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SURFACTANT-ENHANCED CONTROL
OF TRACK-ETCH PORE MORPHOLOGY

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1. Inroduction

The formation of submicron pores of controlled geometry by the chemical etching of nuclear tracks in insulators has been first described by Price and Walker [1]. The technique of particle track etching has found diverse use in science and technology [2]. Mechanisms of track evolution during chemical treatment have been the subject of intensive research aimed at the development of nano- and microstructures with pre-determined characteristics [2-6]. Among other possible track-recording materials, particular attention has been paid to polymers which serve as matrices for the so-called track-etch porous membranes. A number of parameters, such as bombarding particle energy loss, material properties, post-irradiation treatment conditions (storage in air, heating, exposure to ultraviolet light), composition of the etching solution, etc., have been studied with respect to their influence on the porous structure obtained by the track-etch technique. In this study we are focusing on the effect of surfactants on the etching of small pores. The use of surfactants as wetting agents, increasing the track to bulk etch rate ratio, was suggested a long time ago. Numerous experimental works have been performed with the use of surfactant-containing etchants. However, the role of surfactants in the chemical etching of particle tracks is much more complex than is customarily thought.

In the present work we restrict ourselves to a qualitative description of the surfactant effect on the track-etch pore formation. The function of a surfactant in a heterogeneous system always includes diffusion and adsorption of the surfactant molecules. These two processes can be studied by various experimental methods. In this work a conductometric method was used to monitor the pore growth during the chemical treatment [5,6] and, thus, to estimate the influence of the adsorbed surfactant on the rate of the chemical reaction at the

2

etchant/polymer interface within narrow pores. The final etched structures were examined by the scanning electron microscopy to determine the pore channel profile. Combination of the results obtained by these methods made it possible to reveal a special function of a surfactant in the etching of nanopores in a solid.

2. Experimental

Polyethylene terephthalate (PET) films 5, 10 and 12 μm in thickness were "lavsan" (the USSR production), Hostaphan RE5 (Kalle) and Melinex (ICI), respectively. All three types were biaxially oriented foils with the density of about 1.39 g/cm^2. Polycarbonate (PC) film Makrofol KG was obtained from Bayer (Germany), its thickness was 10 μm and the density was 1.2 g/cm^2.

The film samples were irradiated with Kr (253 MeV) and Xe (150 MeV) ions at the cyclotrons of the Flerov Laboratory of Nuclear Reactions. After the irradiation the samples were kept in air under normal conditions. PET samples were additionally sensitized with ultraviolet irradiation from a source with the maximum intensity at 310-320 nm. Chemical etching was performed in alkaline (NaOH, KOH) aqueous solutions of various concentrations. Surfactants such as nonylphenyl-polyethylene glycols (NPPEG) from Fluka, sodium dodecyl diphenyloxide disulphonate (SDDPODS) from Dow Chemical and polyvinylpyrrolidones (PVP) with different molecular masses from Merck were added in small quantities to the etching solutions.

The irradiated samples were etched in a conductometric cell. The electrical resistance of the growing track pores filled with etchant was measured as a function of time. The temperature during etching was kept constant at a given level. A programmable automatic RCL meter (PM6304, FLUKE) controlled by a PC was used for measuring the electrical resistance of the cell R_c during etching. A sine voltage of 50 mV with a frequency of 1000 Hz was applied to the electrodes made of platinum. In separate experiments, the resistance R_e of the cell filled with the etchant, but without the sample in it, was measured. Specific conductivities of the solutions used for etching was measured with a LF325 conductivity meter.

Etched samples were examined in a scanning electron microscope JSM-840 (JEOL). Specimens were covered with a thin gold-palladium electrically conductive layer (thickness of about 20 nm). Freeze-fractured samples were prepared for making cross-sectional views.

3. Results and discussion

3.1. Conductance measurements

The resistance R of the membrane itself was derived by subtraction of the resistance of electrolyte R_e from the resistance of the cell R_c. The effective pore diameter, as a function of the etching time t, was obtained from

$$d_{eff}(t) = [4\,l\,/\,\pi\,k\,N\,R(t)]^{1/2} \tag{1}$$

where k is the specific conductivity of the solution used for etching, N is the number of tracks in the sample, and l is the sample thickness. No correction was made for the additional resistance at the pore channel ends, because in all our experiments the pore diameters were always much smaller that the membrane thickness.

The time dependence of the membrane conductance describes the pore formation and growth as the process of etching develops. As long as no through pores are formed, the conductance is very low. When the first pore channels are etched through, the conductance increases sharply. The incubation time is a parameter from which the track etch rate can be derived. The slope of the $d_{eff}(t)$ function is, in fact, twice the radial etch rate. The track to radial etch rate ratio, V_T/V_r, can be easily found from the conductance measurements. Tracks in all our samples were sensitized by means of oxidation in air under the illumination with visible (PC) or ultraviolet (PET) light. Thus, the etch rate ratio was typically a few hundred which allowed us to consider the forming pore channels as the ones having practically no taper towards the center. In the framework of this approach, we use the parameter d_{eff} for characterizing the pore size. It is obvious from formula (1) that the effective pore diameter is the diameter of a cylindrical pore having the same conductance and the same length as the measured pore with an unknown geometry.

4

The conductance data converted to the $d_{eff}(t)$ functions are shown in figures 1 and 2. When a surfactant-free etchant is used. the pore diameter grows almost linearly starting from the breakthrough point. The curves obtained in the experiments with surfactant-containing etchants are characterized by almost the same breakthrough time which indicates that the surfactant has practically no influence on the etch rate along the track axis. Up to the effective pore diameters of about 25 nm (Fig. 1) and 100 nm (Fig. 2) the curves are parallel for both types of etching solutions. At larger values of d_{eff} the radial etch rate clearly decreases if the surfactant is present in the system.

3.2. Simple model of the phenomenon

To explain the observed phenomenon. let us first consider the influence of a surfactant on the chemical reaction at the interface solid/liquid. Large molecule surfactants are composed of a hydrophobic part. normally an alkyl radical having 8-12 carbon atoms. and a hydrophilic part. that is a polar moiety (ionic or non-ionic). The surfactant molecules orient themselves with their hydrophobic part towards the surface and the hydrophilic part - towards the aqueous solution. The formed surfactant layer is quasi-solid and partially protects the surface from the etching agent. However. the adsorbed layer does not only consist of surfactant molecules but also contains solvent (water) molecules. Transport of water and ionic solutes through the barrier formed by the surfactant is probably similar to that through lipid bilayers (7). The diffusion of H^+ and OH^- ions across such molecular layers is significantly faster that the diffusion of other ions (8). The thickness of the adsorbed layer h is of the order of the fully extended length l_s of the surfactant molecules. For most commonly used surfactants this quantity is 2-4 nm. The conformation of the alkyl chains in the adsorbed layer can vary depending on the nature of the solid substrate (9). The formation of the adsorbed layer leads to a reduction in the bulk etch rate of the surface of a solid that undergoes etching. The kinetics of the process in the absence and in the presence of a surfactant is illustrated by the example of a polymer treated with alkaline solutions (see Table 1). The polymer/solution interface advances 2-3 times faster if there is no surfactant in the etchant. The effect of the surfactant tends to decrease at higher temperatures. Transient defects in the adsorbed layer probably arise from thermal fluctuations and promote easier transport of water molecules and hydroxide ions to the polymer surface.

Table 1. Bulk etch rates with and without SDDPODS under various conditions. PET film with the thickness of 10 μm. The bulk etch rates are found from the weight loss.

Etchant	Temperature 40°C	Temperature 80°C
6N NaOH	4.4 ± 0.2 nm/min	59 ± 4 nm/min
6N NaOH + SDDPODS (0.025%)	1.4 ± 0.1 nm/min	39 ± 2 nm/min

Let us now return to the curves in figures 1 and 2. Initial diffusion of etchant molecules across the surfactant layer initiates the formation of a small hole as in the case when the surfactant is not present in the reaction volume. When the hole attains a few nanometers in diameter, the surfactant molecules penetrate into the pore "mouth" and cover its walls. Further diffusion of the surfactant molecules into the growing pore is hindered. The adsorbed surfactant layer is not permeable for large molecules. At this stage the transport of surfactant molecules into the pore channel can proceed only by lateral propagation on the pore wall surface. This process is slower than the diffusion in the bulk solution. Therefore, the volume inside the pore remains free of surfactant molecules for a substantial amount of time. However, the transport of hydroxide ions into the pore or etch products out of the pore, is not blocked due to their relatively small size. As a result, the inside diameter of the would-be cylinder (in the absence of surfactant molecules) grows at a higher etch rate than the pore entrance. This situation is illustrated by Fig. 3. The configuration shown in Fig. 3 corresponds to the etching time at which the curves measured for the surfactant-containing system coincide with those for the pure alkaline solutions. By this moment "bottleneck" or "cigar-like" pore channels are formed in the membrane. Fig. 3 is a simplified picture showing a sharp (step-like) transition between the narrow pore throats and the inner cylindrical part of the channel. Actually the transition is not so sharp; its real shape will be shown below in SEM photographs.

As time passes, the pore entrance becomes large enough for letting surfactant molecules diffuse into the channel and form a protective coating on the pore walls. Starting from this moment, the etching occurs at the same (reduced) bulk rate at any point along the track axis.

6

Thus, the slope of the $d_{eff}(t)$ curve is going down. Note that in the real pore channel the central cylindrical part is much longer than the narrow "throats" at both ends. Therefore the effective diameter value is close to the diameter of the central long part of the pore. Due to this, the initial segments of the $d_{eff}(t)$ functions are practically the same for these two different recipes of etchants. In the case of the cigar-like profile the effective pore diameter is only an "apparent" pore size, it is almost independent on the diameters of the "throats". The ratio between the diameters inside the pore and in the throats varies depending on the etching conditions such as temperature and alkali concentration. For this reason the penetration of the surfactant into the pores occurs at different effective pore sizes – 25 nm and 100 nm at 30 and 50°C, respectively.

Even in the absence of the above-mentioned steric hindrance effect at the pore mouths, the diffusion of the surfactant molecules into the pore channel should be slower than that of the small ions such as Na^+ or OH^-. The diffusion coefficients for these small species at 25°C are $1.34 \cdot 10^{-5}$ and $5.25 \cdot 10^{-5}$ $cm^2 s^{-1}$, respectively. The diffusion coefficient for large molecules of surface-active species in the bulk solution (for example, sodium dodecylsulfonate in NaCl) is normally of the order of 10^{-6} $cm^2 s^{-1}$, i.e. almost two orders of magnitude smaller than for OH^- [10]. The coefficient of the lateral diffusion of sodium dodecylsulfonate in the adsorbed layer is $5 \cdot 10^{-7}$ $cm^2 s^{-1}$ [11]. For this reason, in the very beginning of etching the alkali ions penetrate into a track faster and attack the polymer surface not covered with the surfactant layer. The filling of the track with the large surfactant molecules occurs with some delay – depending on the difference in the diffusion coefficients. In other words, the surfactant concentration gradient along the pore channel differs from that for the alkali molecules at the initial step of a rapid movement of the etchant into the growing pore channel.

3.3. Influence of molecular mass and type of surfactant

This phenomenon is observed for surfactants of different types. Experiments have shown that both kinds of ionic surfactants as well as non-ionic ones are effective. Of course, the surfactant molecules should be relatively large to produce the described steric-hindrance effect in narrow channels. As to the small-molecule surface-active agents, the commonly used alcohols such as ethanol or methanol do not produce the effect described here. First of all, they do not create the protective layer on the surface of polymers. Instead, they cause an

7

increase in the etching reaction rate, probably, due to the alcoholysis mechanism.

Fig. 4 illustrates the results obtained with the use of another large-molecule surfactant – polyvinylpyrrolidone. In contrast to the case of SDDPODS, PVP has an influence on the breakthrough time: the formation of through pore channels takes a longer time in the PVP-containing solutions. From the presented plots one can see both the effect of concentration and the effect of molecular mass. Comparison of curves 1 and 2 in Fig. 4 shows that the low concentration of PVP with the molecular mass of 40,000 (0.003%, w/w) practically does not change the kinetics of the pore channel growth. An increase in the PVP concentration by one order of magnitude (curve 3) provides a profound reduction in the radial etch rate at $d_{eff} > 100$ nm. Shorter PVP molecules at the same mass concentration produce a stronger effect on the pore growth (see curves 3, 4 and 5). In fact, PVP of lower molecular mass has a higher molecular concentration and, obviously, creates a denser protective layer on the polymer surface.

3.4. Scanning electron microscope observations of the pore shape

An example of a structure produced using surfactant-controlled etching is presented in Fig. 5. A sample of polyethylene terephthalate (PET) film was exposed to accelerated xenon ions which fully traversed the film. The film was subsequently etched in a NaOH solution under standard conditions for the manufacturing of nuclear track membranes, a very small amount of an anionic large molecule surfactant being added. Since both sides of the film are subjected to the surfactant-controlled treatment - the effect takes place simultaneously on each track end. The etched track diameters on the film surface are ≤ 80 nm whereas the inside diameters are of about 450 nm. As a result, the inner porosity of the film is more than an order of magnitude higher than the surface porosity. Similar porous structure was obtained in ion-irradiated polycarbonate foils.

Another example, illustrating the versatility of this geometry control method, is shown in Fig. 6. Here "through" latent tracks in a PET film were partly etched in a surfactant-free concentrated NaOH solution so that the cones of an appropriate depth were formed at each surface of the film ($V_T \approx V_r$). Subsequent etching in a surfactant-enhanced NaOH solution, under new conditions which allow achieving $V_T >> V_{rs}$, results in the "bow tie" shape shown in the SEM photograph.

8

While the effect was first observed during etching of latent tracks, its relatively simple steric (geometric) nature easily leads to predictions of its applicability in other similar situations. Thus, it was expected that already existing pores with entrances of small enough dimensions for forming a "congestion" of surfactant molecules would produce the same effect. An experiment supporting such assumption is illustrated by Fig. 7. A PET foil with 3×10^8 cm^{-2} latent tracks was first treated in a selective surfactant-free etchant so that the narrow cylindrical pore channels were created in the foil. The effective pore diameter, calculated from the gas flow rate through the obtained membrane, was 20 nm. The membrane was then treated in a surfactant-enhanced etching solution. The difference between the etching rates at the pore orifice and inside the pore resulted in the enlargement of the inside pore diameter which is clearly seen in Fig. 7. Such experiments with the pre-existing pores have shown that the surfactant affects the pore shape even when the pore diameter is larger than l_S. Probably, when the surfactant concentration is higher than the critical micellar concentration, the hindrance mechanism is more complex. The micelles may plug the channel entrances providing their own steric-hindrance effect at larger pore dimensions. Experimental tests show that the effect takes place both in the nanometer and micrometer scales.

4. Conclusion

In the present report we explain how the shape of ion track pores can be changed using surface-active species added to etchant in small quantities. We have not seen any evidence in literature that the phenomenon has ever been understood and described before. However, the surfactants were used as components of etching solutions in many earlier works, and their authors obtained the results that were undoubtedly influenced by the surfactant effect. Below we mention only a few of them. In [6] the conductometrically measured $d_{eff}(t)$ curves were strongly distorted by the presence of a surfactant. The enormously large apparent size of the damaged zone around the ion path was erroneously attributed to the action of secondary electrons. The authors of [12] found a cigar-like shape of pore channels in Nuclepore filters. They suggested that the etching process could not be stopped rapidly enough by washing. According to the authors' explanation, water takes more time to reach the center of the membrane and the etchant has more time to act which makes the narrowing towards the pore

ends more pronounced at small sizes. In [13] the commercially available polycarbonate track-etch membranes were used as templates for synthesizing metal nanowires. The produced nanowires were tapered towards both ends thus resembling the shape of the pore channels. The origin of such a taper was ascribed to the change of the spatial absorbed dose distribution produced by secondary electrons near the polymer surface. We believe that in all the mentioned cases the researchers dealt with one and the same phenomenon – surfactant-controlled pore shape.

Although the hindrance effect of surfactant molecules has not been described for track pores, it is known for narrow channels of another nature. In [14] the effect of the surfactant structure on the activity of water-soluble herbicides was studied. It was found that the toxicity index of herbicides decreased with increasing the length of the ethylene oxide chain in the molecule of detergent added to the solution. The authors of [14] assumed that the detergents align themselves at the surfaces of cracks or fissures in the leaf with polyoxyethylene chains oriented away from the surface. Thus a "hydrophilic" channel is formed in the narrow space between short ethylene oxide chains. Water-soluble herbicides are able to diffuse by this route. In contrast, if the detergent has longer polyoxyethylene chains, they block the channel and the herbicide does not pass into the leaf cuticle.

The surfactant-controlled design of track pore shapes provides the most obvious benefits for membrane technology. The membranes containing an array of bottleneck nanocapillaries have high selectivity and, at the same time, high permeability. Apart from filtration, the method can find applications for the cases when porous bodies with special properties are needed. Substrates with high inner porosity can be produced and used for encapsulation of drugs, dyes, chemicals, etc.
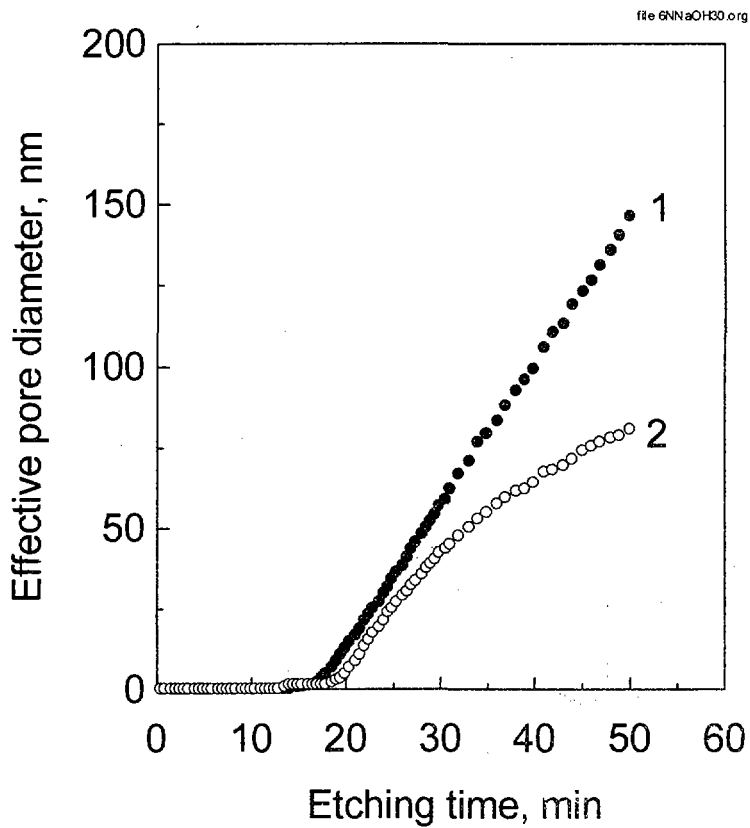
Fig. 1. Effective pore diameter as a function of etching time. A PET foil with the thickness of 10 µm, irradiated with the 1 MeV/u Xe ions. Etching in 6M NaOH with 0.025% (w/w) SDDPODS (open circles) and without SDDPODS (solid circles) at 30°C.
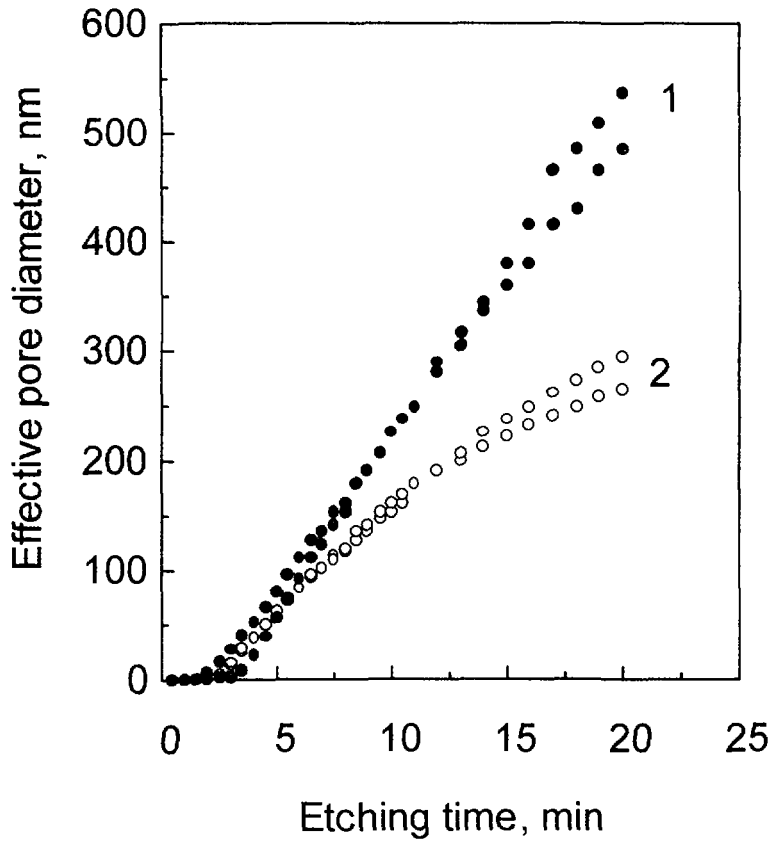
Fig. 2. Effective pore diameter as a function of etching time. Etching temperature 50°C, all other conditions are the same as in Fig. 2. Results of two parallel experiments are shown for both etching regimes.
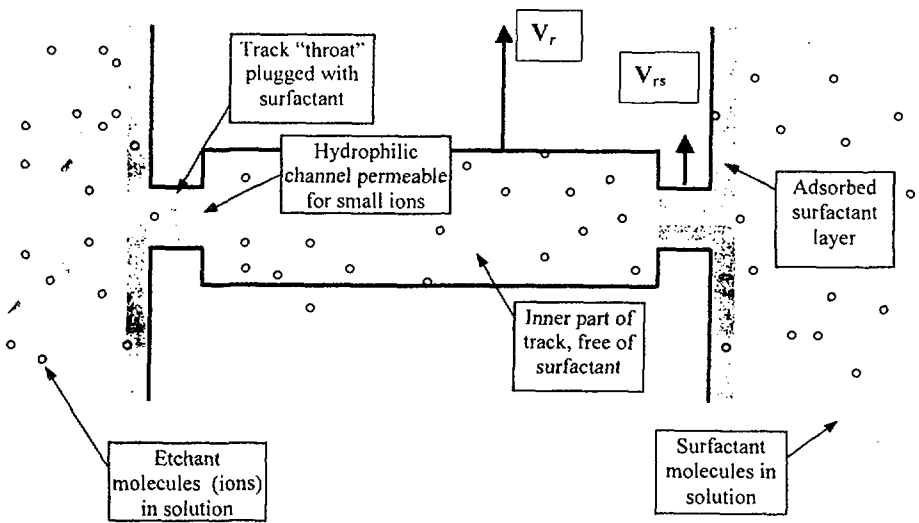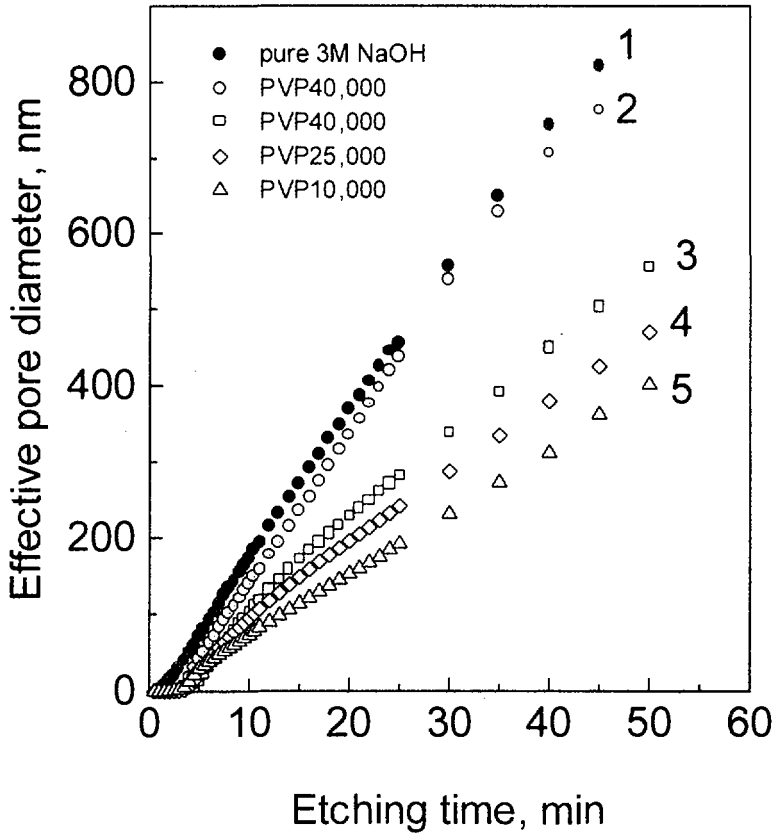
Fig. 3. The pore channel profile formed by etching in a surfactant-containing solution. Note that in reality the length of the pore is much larger than its transverse size. Radial etch rates of a free polymer surface and that covered with surfactant are shown as V_r and V_{rs}, respectively.

Fig. 4. Effective pore diameter as a function of etching time. PET foil with the thickness of 10 μm, irradiated with the 1 MeV/u Xe ions. Etching in 3M NaOH at 60°C.

Solid circles: pure alkaline solution;

Open circles: with 0.003 % of PVP-40,000;

Squares: with 0.025 % of PVP-40,000;

Diamonds: with 0.025% of PVP-25,000;
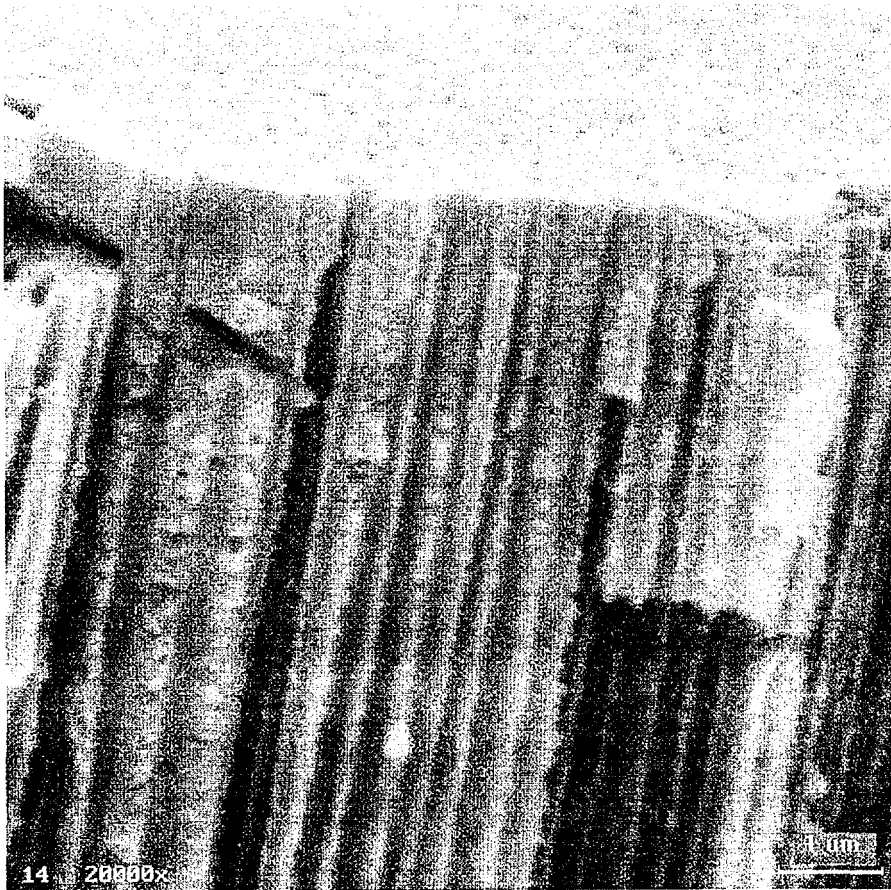
Triangles: with 0.025% of PVP-10,000.

Fig. 5. A SEM photo of the cross section of a PET film sample exposed to a 150 MeV Xe ion beam and etched in a 6M NaOH solution containing a very small amount of an anionic large molecule surfactant. The film thickness is 5 µm. Surface pore density is 7×10^7 cm^{-2}.
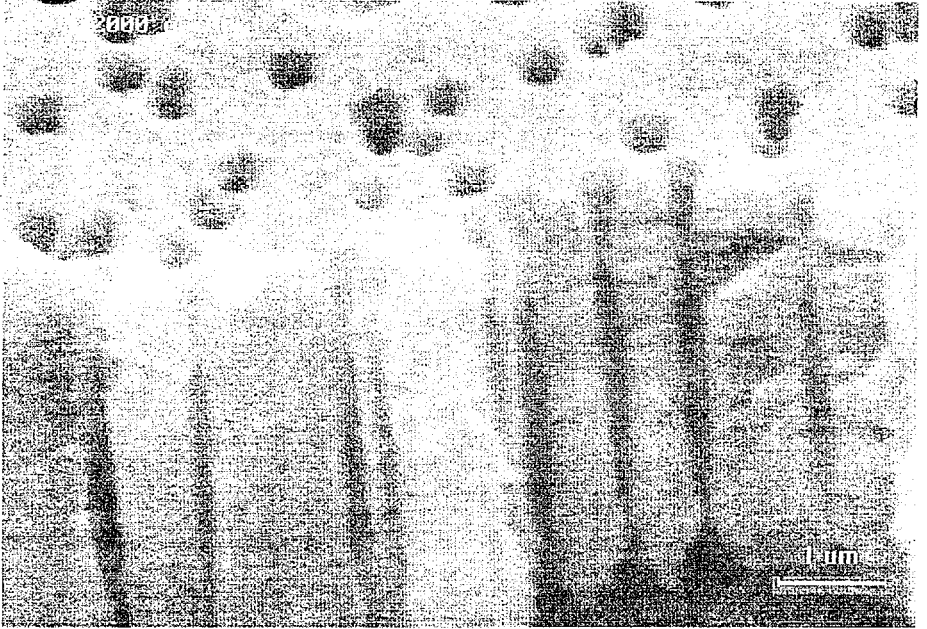
Fig. 6. A SEM photo of the cross section of a PET sample exposed to a 150 MeV Xe ion beam and partly etched in a surfactant-free concentrated NaOH solution to obtain a small cone at each track end. Subsequent etching in a surfactant-enhanced NaOH solution resulted in the "bow tie" shape shown here.
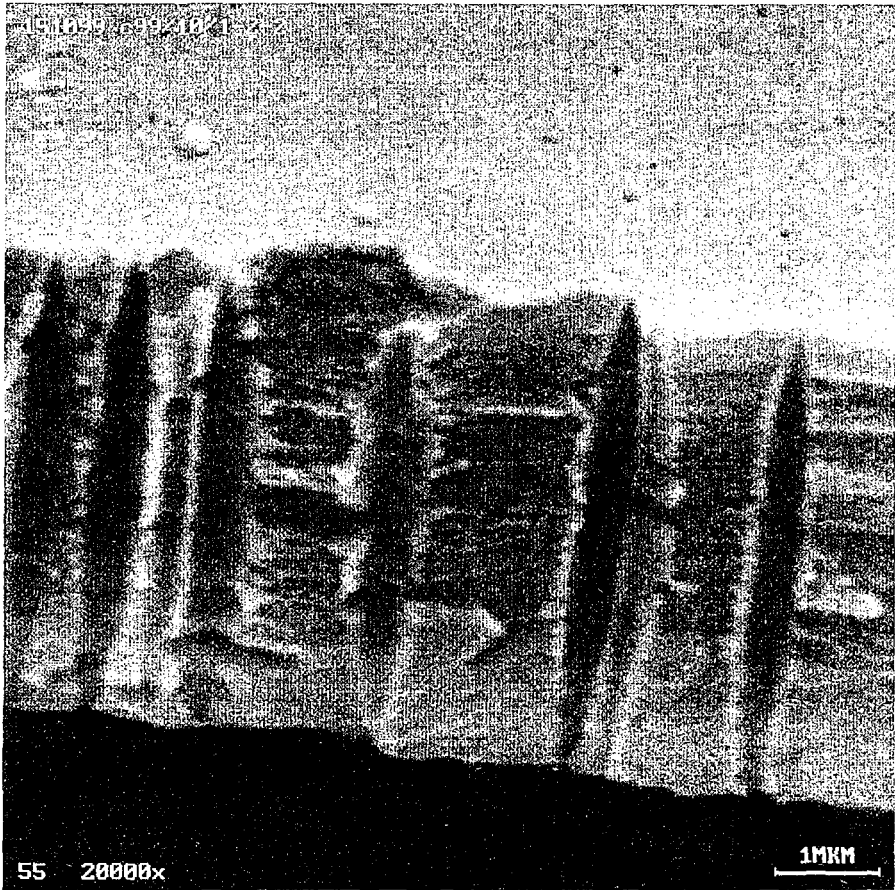
Fig. 7. A SEM photo of the cross section of a PET sample exposed to a Xe ion beam perpendicular to the surface, then exposed to UV light and treated in 0.2M NaOH at 80°C so that the through pore channels with a diameter of about 20 nm were produced. The second treatment was performed in a 3M NaOH solution with 0.03% of SDDPODS at 70°C during 6 min. The film thickness is 10 μm, the track density is 3×10^8 cm^{-2}.

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