

**The heavy ions tracks in polymers investigation by means of high-effective liquid chromatography and atomic-force microscopy.**

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**Abstract**

The method of heavy high-energy ions latent tracks structure in polymers investigations have been proposed. This method includes the irradiated polymer preliminary treatment with water, then with weak alkali solution for different track area visualization and investigation. The products of polyethylene terephthalate radiolysis from the track areas were investigated by means of inverse-phase chromatography. Atomic-force microscopy was used for polymer investigation. It was shown that the latent track has complicated structure and consists of different areas. For Xe- irradiated PET- sample 3 areas (with diameters 7 nm, 17 nm and 50-150 nm) were found. Such track structure allows to explain the discrepancy between the data, previously obtained by using different methods.

**Keywords:** heavy ions, tracks, polymers, atomic-force microscopy, chromatography

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## 1.Introduction.

During the last years the track membranes (TM), obtained by swift heavy ions irradiation of polymers and by subsequent latent tracks (LT) etching, are widely used in the medicine, biotechnology and in the ecological problems solving. In this connection the detailed study of swift heavy ions tracks structure in polymers is of a big interest for the TM pores structure improvement (pores geometry and selective layer parameters variation, pores sizes scattering diminution and etc.).

The polyethylene terephthalate (PET) films are most frequently used for the TM production. It was shown by the studying of LT etching mechanism in PET that the pores formation includes several stages: at the beginning of etching the hillocks at the sample surface are formed on the tracks places. These hillocks are found to be micro-gels (Vilensky and Tolstikhina, 1999a; Vilensky and Tolstikhina, 1999b). It was previously shown by the exclusion chromatography (EC) that these hillocks consist of cross-linked and destroyed polymer and include the set of oligomers (Vilensky, et al., 1997). The considerable changing of polycarbonate (PC) and PET molecular-weight distribution as a result of heavy ions irradiation were found by EC method. Such molecular mass changing indicate the macromolecule branching and cross-linking (Vilensky, et al., 1997; Vilensky and Zhdanov, 1998).

The results on the LT etching cited above and the other literature data (Apel, 1991; Ciesla et al., 1994; Trautmann et al., 1998; Durrani and Bull, 1990; Fleischer et al., 1981; Waligorski et al., 1986; Apel et al., 1997; Smolyansky et al., 1993; Vilensky et al., 1992) show that track has complicated structure. In the heavy high-energy ions tracks in polymer (PET) 2 areas (zones) were found: “the core” (predominating of destruction) and “the cover” (predominating of macromolecules cross-linking) (Apel, 1991; Ciesla et al., 1994). On the other hand, it was found that LT in the polycarbonate (CR-39), irradiated by Kr ions with energy 209 MeV, consists of three areas: with sizes 10-20, 50-100 and 100-500 nm respectively (Rozlosnik et al, 1997). But the features and nature of these areas were not determined.

It may be suggested, that the polymer tracks etching peculiarities connected with the complicated structure of tracks. So, the object of the present work was the complex investigation of LT etching and LT structure using the high-effective liquid chromatography (HELC) and the atomic-force microscopy (AFM) techniques.

## 2. Experimentals.

**Samples.** The biaxially-oriented PET film with thickness 10  $\mu\text{m}$  was used. The samples were irradiated with Xe ions (energy 1 MeV/a.m.u, fluence  $2 \cdot 10^9 \text{ cm}^{-2}$ ) (the cyclotron U-400, Flerov Laboratory of Nuclear Reactions of JINR, Dubna). The linear energy loss of Xe ions at the entrance in polymer was about 10 keV/nm.

**Chemical treatment** . In the present work two chemical techniques were used for LT structure and chemical composition investigation: the method of “layer-by-layer etching”, developed before by one of the authors and the method of “swelling”.

First method consists of consecutive LT areas etching and etching products investigation in solution (Vilensky, et al., 1997; Vilensky and Zhdanov, 1998). The radiolysis products from the core and from the LT area were extracted by water to the full elimination of ones from tracks. After that the radiolysis products from the other track areas were extracted by the combination of etching processes at different temperatures: 15 min at 75  $^{\circ}\text{C}$  and 1.5 h at 20  $^{\circ}\text{C}$  (KOH water solution 0.25 mole/l was used).

The second method: water treatment of the samples leads to different “swelling” of different LT areas and to visualization of these areas.

**Chromatography.** The products separation from the liquid solutions and theirs investigation were carried out on the "Millichrom 4" and on the "Millichrom A-02" chromatographs with the column, filled with modified adsorbents: Diabond and Eurospher C 18-5. The separation was carried out in isocratic and in gradient regimes. The acetonitrile water solutions with the different components ratio (from 0 up to 100% of acetonitrile) were used as the eluent.

**AFM-microscopy.** The surface of the polymer samples was investigated by AFM Solver P-47 (NT-MDT, Russia). Resonance regime (“taping mode”) was carried out using silicon cantilevers (length 90  $\mu\text{m}$ , tip radius less than 10 nm, frequency 300-400 kHz), working in the air at room temperature. Plane and three-dimensional images of the samples surface relief were obtained. Standard NT-MDT computer programs for size determination and statistic calculation were used.

## 3. Results and discussions.

Fig. 1 demonstrates the obtained track structure, which includes three typical areas.

**First area.** The polymer irradiation with heavy swift Xe ions leads to remarkable changing of the surface morphology. The typical cavities at the surface of irradiated polymer (without any chemical treatment) were found using AFM. The surface density of the cavities corresponds to the fluence of irradiation. These cavities average diameter ( $D_1$ )

is equal to  $7 \pm 1.5$  nm. This size corresponds to the value, calculated on the base of absorbed energy value (Durrani and Bull, 1987; Fleischer et al., 1981). The central track area, corresponds to these cavities diameter, can be named as “the track core” (area 1, Fig. 1).

**Second area.** In this area (area 2, Fig. 1) the destruction processes are predominant. This area was discovered after the irradiated PET exposure in water at least 4 hours; this exposure provides, on the base of HELC data, the complete removing and decomposition of radiolysis products from LT. The radiolysis products, passed into water, were studied by HELC.

The typical chromatograms of the irradiated PET radiolysis products, educed after the exposure in water during 15 min, 2h or 4h, are presented on Fig. 3. The chromatograms demonstrate, that the peaks quantity and intensity and spectral ratios are changed with the time. The time of radiolysis products retention on the hydrophobic fixed phase is less than that of terephthalic acid (TPA), i.e. the radiolysis products are more hydrophilic. The kinetic curves of radiolysis products accumulation in water (calculated on the base of HELC) are shown on Fig. 4 (curve 2). It was found that radiolysis products from LT are diffused into water during a few minutes, after that they decomposed with TPA formation (Fig. 4, curve 1). Though these radiolysis products were not exactly identified, we can suppose (on the base of HELC) that they consists of low oligomers with carbonyl, carboxyl and hydroxyl groups.

The radiolysis products removing from the LT results to the increasing of the changed area: the cavities diameter, estimated by AFM, increase up to  $17 \pm 3$  nm. ( $D_2$ ). Such area diameter is approximately corresponds to the secondary electrons run (Apel et al., 1997). The  $D_2$  value is in a good agreement with the track sizes, obtained by means of conductometry method on maximum etching rate (Apel, 1991; Apel et al, 1997). Thus, this area with average diameter 17 nm can be named as “the destruction area”.

**Third area.** Combination of chemical methods (alkali etching), HELC and AFM technique was used at this stage of investigation. The etching products (potassium terephthalate and radiolysis products) from this area were analyzed by HELC method. Fig.5 demonstrates these products accumulation at 20° C. At the beginning of etching curves 1 and 3 are coincides, and the etching velocity deviation is visible only after 2 hours. This data shows that during first 2h the etching velocities of irradiated and control films are equal. The potassium terephthalate concentration in the solution increases only at the TM pore structure formation (right side of curve 1 on Fig. 5). The accumulation of radiolysis products from the destruction track area is differ: after several minutes of exposure the radiolysis products are turning into the solution, but only after 3h, with the

TM pore structure formation, concentration of that products in the solution increases significantly.

At the higher temperature the velocity of the radiolysis products accumulation in the solution is much higher. The radiolysis products from tracks accumulation in KOH solution (0.25 mole/l, 75<sup>0</sup>C) is shown on Fig. 6. The curve has S-like character. The lower part of the curve is analogous to curve 2 on Fig. 5 and describes the radiolysis products removing from the track core and from the destruction area (Fig. 1, areas 1 and 2), and also the TM pore structure formation. Subsequent radiolysis products isolation into solution occurs at the track areas etching, where cross-linking is predominate (Fig. 1, area 3; the diameters range, is from 7 nm up to 60 nm).

During further etching (diameters range from 60 nm up to 100 nm) the radiation destruction product removing into the solution was not observed. So, according to HELC data, the structure of this area is identical to initial polymer structure.

At the beginning of the alkali etching process the “swelling” took place. AFM demonstrated the formation of hillocks at the polymer surface (Fig. 7). The surface density of these hillocks corresponds to irradiation fluence. It was found, that LT area swelling time till the hillocks formation depends on KOH solution temperature and concentration. After the hillocks appearance theirs size increase from 50 nm up to 150 nm . After that hillocks size decrease and then they disappear. On further etching the straight through channels (pores) with diameter ~7 nm are formed on the places of hillocks. The “swelling” confirms the cross-linking of the polymer molecules in this area of LT during the irradiation.

The diameter  $D_3$  (area 3, Fig. 1) is approximately equal to the diameter of total changed polymer area, that is found in works (Vilensky et al , 1997; Vilensky and Zhdanov, 1998; Smolyansky et al., 1993; Vilensky et al., 1992). Appearance of this big area of cross-linked polymer can be attributed to the blast wave presence at the moment of tracks formation or to the “hot” hydrogen atoms diffusion (Goldansky et al., 1975; Apel, 1998; Sokolova et al., 1997).

Thus, HELC and AFM data show that polymer structure in the track area is more complicated that previously shown. The track structure determines the velocity and peculiarities of etching.

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**Inscriptions to pictures.**

- Fig. 1. The scheme of heavy ion latent track structure: 1 – track core (diameter  $D_1$ ); 2 – destruction area ( $D_2$ ) ; 3 – area of cross-linking ( $D_3$ ), 4- initial polymer
- Fig. 2. a. AFM image of PET surface irradiated with Xe ions (fluence  $2 \cdot 10^9 \text{ cm}^{-2}$ ). The dark fields corresponds to cavities) ,  
b. Cross-section profiles: 1-profile of the surface with the cavity,  
2- polymer surface profile.
- Fig. 3. The chromatograms of water solution radiolysis products, extracted from irradiated PET film. Exposure time in water: a – 15 minutes; b – 2 hours; c – 4 hours (corresponds to TPA). Chromatograph "Milichrom A-02", column with Eurospher C18-5. The eluent is water-acetonitrile (linear gradient 5-100%).
- Fig. 4. The water-soluble products extraction from irradiated PET film. (S – relative peaks area). Curve 1 – TPA; curve 2 – other radiolysis products.
- Fig. 5. The accumulation of PET etching products in KOH solution (0,25 mole/l) at  $20^\circ\text{C}$ . (S – relative peaks area). Curve 1 – accumulation of TPA from irradiated PET; curve 2 – accumulation of radiolysis products from irradiated PET ; curve 3 – accumulation of TPA from control (non-irradiated) PET. (Chromatograph "Milichrom 4", column with Diabond C18. The eluent is water).
- Fig. 6. The accumulation of PET radiolysis products in KOH solution (0,25 mole/l) at  $75^\circ\text{C}$ . (Chromatograph "Milichrom 4", column with Diabond C18). The arrows denote the pore size.
- Fig. 7. a- AFM image of irradiated PET surface, after alkali etching (2h at  $20^\circ\text{C}$ ). The white fields indicate the hillocks – the tracks, visualized after “swelling” in alkali.  
b- cross-section profiles: 1-profile of the surface with the hillocks,  
2- polymer surface profile.



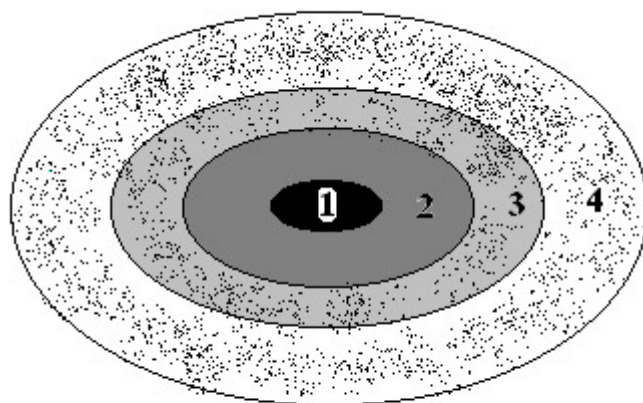


Fig. 1.

Fig.2.

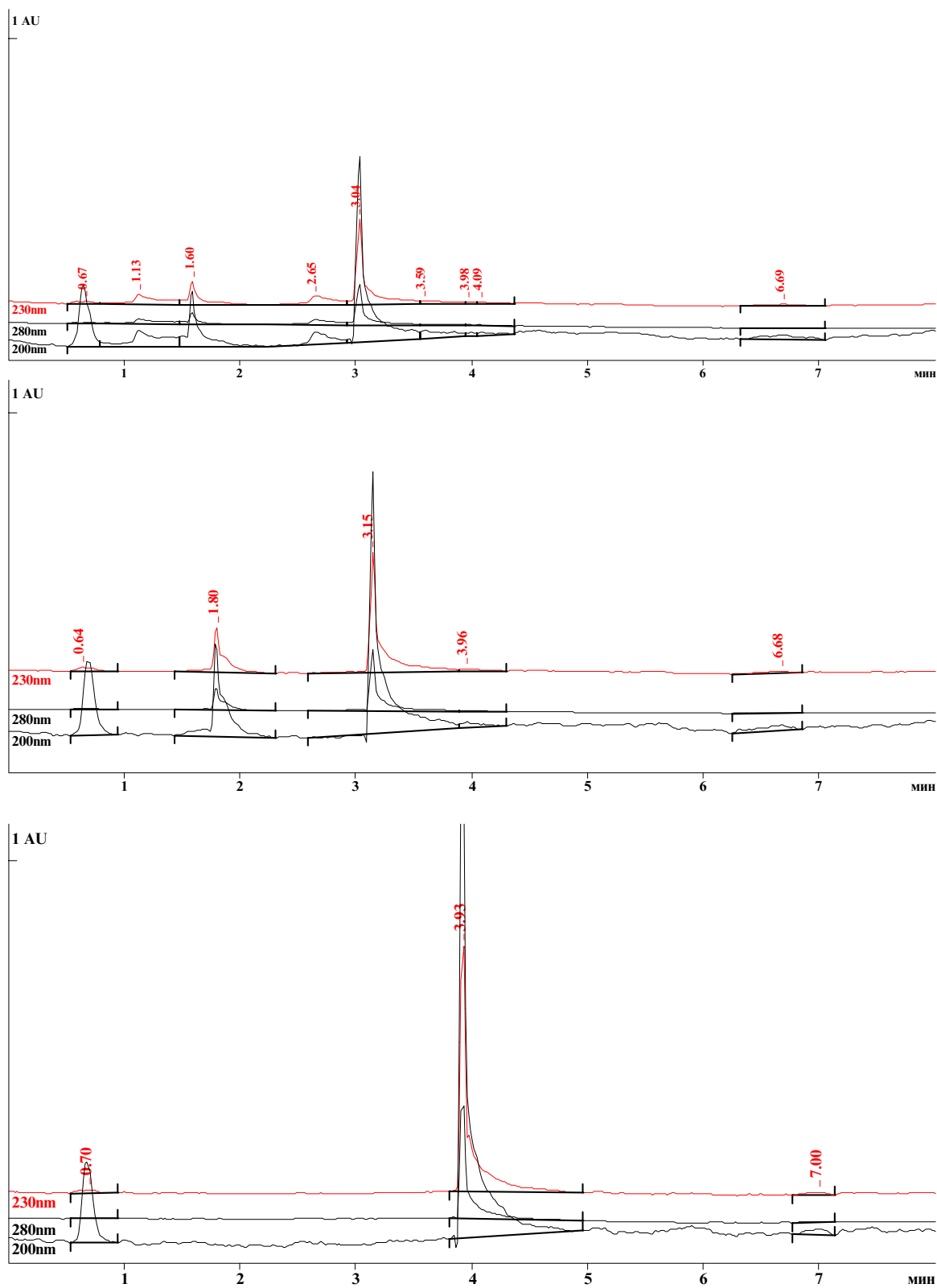


Fig3

Fig. 4.

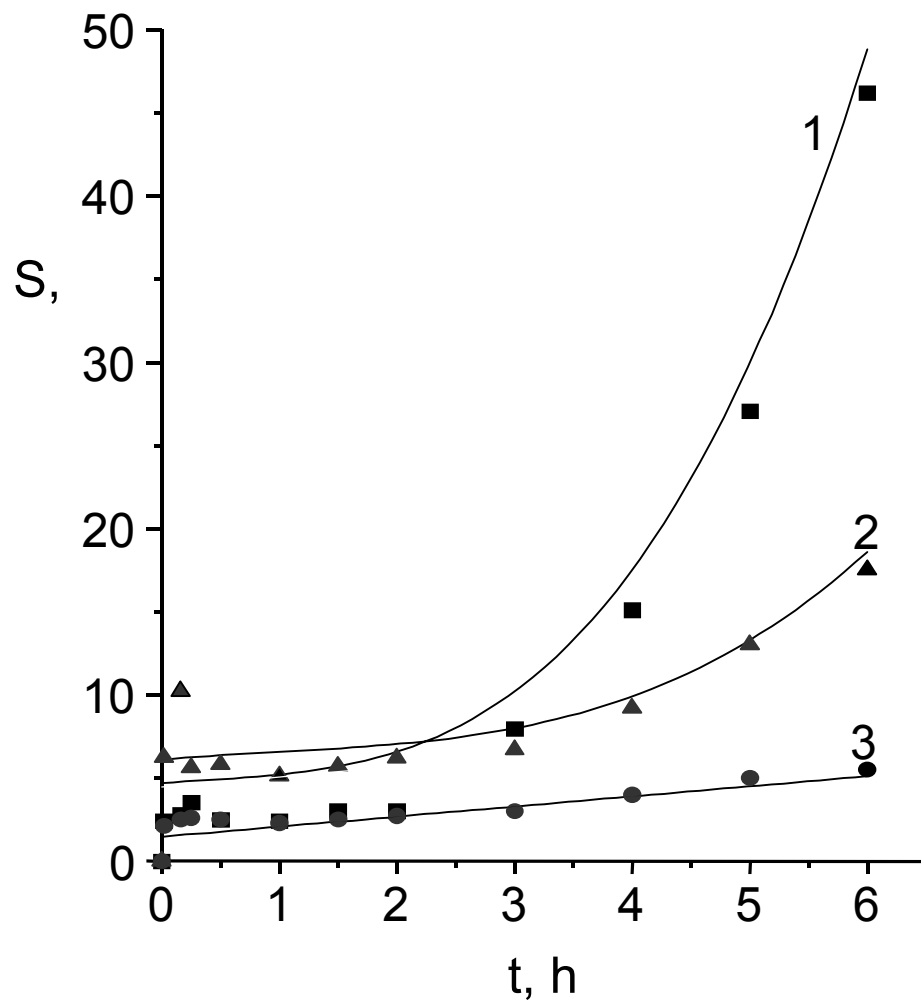


Fig. 5.

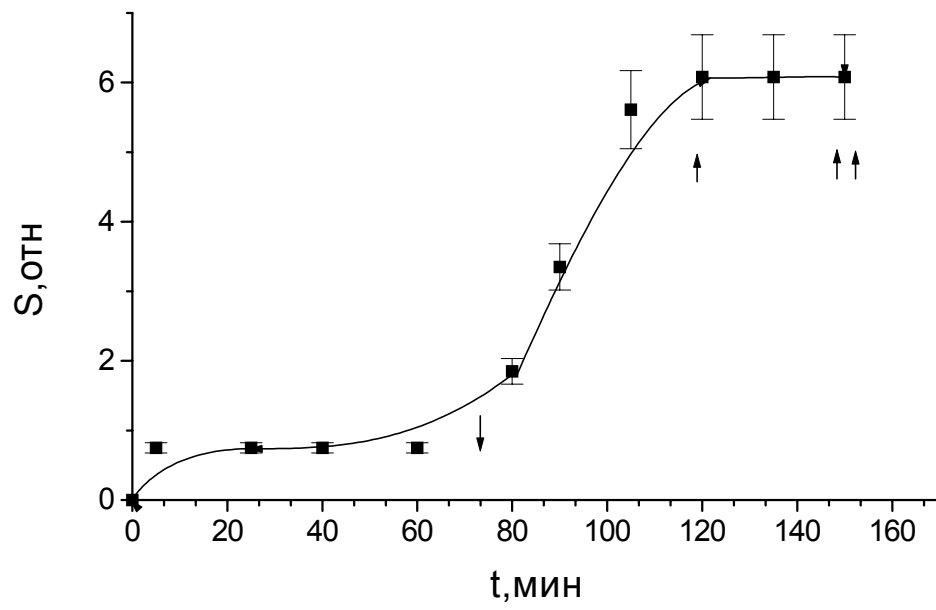


Fig. 6.

Fig. 7 a.

Fig. 7 b.