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Production of nano-pore track membranes based on PET films irradiated by Ar ions

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Changes in diameters and depths of pores were studied in the process of etching polyethyleneterephthalate films irradiated with Ar ions having the energy of 1 MeV/n. Information about the pore diameters and lengths was obtained with electron microscopy methods. 0.5 N and 2 N solutions of NaOH were used as etchants. Etching was performed at 55 and 70°C. Two methods of sensitization were used: the first one by UV illumination and treating in dimethylformamide, the second method just by in UV illumination. It was found that diameters and depths of pores are larger in films treated according to the first sensitization method. Etching duration (breakthrough time) which leads to through-going pores of the minimal radius was established. After sensitization according to the first method the track etch rate grows quicker than the transverse etch rate. This gives a possibility to obtain through pores with diameters ranging from 50 nm to several micrometers.

Методами электронной микроскопии исследованы изменения диаметра и глубины пор в процессе травления полиэтилентерефталатных пленок, облученных ионами Ar с энергией 1 MeV/n. В качестве травителя использованы 0.5 N и 2 N растворы NaOH при 55°C и 70°C. Процесс травления ускорялся сенсибилизацией, которая заключалась либо в облучении пленок УФ и выдержке в диметилформамиде (ДМФ) — первый режим сенсибилизации, либо — только в облучении УФ — второй режим сенсибилизации. Установлено, что диаметр и глубина пор больше в пленках, обработанных по первому режиму сенсибилизации. Измерено время травления (время прорыва), необходимое для формирования сквозных пор минимального радиуса. Выполнены оценки линейной и радиальной скоростей травления пор. Установлено, что после обработки ДМФ линейная скорость травления пор увеличивается значительно больше, чем радиальная. Это дает возможность получать сквозные поры диаметром ≥50 нм.

Track-etched membranes are unique filters because these filters have a system of through pores (parallel or nonparallel) ranging from micrometers to sub-micrometers in diameter. These pores can be shaped as cylinders, tapers or something. The track membranes have wide applications for the finest filtration which is impossible with other types of filters. Conventionally, for track-etched membrane production high energy heavy ions are used: they produce sufficient radiation damages in tracks providing the etching rate along the tracks v_l (track etch rate) were much higher than transverse (i.e. radial) etching rate v_r. With $v_l >> v_r$ it is possible to obtain through-going pores of rather small diameters. For instance, with etching tracks of Xe ions having the energy of 1 MeV/n in PET films through pores ≥10 nm in diameter were obtained [1, 2]. It is believed that lighter ions such as Ar ions cannot be used for obtaining through pores in polyyeethylene-terephthalate (PET) films <0.1 μm in diameter [3–5]. Radiation damages in the core of these tracks are not sufficient to fulfill the condition $\nu_l >> \nu_r$ which is required for etching through pores of a regular cylindrical shape and small in diameter. Our experiments have shown that the proper choice of sensitization conditions allows to increase track etch rate of Ar tracks in PET films significantly and to obtain through-going pores <0.1 μm in diameter [6, 7].

The goal of this work was further investigation of sensitization methods and conditions of etching Ar ion tracks in PET films for obtaining through pores of small diameters. In order to obtain cylindrical pores, the ratio between the track etch rate ν_l and the bulk etch rate ν_0 should be as high as possible. Comparison of the data from literature and our data allows us to expect that ν_l/ν_0 ratio would be the maximal in the case of etching Ar ion tracks in an weak etchant. In such etchant the bulk etch rate is negligibly low, and pore sizes would be mainly defined by etching only the damaged area of tracks. In this work we studied the initial stage of the pore formation in PET films irradiated by Ar ions in the course of etching in 0.5 N and 2 N solutions of NaOH. The distinctive feature of our experiments is the information about pore depths and diameters obtained by measuring of these parameters directly by electron microscopes. In most part of works this information was obtained indirectly (conductometric technique or bubble method [8–12]). At high irradiation doses the information obtained by these methods would be distorted due to presence the overlapped pores and the fact that not all the pores become through- going simultaneously. The method we have used allowed to measure pore depths on the cross sections of films and diameters of only separated through-going pores on the film surface without considering the overlapped pores.

PET films (Lavsan) 6 μm thick were irradiated with accelerated Ar^{3+} ions with the energy of 1 MeV/n at the MILAC heavy ion linear accelerator [13,14]. The fluence corresponded to the track density of 10^7–$5\cdot10^8$ cm^{-2}. All samples were exposed to ultraviolet light in the air at a special optical system with several mercury lamps and glass filters (Department of Optics, Kharkiv National University), which made possible to select the necessary wave range for irradiation. The light was filtered in a way that the light flux has the maximum illumination in the wavelength range 320–360 nm. The intensity of UV illumination was $\approx 10^{15}$ quanta$\cdot$cm$^{-2}\cdot$s^{-1}. All samples were illuminated with UV for 6 h. With such duration of illumination the maximum degree of radiation damage in ion tracks is provided [4,5]. As a solvent the dymethylformamide (DMF) was chosen. This solvent noticeably increased the track etching rate [15–19]. Before etching, a half of samples were soaked in DMF for 15 minutes at the room temperature. The soaking was conducted by immersing the samples in the DMF solution. After DMF treatment the samples were dried out with filtering paper. As the etchant 0.5 N and 2 N solutions of NaOH were used, and the etching was carried out at 55°C and 70°C. For examining the dependence of the pore diameters on the etching duration two samples were etched simultaneously during the same etching period: one was illuminated with UV and treated with DMF (first mode of sensitization), the other was just UV illuminated (second mode of sensitization). Pores in the bulk and on the surface of films were studied by scanning (SEM, JSM-840) and transmission (TEM-125) electron microscopes. For investigation of pores in the bulk of films the etched samples were cleaved in liquid nitrogen. The pore lengths on the cross-section of the film were measured. The duration of etching after which the pores become through (similarly to [1]) we will denote as breakthrough time. In order to find the breakthrough time we etched a large number of samples simultaneously removing them in turns one by one with the interval of 5 minutes (for 0.5 N etchant) and 3 minutes (for 2 N etchant). The pore diameters were measured on the film surface by TEM (with shadow replica method). The replicas were prepared in the following way. In vacuum of 10^{-3} Pa, a gold was deposited at an angle of 10° with respect to the sample surface. The deposited gold formed an island film characterized by islands of radius and separation 5 nm. In the area of pores gold was absent as it caved into the pores. Finally, a carbon layer of 40 nm thickness was deposited on the film surface. The carbon layer together with the

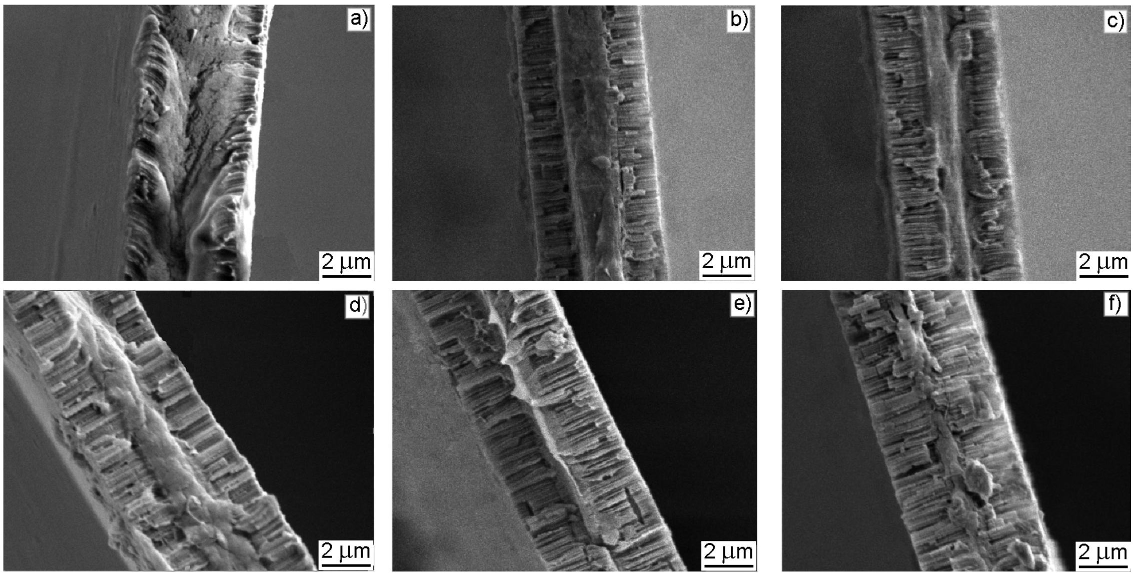

Fig.1. Pores in the cross sections of PET films that were etched in 0.5 N solution of NaOH at 55°C for 2.5h (a, d), 3.5h (b, e) and 3.75h (c, f). The upper row — UV sensitization, the lower row — sensitization with UV and DMF.

gold islands was peeled from PET film surface and examined by TEM.

For both modes of sensitization, the dependence of pore diameters on the film surface and their length on the cross sections on the etching duration was studied. It was found that under same conditions of etching the pore diameter is larger in samples which were soaked in DMF. We present the results obtained in the course of film etching in 0.5 N и 2 N etchants separately. Pores on the cross-section of the films depending on the sensitization method and etching duration at 55°C are shown in Fig. 1. The pores are seen as dashes perpendicular to surfaces. It is seen that with each etching duration the pore length is larger in the samples treated with DMF (first mode of sensitization). After etching for 2.5 h, in UV irradiated samples the pores were etched only near the surfaces (Fig. 1a, upper row). With the same etching duration in the samples soaked in DMF the pores were etched by one third of the film thickness (Fig. 1d, lower row). After etching for 3.45 h, in samples soaked in DMF throughgoing pores were etched (Fig. 1f, lower row); without DMF treatment in the middle of the cross section area a non-etched area remained (Fig. 1c, upper row).

We found that at 55°C the breakthrough time for the first sensitization mode was (200±10) min, and for the second one — (270±10) min. Knowing the breakthrough time we can evaluate the track etch rate for both sensitization conditions. We think that for this time the tracks were etched by a half of the film thickness. It appeared that for the first sensitization mode this rate is 15 nm/min, and for the second — 11 nm/min. For both sensitization modes the data on pore lengths are given in Fig. 2. It is seen that the etch rate is almost 1.5 time larger in the samples treated with DMF. Such influence of DMF on the etch rate of Ar ion tracks is much less than that observed in [15] where treatment with DMF increased the etch rate of Ar ion tracks in polyester by the factor of 37. This difference can be caused by the following reasons:

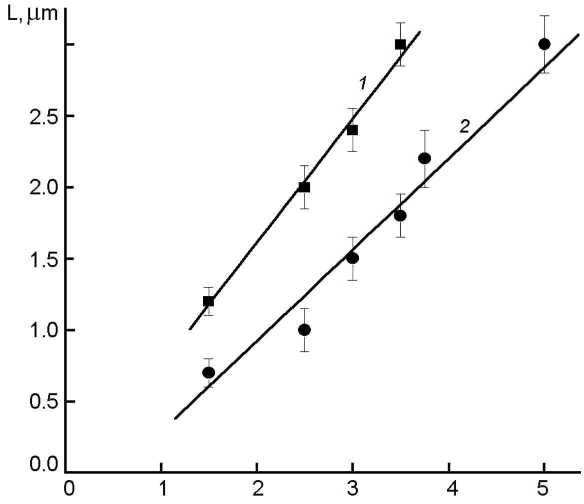

Fig.2. Dependence of the pore length at the cross sections of PET films on the etching duration and sensitization method: *1* – *UV* and *DMF*, *2* – sensitization with UV only.

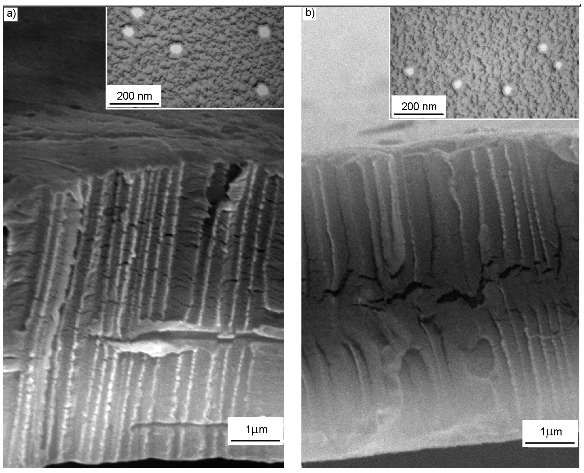

Fig.3. Pores in the cross sections and the surfaces of PET films that were etched in 0.5 N solution of NaOH for 2.5h: (a) — the film was etched after the first sensitization mode, (b) — after the second sensitization mode.

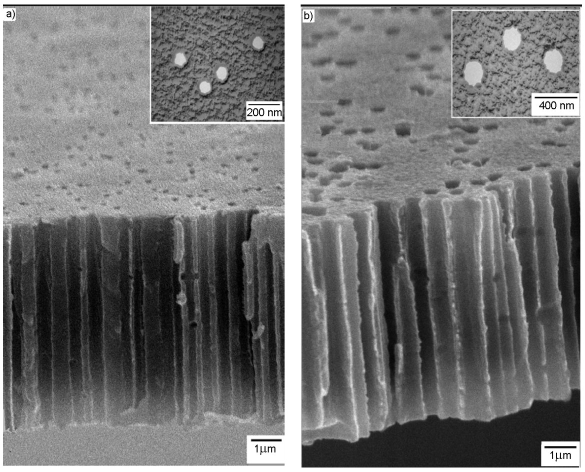

Fig.4. Membranes obtained by etching the PET films in 2 N solution of NaOH for 20min (a) and 40min (b) after the first sensitization mode.

in [15] the energy of Ar ions was significantly higher than 1 MeV/u which leads to high energy losses, that is, to higher damage in the track zone. In [15] treatment with DMF was performed at higher temperature and etching was carried out in more concentrated etchant. Besides that, the etch rate depends on the polymer structure (density, admixtures, porosity etc). The structural difference of the film can also change the etching rate. In [15] it was not indicated which kind of polyester was studied.

The average pore diameter was calculated by averaging diameters of no less than 50 pores on the film surface. Information about the pore diameters depending on duration and temperature of etching is summarized in Table 1(diameters of through-going pores are given in bold). It is seen that for all etching durations the pore diameters are larger in samples treated ac-

Table 1. Dependence of the pore diameters (*d*) on the sensitization mode, temperature (*T*) and etching duration (*t*) in solutions of NaOH

T = 55°C; 0.5 N, of NaOH				
t, min	210	225	255	270
d, nm (UV, DMF)	**65 ± 10**	**75 ± 10**	**110 ± 10**	**130 ± 10**
d, nm (UV)	40±10	50±10	80±10	100±10

T = 70°C; 2 N, of NaOH							
t, min	130	150	180	210	240	270	300
d, nm (UV, DMF)	40±10	**50±10**	**70±10**	**120±10**	**200±20**	**270±20**	**350±20**
d, nm (UV)		40±10	50±10	**80±10**	**120±20**	**180±20**	**220±20**

55°C; 0.5 N, of NaOH						
t, min	30	50	70	90	120	240
d, nm (UV, DMF)	**70±20**	**110±20**	**170±20**	**230±20**	**300±30**	**520±30**
d, nm (UV)		60±20	80±20	130±20	190±30	400±30

70°C, 2 N; of NaOH							
t, min	15	25	35	45	60	120	150
d, nm (UV, DMF)	**60±20**	**100±20**	**200±20**	**250±30**	**300±30**	**480±30**	**530±30**

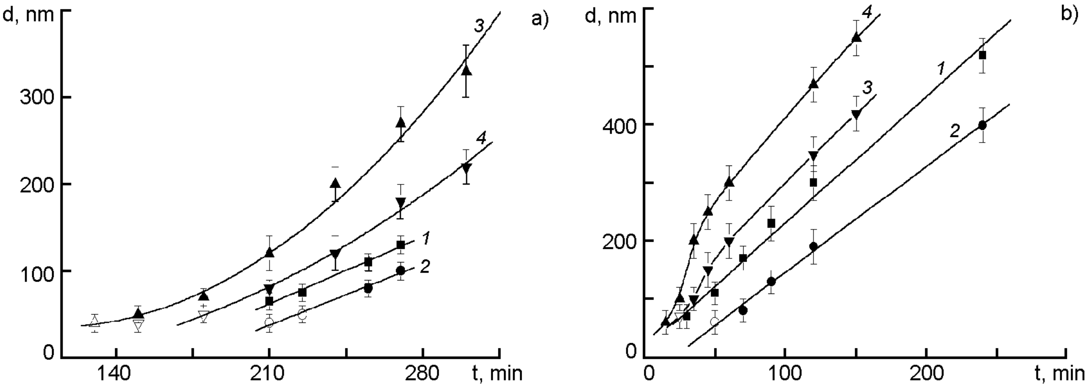

Fig.5. Dependences of the pore diameters on the sensitization mode, duration and temperature of etching in 0.5 N solution of NaOH (a) and 2 N solution of NaOH (b). White dots corresponds to not through pores; *1* – 55 °C, UV, DMF; *2* – 55 °C, UV; *3* – 70 °C, UV, DMF; *4* – 70 °C, UV.

cording to first sensitization mode. Increasement of the etching temperature to 70°C allowed obtaining through-going pores of smaller sizes than those of the pores obtained at 55°C. In Fig. 3 pores at the cross sections and surfaces of films etched in the same etchant are given. It is seen that in the sample treated with DMF through pores were formed (Fig. 3a). In the sample that was not treated with DMF the untreated area remains in the middle of the cross section (Fig. 3b). It is seen that pore diameters are larger in the sample treated according to the first method of sensitization. All the pores are round in shape. Their diameters are (50±10) nm in the case of the first sensitization mode and (40±10) nm in the second. However, the pores in the sample that was not treated in DMF are not through (Fig. 3b).

It was found that in 2 N etchant the rate of etching through-going pores is much larger than in 0.5 N etchant. In the films treated according to the first sensitization mode through pores 60±20 nm in diameter are etched for 15 minutes at 70°C. Without DMF treatment through pores are formed only after etching for 30 minutes. In Fig. 4(a, b) pores at the cross sections and surfaces of the films treated according to the first sensitization mode and etched for 20 minutes (a) and 40 minutes (b) at 70°C are shown. The average pore diameter in these films appeared to be 55 nm (Fig. 4a) and 170 nm (Fig. 4b). It is clearly seen that the pores have a regular round shape and the same diameter through the total bulk of the film. It is seen that with the same etching duration pores are almost twice as large in the case of etching at 70°C (Table 1).

Let us compare our data on etching of Ar ion tracks with the data on etching tracks of heavier ions [1]. In [1] PET films were irradiated with different heavy ions, and information about pore diameters were obtained by measuring electric conductance of the samples in the course of etching in 0.1 N solution of NaOH at 80°C. Authors observed three stages of etching. The first stage corresponds to etching the track core. At this stage the track core 10–15 nm in diameter is etched through. The highly damaged track core manifests itself on the etching curve as a sharp increase in the pore diameter. The second stage corresponds to etching the track halo — area surrounding the track core. In the track halo the etching proceeds at a rate that slowly increases approaching a constant value at large radii. Then the third stage begins that corresponds to etching undamaged polymer where the radial etch rate is a constant value. This value is higher than the etch rate of halo but lower than the ecthing rate of track core.

The pore diameter as a function of etching time and temperature for our data is shown in Fig. 5(a, b). It is seen that at 55°C pore diameters grow linearly with etching duration in both etchants. At this temperature the etching process runs slowly. The pores become through when their diameters are much larger than the halo diameter. Deviation from linearity is observed at 70°C in the region of small diameters. It should be noted that this deviation is different for 0.5 N and 2 N etchants. This deviation is espe-

Table 2. Breackthrough time (τ), the linear (ν_l) and radial (ν_r) etching rates of the pores in solutions of NaOH depending on etching temperature (T) and sensitization mode.

0.5 N, of NaOH				
T°C	τ, min	ν_l, nm/min	ν_r, nm/min	ν_l/ν_r
55°C (UV, DMF)	200	15	0.15	100
70°C (UV, DMF)	140	21.5	0.18	119
55°C (UV)	270	11	0.16	69
70°C (UV)	200	15	0.175	80
2 N, of NaOH				
T°C	τ, min	ν_l, nm/min	ν_r, nm/min	ν_l/ν_r
55°C (UV, DMF)	30	100	1.16	86
70°C (UV, DMF)	15	21.5	2.0	100
55°C (UV)	70	43	0.57	75
70°C (UV)	30	100	1.16	86

cially clearly seen for samples treated according to the first sensitization mode. In the case of 0.5 N etchant, the pore diameter slowly increases at the initial stage. Constant etch rate would be reached only after pore diameters become ≥100 nm. In the course of etching in 2 N etchant the pore diameter grows quickly with etching duration and constant rate would be reached after the pore diameter is ≥200 nm. Several factors can possibly cause the different behavior of the etching curves at 70°C in 0.5 N и 2 N etchants. Behavior of the curves may depend on different rates of the fresh etchant supply in the case of etching in solutions of different concentrations. We did not carry out these studies. The pore sizes should also depend on the relation of the core etching rate, area of halo and un-irradiated film areas in the etchant of different concentrations. Possibly in the 0.5 N etchant the stage of slow etching corresponds to etching the halo regions in the Ar ion tracks. We do not observe the first fast stage of etching as it was observed in [1]. It may be associated with the fact that the radiation damage in the Ar track core is much less than in the core of heavy ion track. Besides that, the Ar ion core track diameter is very small: about 7 nm [1]. Pores of such small diameter are not through-going. If the halo diameter is much larger than the core diameter it is possible to observe changing of the radial etch rate associated with etching the halo area. As well as in [1], in the halo area the radial rate slowly increases approaching a constant value in the undamaged area around the halo. In 2 N etchant we do not observe the stage of slow rise of pore diameter. The possible reason of this difference may be associated with the fact that 2 N etchant is much more aggressive than 0.5 N etchant. High radial and linear rates of etching leads to the fact that both the track core and the halo were etched off completely at the initial stage of etching. After that the etching process runs at a constant rate. From the dependences given in Fig. 5 we can conclude that the diameter of the Ar ion tracks halo is rather large. Nevertheless we are not acquainted with the works where propagation of the radiation inducing cross-linking of polymer molecules at irradiation by Ar ions is studied. In the case of the heaviest ions the track halo was detected at a radial distance as long as 100 nm.

Knowing the breakthrough time and diameters of the pores etched during this period, we can estimate radial and linear rates of pore etching. The linear etch rate was determined as $h/2\tau$, where h is the film thickness and τ is the breakthrough time. The radial etching rate was determined as the ratio of the minimal radius of a through-going pore to the breakthrough time. It should be noted that such estimation of the radial etching rate is made without account of the fact that radial rates of the track core and the halo may be rather different. Our estimations give the average radial rate of the formation through pores of the minimal diameter. Data on the breakthrough time, radial and linear rates of pore etching for both methods of sensitization are summarized in Table 2. In the right columns of Table 2 the ratio of the linear rate to the radial rate are given. It is seen that this ratio is much larger for the first sensitization mode. High linear rate of track etching at the first sensitization mode enables obtaining narrow through-going pores.

In conclusion, treating PET films with dimethylformamide increases both linear and radial rates of Ar ion track etching; but growth in linear etch rate appeared to be higher than the radial one. This allows obtaining track-etched membranes with pore diameters ranging from 50 nm to several micrometers.

In the 0.5 N etchant increase in pore diameters runs slowly that allows obtaining membranes with pores which diameters differ by a small value of about 10 nm (see Table 1). Low radial rate of etching provides a possibility to observe the halo in the Ar ion track structure. The main drawback of using 0.5 N etchant is the prolonged time of etching through-going pores.

With etching in 2 N etchant the pore depth and diameter grow quickly. High radial and linear etch rates allow one to obtain membranes with different pore diameters during relatively short etching procedure.

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Отримання трековіх мембран з нанорозмірними порами на основі ПЕТ плівок, опромінених іонами Ar

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Методами електронної мікроскопії досліджено діаметри та глибину пор у процесі травлення поліетилентерефталатних плівок, опромінених іонами Ar з енергією 1 MeV/n. В якості травника використовувалися 0.5 N та 2 N розчини NaOH при 55°C та 70°C. Процес травлення прискорювався сенсибілізацією, яка полягала або в опромінюванні плівок УФ та вимочуванні у диметилформаміді (ДМФ) — перший режим сенсибілізації, або — лише в опромінюванні плівок УФ — другий режим сенсибілізації. Встановлено, що діаметр та глибина пор більші у плівках, оброблених за першим режимом сенсибілізації. Знайдено тривалість травлення (тривалість прориву), що необхідна для травлення наскрізних пор мінімального радіуса. Виконано оцінки лінійної та радіальної швидкостей травлення пор. Встановлено, що після обробки ДМФ лінійна швидкість травлення пор значно більша, ніж радіальна. Це дає можливість отримувати наскрізні пори діаметром $\geq$ 50 нм.