NUKLEONIKA 2012;57(4):575–579

ORIGINAL PAPER

Nanopores with controlled profiles in track-etched membranes

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Abstract. Track-etched membranes are porous systems consisting of a polymer foil with thin channels-pores – from surface to surface. The increasing interest in this kind of material is connected with the development of nanoporous materials with unique properties such as diode-like effects in membranes with highly asymmetrical nanopores. The materials can be used for molecular sensors and atom beam optics, development of nanocapillary bodies for modelling the transport of molecules and ions in constrained volumes. Control over pore geometry opens the way to a number of new applications of track-etch membranes (TMs). The nanopores were obtained by the ion-track etching method using surfactant-doped alkaline solutions. Control over the pore profile and dimensions was achieved by varying the alkali concentration in the etchant and the etching time. The pore geometry was characterized in detail using field-emission scanning electron microscopy (SEM). SEM images of the surfaces and cleavages of TMs with different pore morphology are shown.

Key words: nanopore • scanning electron microscopy (SEM) • surfactant • track-etched membranes (TMs)

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Received: 9 September 2011
Accepted: 20 January 2012

Introduction

The production of the track-etched membranes is well known in membrane science. Latent ion tracks are the result of the passage of swift ions through solid matter, they can be etched selectively in many materials. As a result, conical, cylindrical or other shape channels can be obtained. The increasing interest in polymer track-etched membranes with nano-channels is connected with the development and creation of nanoporous materials with unique properties. The main directions of the research work include: (i) development of membranes with diode-like pores, highly asymmetrical nanopores for molecular sensors; highly asymmetrical nanopores for atom beam optics [1, 6], (ii) development of high-performance asymmetrical track membranes [1], (iii) study of propagation of X-rays and acoustic waves through track-etched membranes as model porous medium [7] and (iv) development of nanocapillary bodies for modelling the transport of molecules and ions in constrained volumes [6].

Ion and molecule transport, sensing and separation with nanopores are the potential applications of membranes. Narrow track-etched pores in a polymer have similar properties of biological ion channels [4, 13, 14]. It has been found that conical nanopores are cation selective and have diode-like voltage-current characteristics [4, 13]. Also the shape of pore tip determines the transport properties of the asymmetric narrow channels and, therefore, the control over the profile

of the asymmetric nanopores is of primary importance [5, 11]. But the exact dimensions of track etched pores, especially geometry of the pore tip are not known in many experimental works.

The process of polymer track-etched membrane is well known in the literature [1–4]: polymer foil is irradiated with accelerated heavy ions that must have enough energy to penetrate and to create latent tracks in the bulk of polymer foil to make it possible their subsequent etching process. The final results of this process – pores with predicted geometry – can be controlled in different stages of the production process, for example ion beam parameters (ions energy, ions density) and physicochemical treatment (sensitization, etching process parameters). Different etching methods have been developed to allow the enlargement of the cone angle [8, 12] or to form other than conical nanopores [2, 3].

Asymmetric pores have been produced by the surfactant-controlled etching of heavy ion tracks in a polymer foil. The formation of nanopores with different tip shapes is based on the interplay between the chemical attack by alkaline solution and the protection effect of surfactant. These two components of the etching solution diffuse into the pore at different rates, which results in the formation of a channel with a narrow neck at the surface. By varying the etchant component concentrations, it is possible to control the degree of tapering. A scheme of the etching process is presented in Fig. 1. The film surface on the one hand side become hydrophilic by photo-oxidation which prevents adsorption of surfactant and makes the surface more susceptible to chemical attack.

A key question is the detailed knowledge about geometrical characterization of the nanoporous materials produced by ion-track technique. High resolution SEM observations make it possible to reveal important features of asymmetric track membranes.

The goal of this work was to obtain pores in PET foils with new special shape – "bullet-like" tips with diameter in nanoscale. Nanopore membranes with tip geometries gradually changing from slightly tapered to highly tapered were produced and investigated. Geometric characteristics of the asymmetric nanopores including determination of the shape and the size of pore tip region are presented in this paper.

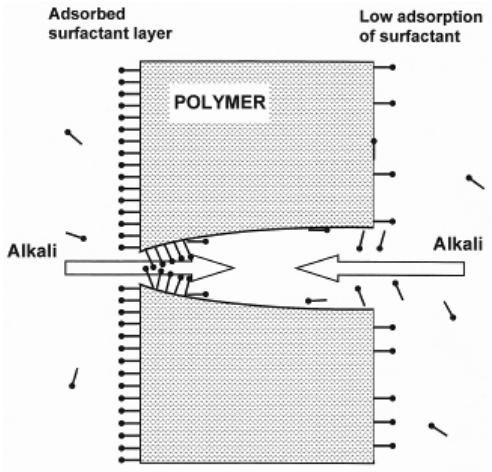


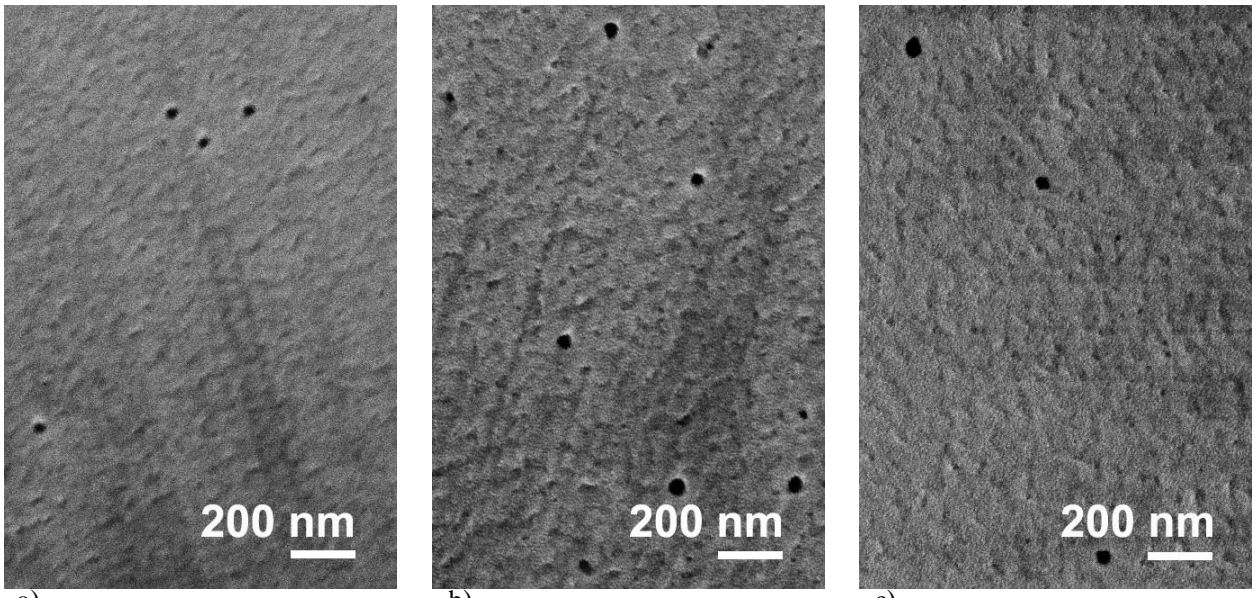
Fig. 1. Scheme of track etching in an ion-irradiated polymer film in the presence of nano-sized surfactant molecules.

Experimental

For fabrication of the membranes the method – described in details previously – was employed [1, 3]. Polyethylene terephthalate (PET) film 12-μm thick (Hostaphan RNK, Mitsubishi Polyester Films) was irradiated with accelerated heavy ions: 170-MeV Xe-ion beam with an ion fluence in the range of 5×10^4 to 1×10^8 cm^{-2} from the IC-100 accelerator at the Flerov Laboratory of Nuclear Reactions (Dubna, Russia). IC-100 heavy ion cyclic implanter is designed for acceleration of ions from carbon ($^{12}C^{+2}$) to argon ($^{40}Ar^{+7}$) with a fixed energy of 1.2 MeV/nucl at high frequency (HF) system forth harmonic and of 0.6 MeV/nucl at HF sixth harmonic. IC-100 main parameters are as follow: (i) accelerated ions: $^{22}Ne^{+4}$, $^{40}Ar^{+7}$, $^{56}Fe^{+10}$, $^{86}Kr^{+15}$, $^{127}I^{+22}$, $^{132}Xe^{+23}$, $^{132}Xe^{+24}$, $^{182}W^{+32}$, $^{184}W^{+31}$, $^{184}W^{+32}$, (ii) range of accelerated ions A/Z = 5.545.95, (iii) ion energy 0.9÷1.1 MeV/nucl, (iv) uniformity of track membrane pore density ±10%. Special purpose beam transportation line with a polymer film irradiation unit has been created. The 320-mm wide and several metres long film was transported at a constant speed across the scanning ion beam. A scanning system provided a homogeneous distribution of ions over the target. In the next step of asymmetric membrane production one surface of the irradiated foil was exposed to ultraviolet (UV) radiation from a source (LE-30 lamp, LISMA, Russia) that provided approximately 3 W·m^{-2} and 4 W·m^{-2} of electromagnetic power in ranges B (280 to 320 nm) and A (320 to 400 nm), respectively, on the specimen surface area. After UV exposure, the samples were etched during different times with sodium hydroxide solutions to which 0.05% (w/w) Dowfax 2A1 (Dow Chemicals) was added at a constant temperature of 60°C. Alkaline solutions with NaOH concentrations of 4M, 5M and 6M were used to produce membranes with gradually increased tapering of the pore tips. After etching, the samples were rinsed with ultra-pure water and air-dried. Parameters of etching process are presented in Table 1. The etched samples with a high pore density (1×10^8 cm^{-2}) were examined using an LEO 1530 (Zeiss, Germany) field-emission scanning electron microscope (FESEM). Small pore density and pore diameters (tip region) were estimated by observing the membrane surface. The pore profiles were determined via imaging of fractures of the samples. A special technique was used to render the polymer brittle and avoid residual strain in the fractured specimens [9, 10]. The technique entails the degradation of the membrane matrix under exposure to soft UV light, such that the sample becomes as brittle as glass without alterations in the pore structure. The fractures with pore channels cleaved along

Table 1. Etching conditions for samples with different pore geometries

Etching time	Concentration of NaOH in surfactant-doped etchant		
	4M	5M	6M
T1	4 min 12 s	3 min 30 s	2 min 30 s
T2	6 min	5 min	3 min 30 s
T3	7 min 48 s	6 min 30 s	5 min
T4	9 min 36 s	8 min	6 min 30 s



a) b) c)

Fig. 2. FESEM images of small-pore-size surface of membranes with profiled pores etched in surfactant-doped alkaline solutions: (a) 4M NaOH, 7 min; (b) 5M NaOH, 6.5 min; (c) 6M NaOH, 5 min.

Table 2. Pore radii (nm) in membranes with different pore profile

Etching time	Concentration of NaOH in surfactant-doped etchant		
	4M	5M	6M
T1	60	83	67
T2	90	110	109
T3	100	140	173
T4	137	161	205

the axes were observed and analysed. The surface of the observed samples was coated with a thin layer of gold (10 nm) obtained using a thermal evaporation method with vacuum evaporator (JEE-4X, JEOL, Japan). Based on the results obtained in [9], we assumed that a thin layer of cover we made would not lead to a reduction in the pore openings on the surface.

Results and discussion

As a result of PET foil Xe-ions irradiation, one-side UV irradiation and etching using NaOH with surfactant addition a set of membranes with different size and shape of pores was obtained. The FESEM images of the small pore size surface showing the pore tip diameters are presented in Fig. 2. Several tens of pores were measured in each membrane. The average values of pore radii for obtained membranes are presented in Table 2. Obtained values of main pore radii depend on both parameters of etching procedure: etching time and concentration of NaOH in surfactant-doped etchant. The experimental factors that contributed to random uncertainties are estimated as follow: (1) pore density, ±6%, (2) sample thickness, ±3% and (3) specific conductivity ±3%. Independent uncertainties associated with factors 1, 2 and 3 were combined in quadrature to provide an estimate of random error in the main pore radii in membranes measurements of ±5%.

With the etching conditions used, such pore shape control was possible that the channels with different longitudinal profiles could be produced [2]. Figure 3 shows a fracture of the asymmetrical track-etched membrane. The fracture surface is perpendicular to membrane surfaces. It can be clearly seen a full length of parallel pore channels. The channel consists of a cylindrical part and of the tapered part that is bullet-like in shape.

The FESEM images of pores with highly tapered tips with the bullet-like shape produced by etching at three different alkali concentrations are shown in Fig. 4. It can be clearly seen that the use of the lower alkali concentrations (4M and 5M) provides a less pronounced bullet-like tip. The details of the pore geometry can be also seen in Fig. 5 where fracture of the membrane is presented at higher magnifications. However, the diam-

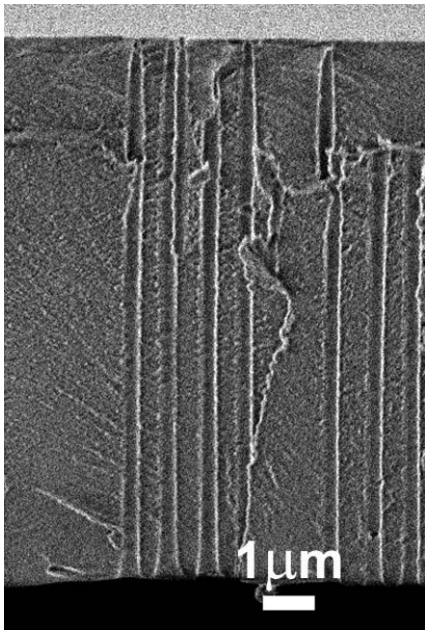


Fig. 3. SEM image of profiled asymmetric pore etched in surfactant-doped alkaline solutions 6M NaOH, 5 min.

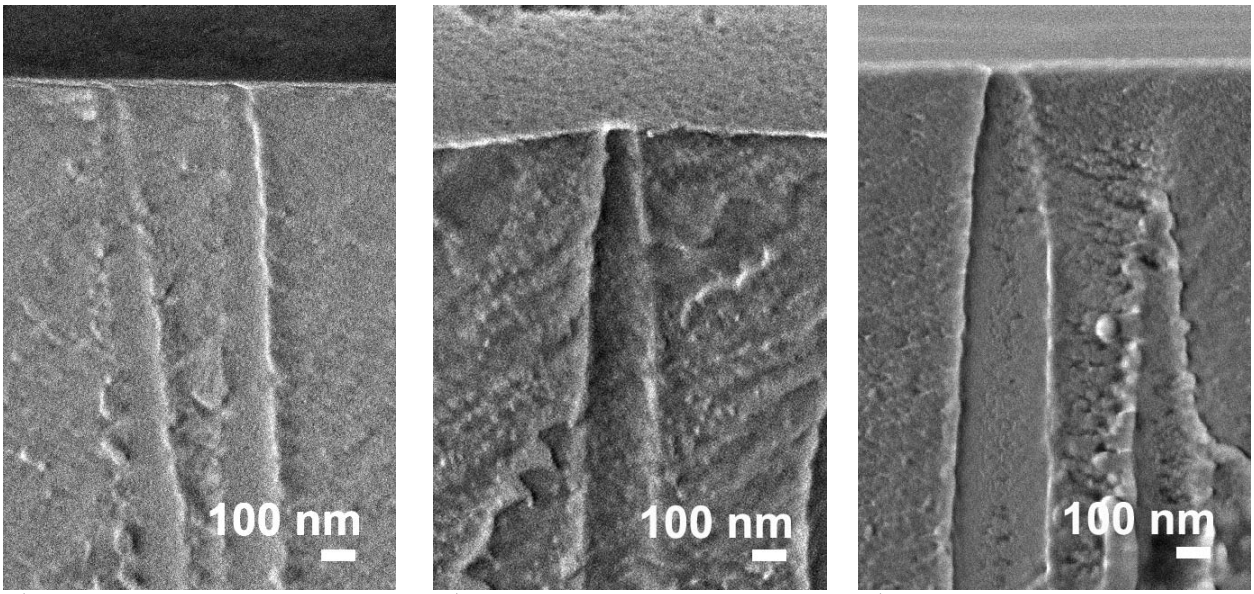


Fig. 4. FESEM images of typical pore tip in membranes obtained by etching in surfactant-doped alkaline solutions: (a) 4M NaOH, 7 min; (b) 5M NaOH, 6.5 min; (c) 6M NaOH, 5 min.

eter of the pore mouths cannot be determined on the fractured pores. Apparently, the lips of the sectioned pore mouths were strained and destroyed in the process of fracturing. The visible size of cleaved pore mouth is noticeably larger than the size of the pore entrance on the surface. The FESEM image presented in Fig. 5 illustrates this situation. One pore cleaved along the axis is visible at this photo. The bullet-like shape of the pore tip as well as the pore mouth can be seen. An arrow in the picture points to the position of the other pore entrances.

From the images of membrane fractures, one can extract quantitative information on the pore profile. The pore profiles imaged, using FESEM were analysed to find a quantitative relationship between the pore radius a and the distance x from the surface. The data measured for several single channels were averaged to obtain a profile typical for used etching conditions. The samples etched with 4M, 5M, and 6M NaOH were analysed. Experimentally obtained tip profiles of the observed membranes are presented in Fig. 6. The pore profile $a(x)$ was fitted using an exponential function suggested by Ramirez [11]:

$$a(x) = a_R - (a_R - a_L) \exp[-(x/d)^n (d/h)^n]$$

where: a_R – pore diameter on the foil side exposed to UV irradiation after etching process, a_L – pore diameter on the foil side not exposed to UV irradiation after etching process, d – pore length; it means thickness of used polymer foil, n and h – parameters of the pore profile; here: $n = 1$.

Profiles shown in Fig. 6 were calculated using this equation. The fitting curves (lines) and obtained experimental data (points) are presented in the diagram. The geometrical parameter h was found to be 570 ± 24, 790 ± 100 and 840 ± 40 nm taking into consideration

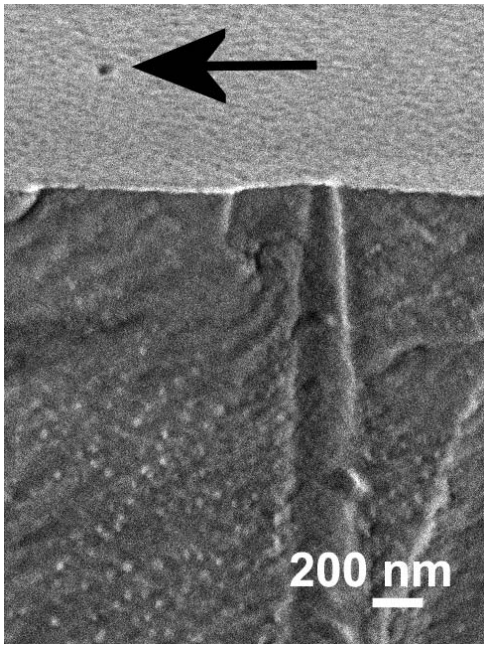


Fig. 5. FESEM image of pore tips in a membrane obtained by etching in 5M NaOH 6.5 min. The black arrow indicates a pore entrance on the upper surface.

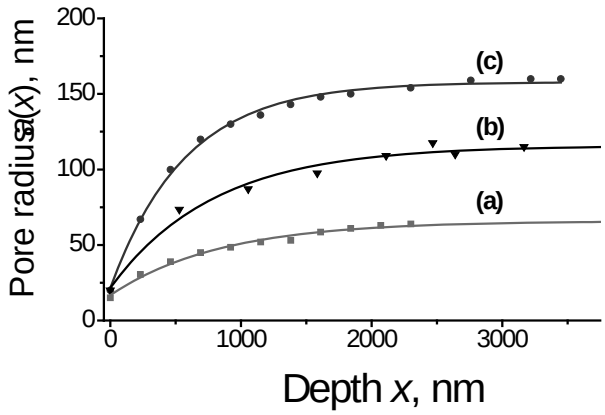


Fig. 6. Tip profiles of pores obtained by etching in surfactant-doped alkaline solutions: (a) 4M NaOH, 7 min; (b) 5M NaOH, 6.5 min; (c) 6M NaOH, 5 min.

accuracy of individual microscopic measurements for 6M, 5M, and 4M etchant concentration, respectively. The conclusion is: the higher the taper, the smaller is the value of the parameter h observed for the respective membrane series. The degree of tapering is correlated with the etching process conditions (etching solution concentration and time of etching process).

Conclusions

1. A surfactant-controlled etching method presented in this work allows us to control the shape of track--etched pores in polymeric – PET-membranes.
2. Use of the described controlled etching method can give pore channels unique properties with potential practical applications, for example: ultrafiltration and microfiltration processes, cation selectivity, mimicking the properties of biological ion channels, nanocapillary bodies for modelling molecules transport in constrained volumes.

Acknowledgment. This work has been partially supported by the cooperation programme between the Polish scientific institutes with the Joint Institute for Nuclear Research (JINR), Dubna, Russia in 2010, according to the subject number 04-5-1076-2009/2011. This work has been partially supported by the Polish Ministry of Science and Higher Education under project with decision 766/W-ZIBJ DUBNA/2010/0.

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