

## Factors Determining Pore Shape in Polycarbonate Track Membranes

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**Abstract**—The formation of pores in polycarbonate films irradiated by accelerated ions upon their treatment with alkali solution containing a surfactant was studied. It was found that the pore shape is determined by both the structure of the initial film and the peculiarities of interaction of a surfactant with a polymer surface and its transfer to a track. Because of the inhomogeneity of the initial material, the “track” pore cross section varies along the pore length. The presence of a surfactant leads to an additional effect. Being adsorbed onto the film surface and at the entrances of etched tracks of heavy ions, surfactant molecules tend to decrease the etching rate, thus leading to the formation of “spindle-shaped” pores. Thus, the use of a surfactant as a component of the chemical etching solution makes it possible to vary the pore shape of track membranes in a directional manner, optimizing their efficiency and selectivity.

### INTRODUCTION

The pore shape of track membranes (TMs) has been repeatedly discussed in previous publications, because materials of this type are used as model porous media. Track membranes are often considered as “ideal” objects containing an array of straight cylindrical pores. Commercial polycarbonate (PC) track membranes are preferred in many applications, because this polymer is characterized by the highest selectivity of track etching [1]. As a consequence, pores are not narrowed in the film depth contrary to, for example, poly(ethylene terephthalate) TMs [2]. However, thorough studies showed that, even in PC, the track pore shape is not always a circular cylinder. In some works, a “paradoxical” cigar-shaped profile was observed, which contradicted a conventional model of etching of heavy particle tracks in a homogeneous isotropic material [3–10]. Repeated attempts were made to explain the origin of this pore shape [6, 8, 9]. Nevertheless, many aspects of this problem still remain unclear.

The aim of this work is the detailed study of the factors determining the channel (pore) shape of polycarbonate TMs. The emphasis was on surface phenomena that can affect the formation of track channels of micro- and nanometric radii.

### EXPERIMENTAL

Polycarbonate films Makrofol KG (Bayer, Germany) and Pokalon N38EM (LOFO, Germany) with a nominal thickness of 10, 12, and 20  $\mu\text{m}$  were used as initial materials. According to producer's data, the films were prepared by solution casting. After casting and

drying, the Makrofol KG films (in contrast to Pokalon N38EM films) were subjected to stretching and crystallization.

The films were irradiated by the extracted beam of accelerated krypton ions with an energy of 250 MeV on an U-400 cyclotron at the Flerov Laboratory of Nuclear Reactions of Joint Institute of Nuclear Research. At a given energy, the ions passed through the film, forming tracks penetrating through the sample from one surface to another. The angle of track inclination was from  $-30^\circ$  to  $+30^\circ$  with respect to the normal to the film surface. Track density was  $(2-5) \times 10^6$  or  $2 \times 10^9 \text{ cm}^{-2}$ . After irradiation, the films were kept in air for several months and longer. A contact with oxygen-containing atmosphere provided the oxidation of radiolysis products, thus ensuring a high selectivity of track etching during subsequent chemical treatment.

Tracks of irradiated samples were developed by the etching with sodium hydroxide solution (6 M NaOH) at  $60^\circ\text{C}$  for a given time (16 min). The samples were treated in parallel under analogous conditions with 6 M NaOH solution containing surfactant. The latter was sodium dodecylbenzene sulfonate (SDBS) (Chameleon Osaka, Japan) with a concentration of 0.01 wt %. A part of the samples of polycarbonate films was etched chemically prior to the irradiation by accelerated ions (6 M NaOH,  $60^\circ\text{C}$ , 60 or 120 min). This procedure ensured the removal (from both sides) of the surface layer 1 or 2  $\mu\text{m}$  thick, depending on treatment time. The modified samples were then irradiated by accelerated ions, and the etching of their tracks was studied by the same procedure that as was used for the unmodified samples.

Gas permeability of the TM samples obtained was measured with the calibrated float rotameters, as described in [2]. The pore density on the surface, as well as pore size and shape, was determined on a JSM-840 (JEOL, Japan) and a LEO-1530 (LEO, Germany) scanning electron microscopes. Sample fractures were prepared by the special procedure described in [11]. The PC films are distinguished by their unequal sides; their surfaces are differed in microrelief. The pores on the rougher (dull) film side are characterized by a higher diameter scatter, thus hindering the exact determination of the average size. Therefore, the diameters of pore entrances were measured by scanning electron microscopy (SEM) only on a smooth (glossy) sample side.

Contact angles were determined by the sessile drop method with a BIOLAM microscope equipped with a projection adapter. The average value of contact angle was calculated from 10–15 measurements made on different sample parts.

## RESULTS AND DISCUSSION

### *Etching of Unmodified Polycarbonate Films*

The samples of polycarbonate films that were not subjected to preliminary modification were studied in a first series of experiments. Comparison of diameters and shapes of etched channels showed a marked difference between the samples treated with the alkali solution containing the surfactant and those treated without the surfactant. The most typical SEM images of the surface and fractures selected from the examination and analysis of a large number of samples are presented in Figs. 1 and 2. Sodium dodecylbenzene sulfonate tends to decrease the rate of chemical reaction at the polymer–solution interface. This effect can be quantitatively evaluated from the ratio of the diameters of pore entrances. The average pore entrance diameter for the Makrofol PC films treated with aqueous solution containing only NaOH was 0.89  $\mu\text{m}$ , whereas the presence of SDBS decreases this value down to 0.54  $\mu\text{m}$ . For the Pokalon PC films, these values were 0.70 and 0.54  $\mu\text{m}$ , respectively. Thus, under these conditions, the surfactant decreases the etching rate of Makrofol and Pokalon films by a factor of 1.65 and 1.30, respectively.

The study of membrane fractures showed that, in all cases, the pores are not cylindrical. After the etching with alkali solution, the channels are slightly narrowed towards the film surface (Figs. 1a and 2a). Narrowing is greater near to the dull (the lower in the SEM images) film side. (Hereafter, in all fracture images, the samples are oriented by the smooth side upward). Surface polymer layers seem to have another structure differing in higher chemical stability. This can be caused by the preparation procedure for PC films. The films are formed by polymer solution casting followed by the removal of a solvent and film stretching at elevated temperature. Possibly, the PC macromolecules are more densely packed in the surface layer due to the var-

ious conditions of polymer crystallization in the bulk and near the surface. This phenomenon is observed for many film materials [12].

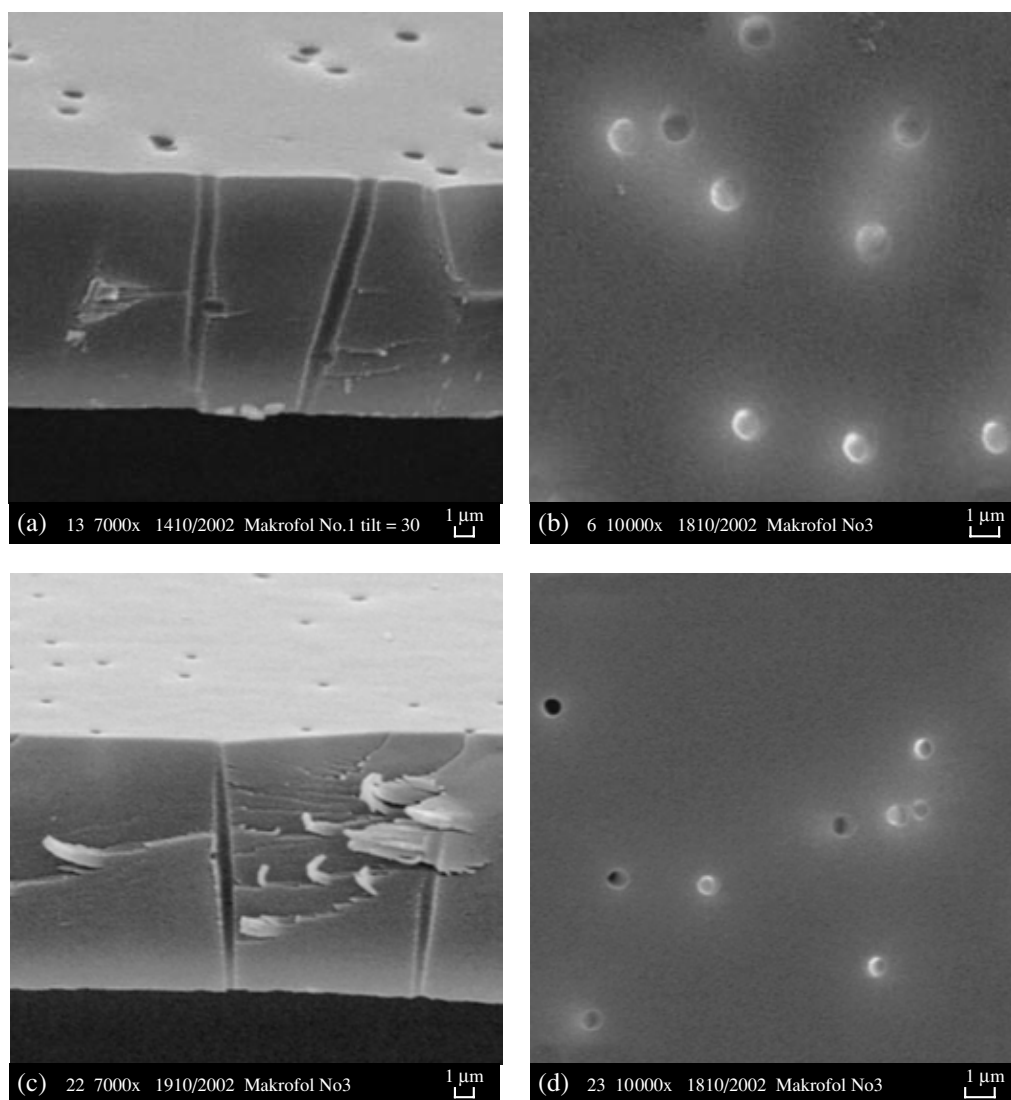
The clearly expressed spindle-shaped pores observed in Figs. 1c and 2b indicate that the presence of surfactant in the etching solution leads to a further decrease in the rate of chemical degradation of a polymer in the pore entrances. As is well seen in photomicrographs, the effect of the surfactant is mainly exhibited near the both surfaces of PC film, whereas the pore diameters in the film depth almost did not decrease.

Let us emphasize that the pores in the obtained samples are not narrowed towards the film core, in contrast to the TMs made of other polymers. This is associated with the fact that, in the PC irradiated by heavy ions, the track-to-bulk etch rate ratio,  $V_t/V_b$ , is very large and, at the corresponding choice of etching conditions, can reach  $10^4$ – $10^5$  [1]. It is known that maximal  $V_t/V_b$  values are reached at an alkali concentration of 6 mol/l. The etching agent permeates very rapidly along the narrow (several nanometers in diameter) track core; after this, the pore grows in the radial direction. In most of the other polymers, the etching agent penetrates along the track slower. By the time when the through pores are formed in poly(ethylene terephthalate) or polypropylene film, the diameter of pore entrances increases up to tens or hundreds of nanometers, and arising channels resemble strongly elongated hourglass [1, 2, 11].

### *Etching of Preliminarily Modified Polycarbonate Films*

In this series of experiments, the PC films, which were preliminarily treated with sodium hydroxide solution to remove surface layers, were studied. We believe that the experiments with the samples modified in this manner allow us to eliminate the effect caused by the inhomogeneity of film structure and to study the direct influence of a surfactant. The results obtained for the Pokalon PC films are illustrated by Fig. 3. After etching with both the pure alkali solution and the alkali solution containing SDBS, the spindle-like shape of tracks is much less pronounced in the preliminarily modified film. The appearance of funnel-shaped pore entrances turned out to be characteristic of this type of PC film (Fig. 3b). Their formation can be caused by the partial degradation of the material in the course of preliminary etching. It was recently shown that, in the alkali etching of poly(ethylene terephthalate) or polycarbonate, the reaction zone is not confined only to the polymer–solution interface, but extended into the polymer depth by several hundreds of nanometers [13].

In the preliminarily etched Makrofol film, the funnel-shaped pore entrances are not formed. The removal of its surface layers leads to a less pronounced change in the channel diameter across the film than it was observed for the initial material (Fig. 4a). As seen from Figs. 4a and 4b, the presence of the surfactant in a solution also affects the pore shape. The channel narrowing



**Fig. 1.** SEM images of Makrofol film irradiated by krypton ions and treated with (a, b) 6 M NaOH and (c, d) 6 M NaOH solution containing 0.01 wt % of SDBS at 60°C for 16 min. (a, c) TM fracture and (b, d) its front surface.

toward the smooth (upper) surface is well seen in Fig. 4b. Decreasing etching rate of the polymer near the surface under the influence of surfactant was estimated from the ratio of average pore diameters in the SEM images. This ratio was equal to 1.3, being significantly less than for the same Makrofol film not subjected to preliminary etching.

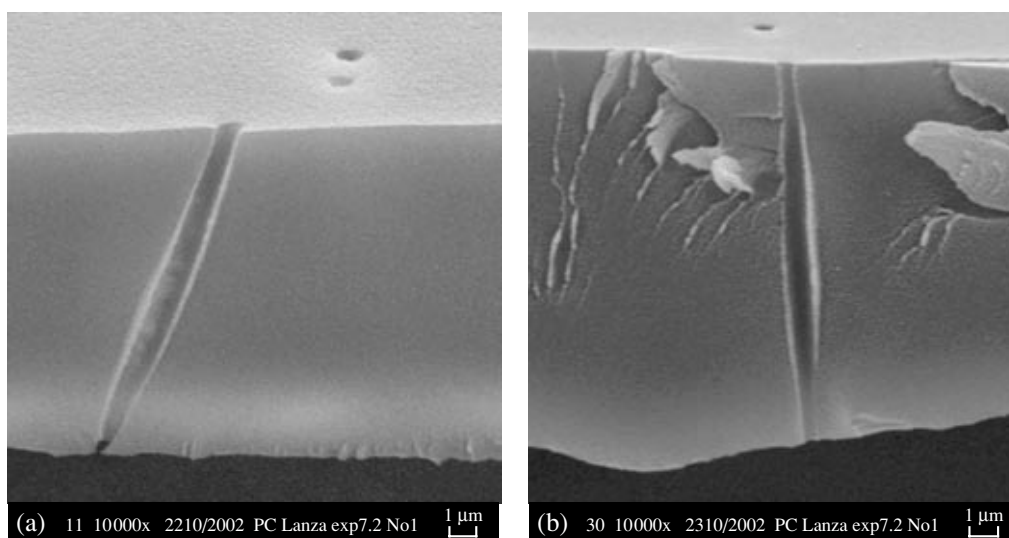
Structural defects in the form of submicron- and micron-sized bubbles in the film depth are well seen on some fractures (Fig. 4c). Such inhomogeneities of cast films were described earlier [14]. The zone of predominant localization of defects seems to be characterized by a looser structure, whose etching rate is higher than for the polymer with the dense packing of macromolecules.

#### *Interpretation of Surfactant Effect*

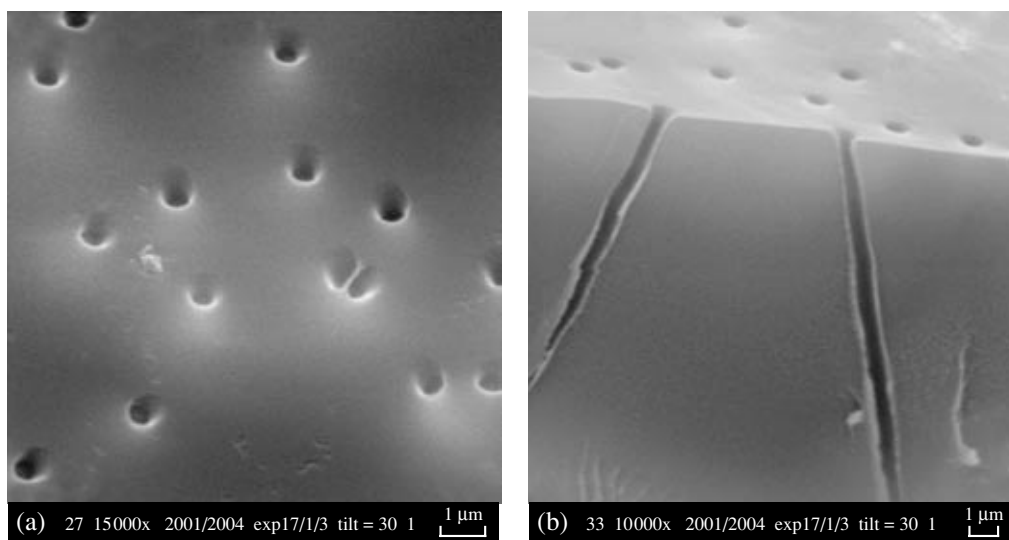
In order to explain the influence of surfactant on track chemical etching, the attention should be drawn to

the following circumstances. First, the adsorption of surfactant on the polymer surface must decrease the susceptibility of macromolecules to the chemically active component of the etching solution. Second, the size of surfactant molecules is of the order of several nanometers that is comparable with the track core radius. Third, the diffusion coefficient of surfactant molecules, is less at least by the order of magnitude than that of etching ions, particularly, hydroxide ions.

Taking the preceding into account, the mechanism of the initial stage of the development of heavy ion track in polymer should be as follows. When polymer is in contact with the etching solution, the surfactant molecules are adsorbed on its surface and oriented by their hydrophobic fragments towards polymer and hydrophilic groups, into the aqueous phase (Fig. 5). The adsorbed surfactant layer 1.5–2 nm thick forms the



**Fig. 2.** SEM images of fractures of Pokalon film irradiated by krypton ions and treated with (a) 6 M NaOH and (b) 6 M NaOH solution containing 0.01 wt % of SDBS at 60°C for 16 min.

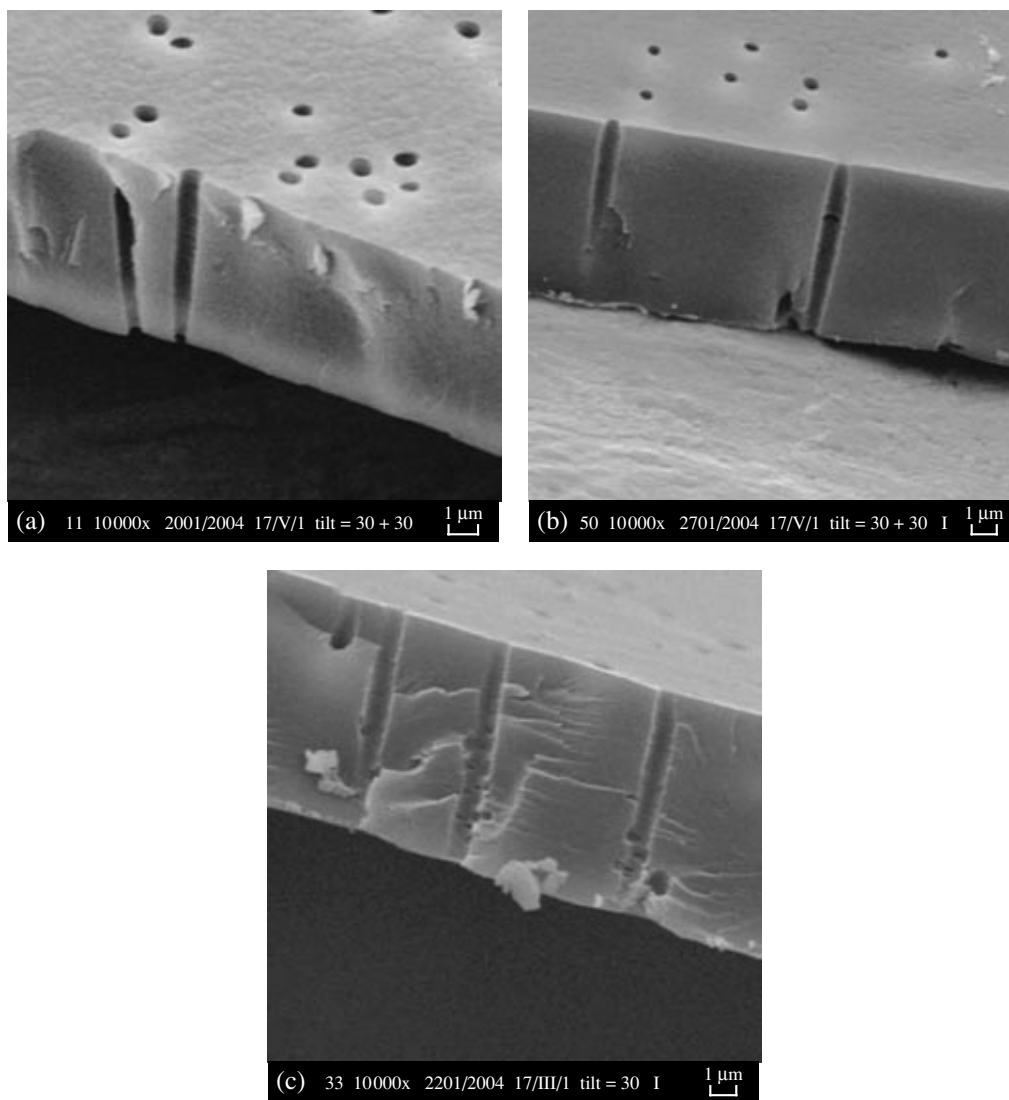


**Fig. 3.** SEM images of (a) surface and (b) fracture of Pokalon film irradiated by krypton ions and treated with 6 M NaOH solution containing 0.01 wt % of SDBS at 60°C for 16 min. Prior to irradiation by the ions, the film was etched for 60 min.

barrier that must be overcome by the hydroxide ions before their reaction with ester groups on the polymer surface. Alkali ions penetrating through the adsorbed surfactant layer react with the polymer surface and with its damaged parts (tracks). After a short time, the track cores are etched and the pores with a radius of several nanometers are formed instead of them. The adsorption of surfactant molecules in the pore entrances leads to the “plugs,” which prevent further diffusion of the surfactant inside the pores. Nevertheless, hydroxide ions continue to diffuse inside the track through the hydrophilic channel of the forming pore. As a result, the pore volume appears to be free of surfactant molecules. Channel walls are not protected with the adsorbed sur-

factant layer; therefore, the channel diameter  $d_i$  in a polymer depth increases faster than the diameter  $d_p$  of the pore entrance. It is evident that length  $l_p$  of narrowing at the pore entrance depends on the rate of the surfactant penetration into the channel. The slower the surfactant diffusion inside the channel, the sharper the change of pore profile with the length. As the pore entrance increases, the channel is also gradually accessed to the surfactant molecules. They penetrate into the channel and are sorbed on the entire channel surface. Further etching proceeds at an equal (decreased) rate in each point of the polymer–solution interface.

Undoubtedly, the suggested qualitative description of track etching in the presence of a surfactant is a sim-



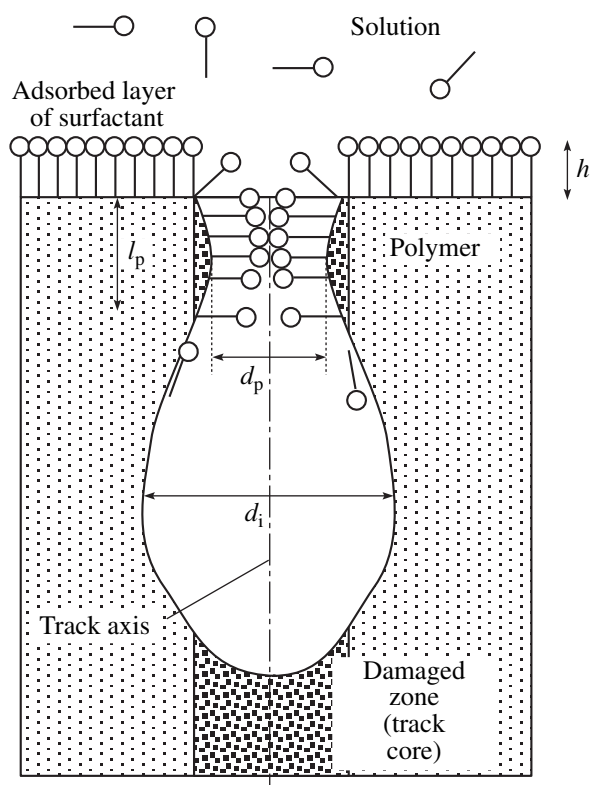
**Fig. 4.** SEM images of the fractures of Makrofol film irradiated by krypton ions and treated with (a, c) 6 M NaOH and (b) 6 M NaOH solution containing 0.01 wt % of SDBS at 60°C for 16 min. Prior to irradiation by the ions, the film was etched for (a, b) 120 and (c) 60 min.

plified model. In the used solutions, the surfactant is mainly present in micelles. As is known, dissolved sodium hydroxide considerably decreases the critical micellization concentration of surfactant due to the salting-out effect. The size of micelles is significantly larger than that of individual surfactant molecules. Therefore, sterical restrictions to the penetration of surfactant into the track are stronger than it follows from the scheme shown in Fig. 5.

The adsorption of surfactant on the nanopore surface is similar to the formation of an internal layer of a vesicle. Conditions of molecular packing on the concave surface differed from those in both the plane monolayer and the micelle [15]. For the cylindrical geometry of the surfactant monolayer where the polar groups of molecules are oriented inward, the following relation can be derived

$$a = v/l(1 + l/2r), \quad (1)$$

where  $a$  is the area per molecule,  $v$  is the volume of hydrocarbon radical,  $l$  is the thickness of hydrocarbon layer, and  $r$  is the inner radius of hydrocarbon layer. As radius  $r$  decreases, the area occupied by a molecule must decrease also. At the densest packing of hydrocarbon radicals  $a = \tilde{a}$ , where  $\tilde{a} = v/l_c$ , where  $l_c$  is the length of stretched radical (here we retain the notations used in [15]). This condition limits the size of polar groups: if the area per polar group  $a_0 > a$ , such molecules cannot be packed into the cylindrical monolayer of small radius. It is evident that there is critical radius  $r_{cr}$  of the concave surface when the ordered monolayer is no longer formed. In view of the preceding, at small pore radii (seemingly, of the order of several nanome-



**Fig. 5.** Scheme illustrating the initial stage of etching of heavy ion track in polymer in the presence of surfactant.

ters), the protective effect of the surfactant must be weak or even completely absent.

Thus, several stages of the interaction between the pore surface and the dissolved surfactant in the etching can be distinguished. At  $r < r_{cr}$ , there is no ordered adsorbed surfactant layer on the inner pore surface, and the hydroxide ions have direct access to the surface. At  $r \approx r_{cr}$ , the ordered monolayer begins to be formed on the surface and the rate of surface etching decreases. At the third stage, when  $r > r_{cr}$ , the dynamic equilibrium is attained. The surface is covered with the surfactant monolayer, through which the hydroxide ions diffuse from the solution to the surface and the etching products diffuse from the surface to the solution. Tentative

Water contact angles on the initial and modified by chemical etching polycarbonate films. Measurements were performed on (a) glossy and (b) dull film sides

Material, film thickness	Side	Initial film	After 60-min etching	After 120-min etching
Pokalon, 20 $\mu\text{m}$	(a)	$81.1 \pm 2.0$	$72.5 \pm 0.8$	$72.9 \pm 0.8$
	(b)	$94.8 \pm 1.3$	$86.0 \pm 2.1$	$86.2 \pm 2.0$
Makrofol, 10 $\mu\text{m}$	(a)	$80.0 \pm 1.1$	$77.6 \pm 1.6$	$75.3 \pm 1.7$
	(b)	$82.2 \pm 1.2$	$90.1 \pm 1.8$	$80.0 \pm 1.6$

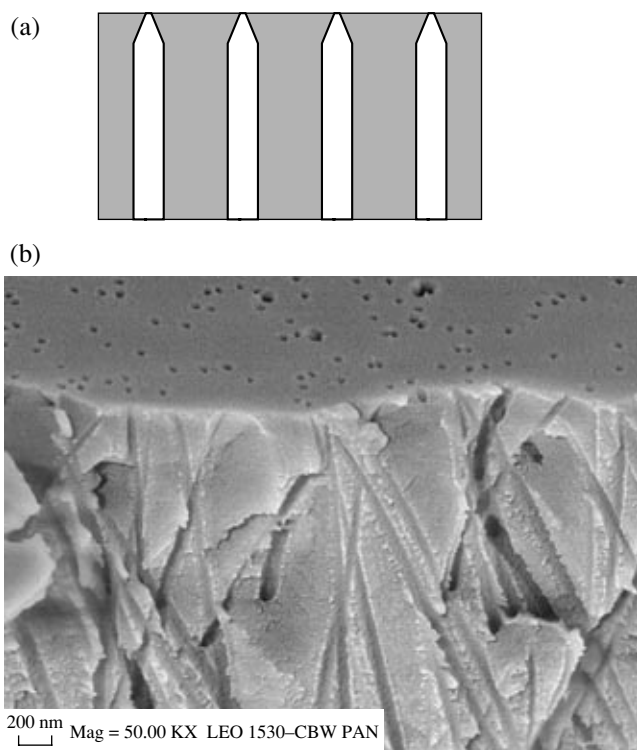
studies of the growth dynamics of pore entrance performed with high-resolution electron microscopy demonstrated that, already at  $r > 10$  nm, we deal with the steady-state process.

Let us emphasize that formula (1) and the preceding speculations refer only to the channel entrance, which interacts with the surfactant from the first seconds of its appearance. In the pore core, the situation is different. Because of the constrained transport of surfactant molecules through the pore entrances at the first stage, the surfactant-free etching solution penetrates into the pore core. An increase in pore diameter for first several minutes is determined by the rate of reaction with pure alkali. When the surfactant penetrates into the pore core, its diameter already reaches tenths of micrometer. Thus, the "delaying" adsorption of amphiphilic molecules on the pore walls does not differ from that on the flat surface because  $r \gg l$ .

It is known that wetting agents are added to the etching solutions in the industrial production of track membranes to ensure more uniform treatment of membrane cloths. In the cases when the conditions of the aforementioned process are realized, the commercial TMs have spindle-shaped pores. The effect is most pronounced for the pores of small diameter (15–50 nm) [3, 8, 9] that, naturally, follows from the mechanism responsible for the formation of the "anomalous" channel profile. Upon the measurement of a flow rate of liquid or gas through the polycarbonate membranes with such a pore morphology, these membranes demonstrate the characteristics corresponding to larger effective pore diameter than pore diameter on the surface determined by the SEM.

It can be expected that the formation of surfactant adsorption layer and its effect on the rate of polymer chemical degradation depend on the state of polymer surface, in particular, on its hydrophilicity–hydrophobicity. Our experiments with the initial and chemically modified PC films allow us to compare the effect of surfactant on the surfaces with various hydrophilicity.

The data on the wettability (by water) of the initial PC films and those modified by etching are listed in the table. In the case of the Pokalon film, the preliminary etching leads to a regular decrease in the water contact angle on both surfaces. One can suggest that the adsorption of amphiphilic molecules on the hydrophilized surface is less effective, leading to the deterioration of the protective effect of the surfactant. The effect of surfactant on the pore channel shape is deteriorated simultaneously that can be associated with the changes in the properties of a polymer at a certain depth. In the case of the Makrofol films, the water contact angle varies in a complex manner, as the polymer is removed (etched) from the surface. As the thickness of the removed layer increases, the contact angle on the rough surface first rises and then lowers. Such a behavior can be caused, for example, by the evolution of a microrelief affecting the measured macroscopic contact



**Fig. 6.** (a) Schematic representation of the structure of asymmetric track membrane and (b) the SEM image of selective layer of asymmetric ultrafiltration polycarbonate TM. Total membrane thickness is  $10\ \mu\text{m}$  and pore density is  $2 \times 10^9\ \text{cm}^{-2}$ .

angle [16]. Seemingly, the short-time etching partly smoothes the microrelief roughness. However, in all cases, independently of the behavior of water contact angle, the preliminary etching of polycarbonate lowers the effect of surfactant in subsequent track development. It is clear that the factor mainly determining the pore profile in the polycarbonate TM is the adsorption of surfactant on the initial surface at the initial etching time.

The influence of surfactant on the track etching exemplifies the self-organization of supramolecular system that can have important practical applications. One of them is the preparation of asymmetric TMs with a high specific efficiency. If the protective effect of surfactant is localized on the one side of a film, the asymmetric structure can be formed, as is shown in Fig. 6a. Selecting the conditions (the type and concentration of surfactant, temperature, and alkali concentration), one can control the  $l_p$  value and the ratio between the  $d_i$  and  $d_p$  values [17, 18]. The prepared membrane with a thin selective layer is characterized by a considerably lower hydraulic resistance than conventional TM. The SEM image of the structure of the selective layer of such a membrane is represented in Fig. 6b. (Note that the pore channels of the membrane are not parallel to one another that is ensured by the special geometry of irradiation to decrease the number of “multiplet” pores.) The pore diameter on the selective surface is 30 nm, and

the thickness of the selective layer does not exceed  $1\ \mu\text{m}$ . Pore channels are broadened up to 80–100 nm with the distance from the surface. The specific efficiency of the membrane with respect to water and air at a pressure drop of 0.1 MPa is  $0.5\ \text{ml min}^{-1}\ \text{cm}^{-2}$  and  $0.8\ \text{l min}^{-1}\ \text{cm}^{-2}$ , respectively. This is by several times higher than the efficiency of TM with the cylindrical pores of the same diameter and the same volume porosity. Advantages of the TMs with the thin selective layer were demonstrated in [19], where the membrane selectivity was studied in the filtration of latex suspensions with the particles of 40–100 nm. Asymmetric poly(ethylene terephthalate) and PC track membranes prepared by this method showed significant advantages in protein ultrafiltration [20].

## CONCLUSIONS

We showed that, in general, the profiles of pore channels of polycarbonate track membranes are determined by two factors: the inhomogeneity of a PC film and the decelerated transfer of surface-active additives into the etched track. The derived detailed information on the pore shape is important for the correct interpretation of studied transport, electrokinetic, sorption, and other characteristics of TMs and TM-based secondary structures [3–10]. The method of the pore shape control based on the controlled decrease of the etching rate in the surface layer seems to be rather promising for both the improvement of parameters of micro- and ultrafiltration TMs and the design of other porous nanostructures.

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## REFERENCES

1. Apel, P.Yu., *Radiat. Meas.*, 2001, vol. 34, p. 559.
2. Apel', P.Yu., Didyk, A.Yu., Zhitaryuk, N.I., *et al.*, *Kolloidn. Zh.*, 1994, vol. 56, p. 746.
3. Cannell, D.S. and Rondelez, F., *Macromolecules*, 1980, vol. 13, p. 1599.
4. Guillot, G., Leger, L., and Rondelez, F., *Macromolecules*, 1985, vol. 18, p. 2531.
5. Hernandez, A., Martinez-Villa, F., Ibanez, J.A., *et al.*, *Sep. Sci. Technol.*, 1986, vol. 21, p. 665.
6. Hernandez, A., Ibanez, J.A., Martinez-Diez, L., *et al.*, *Sep. Sci. Technol.*, 1987, vol. 22, p. 1235.
7. Kim, K.J., Stevens, P.V., and Fane, A.G., *J. Membr. Sci.*, 1994, vol. 93, p. 79.
8. Schoenenberger, C., Van der Zande, B.M.I., Fokkink, L.G.J., *et al.*, *J. Phys. Chem.*, 1997, vol. 101, p. 5497.

9. Ferain, E. and Legras, R., *Nucl. Instrum. Methods*, 1997, vol. 131, p. 97.
10. Kim, K.J. and Stevens, P.V., *J. Membr. Sci.*, 1997, vol. 123, p. 303.
11. Orelovich, O.L. and Apel', P.Yu., *Prib. Tekh. Eksp.*, 2001, no. 1, p. 133.
12. Lipatov, V.S., Moysya, E.O., and Semenovich, G.M., *Polymer*, 1975, vol. 16, p. 582.
13. Baur, D., Apel, P., Korchev, Y.E., *et al.*, Abstracts of Papers, *EuNITT Workshop*, Ciril-Ganil Caen, France, 2002, p. 9.
14. Hipper, Z. and Mauberg, W., *Przem. Chem.*, 1963, no. 3, p. 311.
15. Rusanov, A.I., *Mitselloobrazovanie v rastvorakh poverkhnostno-aktivnykh veshchestv* (Micellization in Surfactant Solutions), St. Petersburg: Khimiya, 1992.
16. Zisman, W.A., in *Contact Angle, Wettability, and Adhesion, Adv. Chem. Ser.*, Gould, R.F., Ed., Washington, DC: Am. Chem. Soc., 1964, vol. 43, p. 1.
17. Apel, P.Yu., Blonskaya, I.V., Didyk, A.Yu., *et al.*, *Nucl. Instrum. Methods*, 2001, vol. 179, p. 55.
18. Apel, P.Yu., Blonskaya, I.V., Orelovitch, O.L., *et al.*, *Nucl. Instrum. Methods*, 2003, vol. 209, p. 329.
19. Oganesyanyan, V.R., Orelovich, O.L., Yanina, I.V., and Apel', P.Yu., *Kolloidn. Zh.*, 2001, vol. 63, p. 825.
20. Nechaev, A.N., Apel', P.Yu., Cherkasov, A.N., *et al.*, *Krit. Tekhnol. Membr.*, 2003, no. 4 (20), p. 18.