Apparently, they are formed due to the swelling of tracks in the etching agent. This diameter of the knolls agrees with the size of the changed polymer layer around the tracks, determined by other methods.[4,8,9]

On further etching, through channels are formed in place of swollen tracks and the film becomes permeable to water ($D_p \cong 100$ Å). Cavities with an outer diameter $D \cong 250$ Å (etching time 40 min) can be seen on the surface images.[1] These cavities are entrances into the through channels, from which the gel has been removed.[1,9]

Figure 3, *a* shows a TM surface (the contact mode, etching time 80 min) in which a pore can be seen. Its magnified image and the surface profile are presented in Fig. 3, *b*, *c*. In this case, the diameter (*D*) of the pore entrance is also 2500 Å, whereas $D_p$ is 600 Å. As the etching time increases to 120 min, no noticeable growth of the outer diameter of the pore was detected, whereas the average $D_p$ increases to 800 Å over the same period.

Since a nanometer-scale image of surface elements in AFM is actually a convolution of the images of the probe shape and the surface element, it is impossible to judge the real shape of the pore taking into account only its profile (see Fig. 3, *c*). However, in view of the average hydrodynamic pore size in this membrane, it can be assumed that a pore is shaped like a double cone.

The AFM data confirm the assumption[1] that in the range of $D_p \cong 200$ to 800 Å, pores are formed as a result of segregation of the cross-linked polymer (as a microgel) from the narrowest pores into the solution. Therefore, first a cone pore is formed and then the microgel segregates in such a way that the conicity decreases. After all the cross-linked polymer has been removed, the pores acquire a cylindrical shape with $D_p \cong 800$ Å and only then does radial etching of the cylinders occur.

The AFM method allowed estimation of the roughness parameters of the TM surface (see Table 1). It

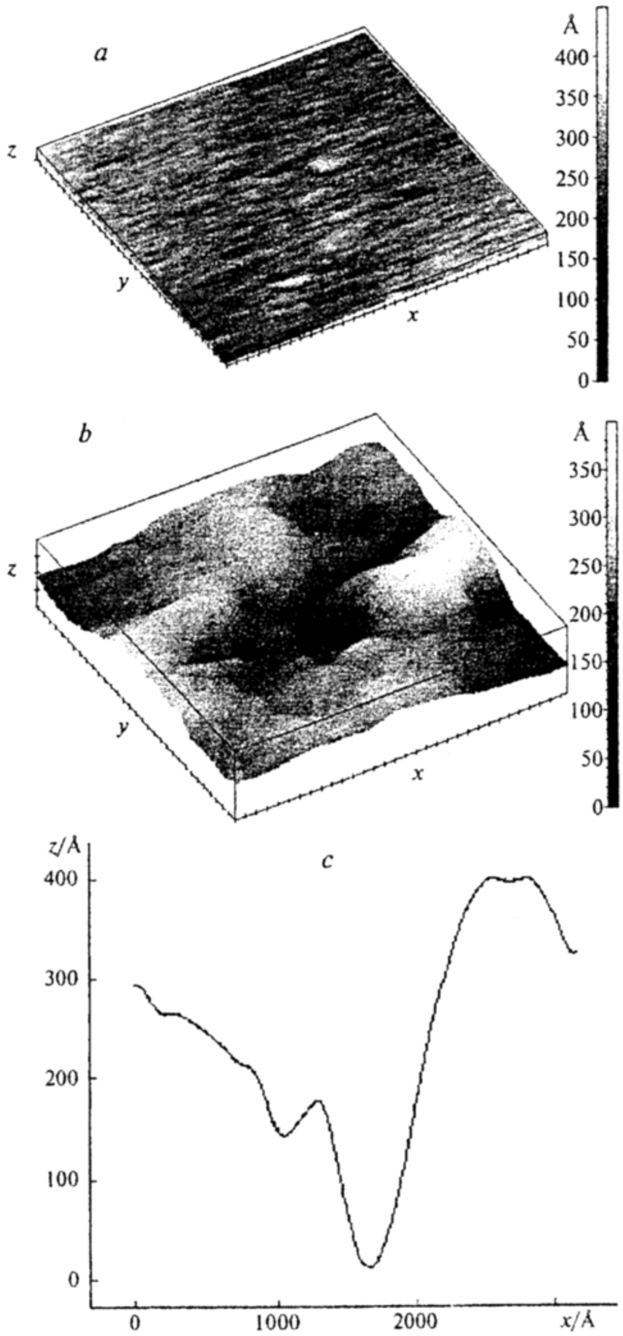


**Fig. 3.** (*a*) Topographic image of the surface of a PETP film irradiated with Xe ions and etched for 80 min (the scale factors on the *x*, *y*, and *z* axes are 1000 Å, contact mode), (*b*) magnified image of a separate pore (the scale factors on the *x*, *y*, and *z* axes are 100 Å, contact mode), (*c*) profile of the pore surface.

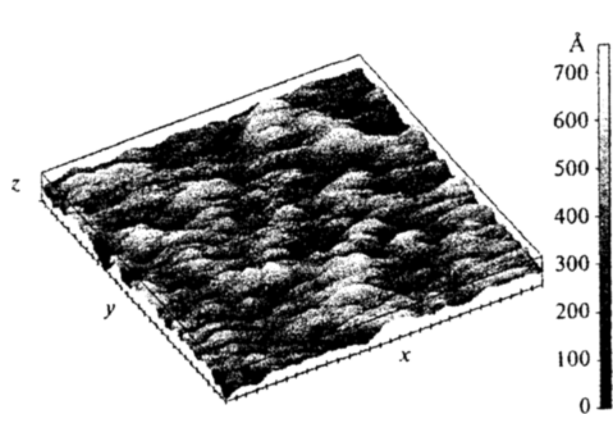


**Fig. 4.** Topographic image of the surface of a PETP film irradiated with Xe ions, sensitized by UV radiation, and etched for 80 min (the scale factors on the *x*, *y*, and *z* axes are 1000 Å, contact mode).

follows from Table 1 that as the etching time increases, the root-mean square roughness of the surface is markedly enhanced (5—6-fold). UV sensitization also increases roughness. It can be seen from Fig. 4 that the morphology of the surface of films that have been exposed to UV radiation is more developed than the normal one (see Fig. 3, *a*). On such a loosened surface, the pore entrances ($D \cong 4800$ Å) are less clearly defined than those on a smoother surface (see Fig. 2, *a*). The diameter of a pore of this type is 840 Å.

The performed studies showed that, after the radiolysis products have been removed, the areas of the cross-linked polymer around the tracks become swollen, which is manifested as the formation of knolls with $D \cong$ 80 to 100 Å and a density of $2 \cdot 10^9$ tracks $cm^{-2}$ on the surface of the irradiated film. The size of these knolls coincides with the area of the cross-linked polymer around the track axis, found by other methods.[4,8,9] The swollen tracks are impermeable to water but permeable to ions.[1] On further etching, through pores (etching for 40 min), shaped apparently like cylinders with cone entrances, are formed instead of knolls.[1] Thus a TM with the minimum possible pore size ($D_p$ = 80 to 100 Å) is formed. After that, TM with pores looking like symmetrical double cones sharing the vertices ($D_p$ = 240 to 300 Å) appear.[1] On further etching, the pore taper decreases, and at $D_p$ = 800 to 100 Å, TM contain cylindrical pores. UV sensitization causes partial destruction of the PETP macromolecules; therefore, etching increases roughness of the TM surface. However, studies showed that these membranes have smaller specific surface areas due to the partial destruction of cross-linked macromolecules in the region of tracks and due to the formation of a less dense gel-like layer on the pore surface.[1]

Thus, we found that the AFM method can be used successfully to study the structure of tracks in polymers. A necessary condition for this is a preliminary treatment of the polymer, which results in its swelling around the track. This treatment facilitates visualization of tracks on an extensive polymer surface.

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