NUKLEONIKA 2009;54(3):157–161

ORIGINAL PAPER

Investigation on polycarbonate nanomembrane production based on alpha particles irradiation

Farhood Ziaie,
Muhammad Shadman,
Saeid Yeganegi,
Ali Mollaie,
Abbas Majdabadi

Abstract. Track-etched membranes were prepared in the Dosimetry Laboratory of Agricultural, Medical and Industrial Research School by exposing polycarbonate (PC) films with a thickness of about 20 μm to alpha particles emitted from ^{241}Am followed by chemical etching in sodium hydroxide (NaOH) at different temperatures and solution concentrations. The PC films were prepared using the method of chemical solving, forming and drying in a vacuum oven. The etching rate of PC was related to the concentration of etching solution, etching temperature and time. Therefore, a series of track-etched membranes were produced using different etching parameters. The relation between the etching rate and the etching parameters were established from experimental data and can be used to control the average pore sizes of the PC track-etched membrane. The pore sizes and their structures were studied by an optical microscope (OM) and a scanning electron microscope (SEM) and the obtained results indicated that the pores across the PC films are cylindrically shaped.

Key words: track-etched membrane • micro/nanofilter • alpha particles • chemical etching • polycarbonate

F. Ziaie✉, A. Majdabadi
Agricultural, Medical and Industrial Research School,
Nuclear Science and Technology Research Institute,
P. O. Box 31485-498, Karaj, Iran,
Tel.: +98 2614424073, Fax: +98 2614464058,
E-mail: fziaie@nrcam.org

M. Shadman
Agricultural, Medical and Industrial Research School,
Nuclear Science and Technology Research Institute,
P. O. Box 31485-498, Karaj, Iran
and Department of Physical and Inorganic Chemistry,
Mazandaran University,
Babulsar, Iran

S. Yeganegi
Department of Physical and Inorganic Chemistry,
Mazandaran University,
Babulsar, Iran

A. Mollaie
Science and Technology Unit,
Azad University,
Tehran, Iran

Received: 24 September 2008
Accepted: 23 April 2009

Introduction

Recently, extensive studies demonstrated the preparation of ion-track membranes produced from different polymers like polyethylene terephthalate (PET), polycarbonate (PC), cellulose nitrate and allyl-diglicol-carbonate [3, 6]. The nuclear track micro/nanofilter is a kind of novel material used successfully in various fields such as precise separation of biological cells, filtering of polluted air streams, microelectronics, pharmaceutical industry, biotechnology, waste water recycling and even fuel cells [1, 5, 7–11]. The pore size, shape and density can be varied in a controllable manner depending on the irradiation process parameters and chemical etching process so that a track-etched membrane with the required transport and retention characteristics can be produced. Parameters of etching process like temperature, pH and etching time, which should be experimentally defined, are the effective factors in production of pores [4]. Ionizing particles travel through polymers, displace electrons and produce localized chemical changes along the path where the particle travels. When the trajectory of a particle is defined by permanent physical or chemical damages, the disrupted regions surrounding the particle path can be chemically etched at rates faster than the surrounding

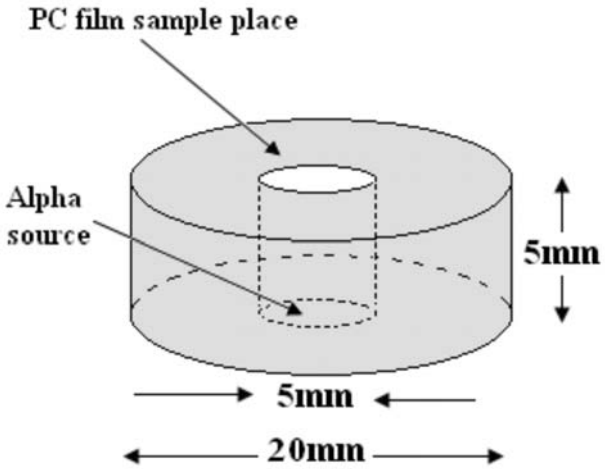

Fig. 1. Scheme of the brassy collimator, alpha particle source and PC film position.

Table 1. Alpha particle energies emitted from ^{241}Am

E_α (keV)	Branching ratio (%)	Half-life (years)
5544.50	0.36	
5485.56	85.10	456.6
5442.80	13.30	

undamaged material to produce microscopically visible tracks [2]. This is due to the fact that the track etching rate, V_t, is higher than the bulk etching rate, V_b, in the irradiated polymers.

In the present study, nuclear track micro/nanofilters are fabricated by exposing PC films to alpha particles emitted from ^{241}Am and subsequently followed by chemical etching with an alkaline solution.

Materials and methods

Materials

Polycarbonate film manufactured by General Electric (GE) with trade name of Lexan, with a thickness of 2 mm and a density of 1.2 g/cm^3 were used in this experiment. NaOH with 99% purity was used as the etching reagent and tetrahydrofuran (THF) was used as the polycarbonate solvent, both are provided by Merck Chemical Company, Germany.

Methods

Film thickness calculation

To calculate the energy loss of the alpha particles passing through the air contained in a collimator (Fig. 1), the SRIM code was used. The alpha particle energies emitted from ^{241}Am are denoted in Table 1. The stopping power for the most probable energy, 5.48556 MeV, calculated in air media was 0.16299 MeV/mm. Therefore, the amount of energy loss through 5 mm of air is 0.81495 MeV, and the remaining energy of alpha particles that reaches the PC film samples is 4.67061 MeV. Then, the SRIM code was used again for PC media, and the alpha particle maximum range obtained was 28.44 μm. Figure 2 shows the alpha particle trajectory through the PC film calculated by SRIM computer code. The result shows that the alpha particles with 4.67061 MeV of energy can pass through a 20 μm thick PC film.

Film casting and curing

A thick PC film was cut to small pieces to obtain mass values according to Eq. (1) presented below:

$$m\ [\mathrm{g}] = \rho\ [\mathrm{g/cm^3}] \times A\ [\mathrm{cm^2}] \times t\ [\mathrm{cm}] \quad (1)$$

where m is the PC required mass (47.1 mg), ρ is the film density (1.2 g/cm^3), A is the teflon mold area (19.625 cm^2), and t is the final film thickness (20 μm). The prepared mass of PC was dissolved in THF solvent and a layer of the solution was spread over the teflon mold and baked in a vacuum oven under 300 Torr pressure at an ambient temperature of 25°C for 3 h. The prepared film thicknesses were 19.6±1.5 μm.

Film irradiation

A cylinder shape brassy collimator with 5 mm and 20 mm inside and outside diameters respectively, hav-

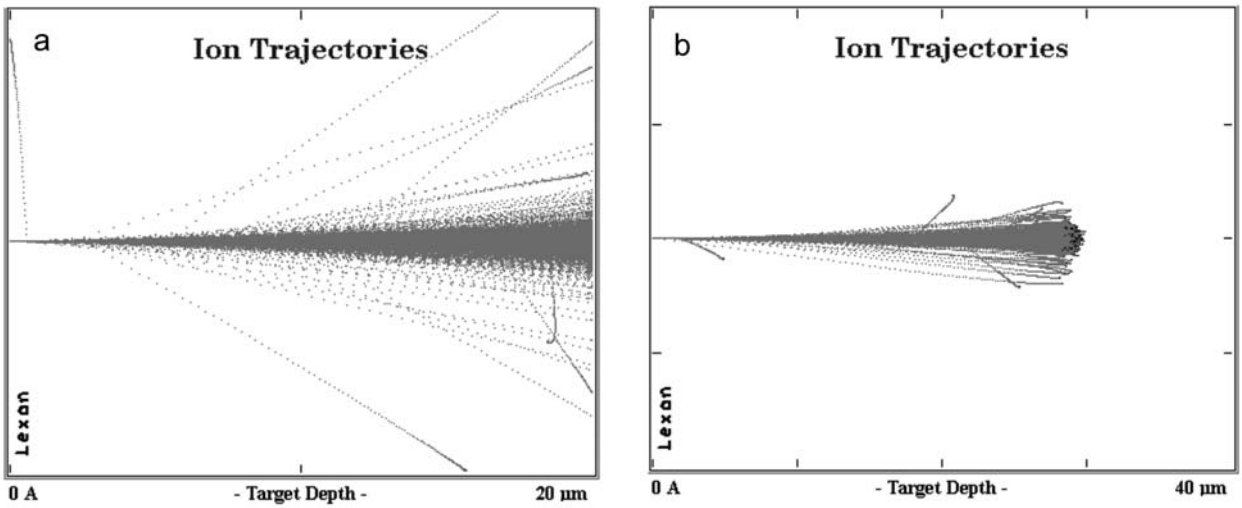

Fig. 2. SRIM calculation results of 4.6 MeV alpha particle trajectories in PC for film thickness of (a) 20 μm and (b) 40 μm.

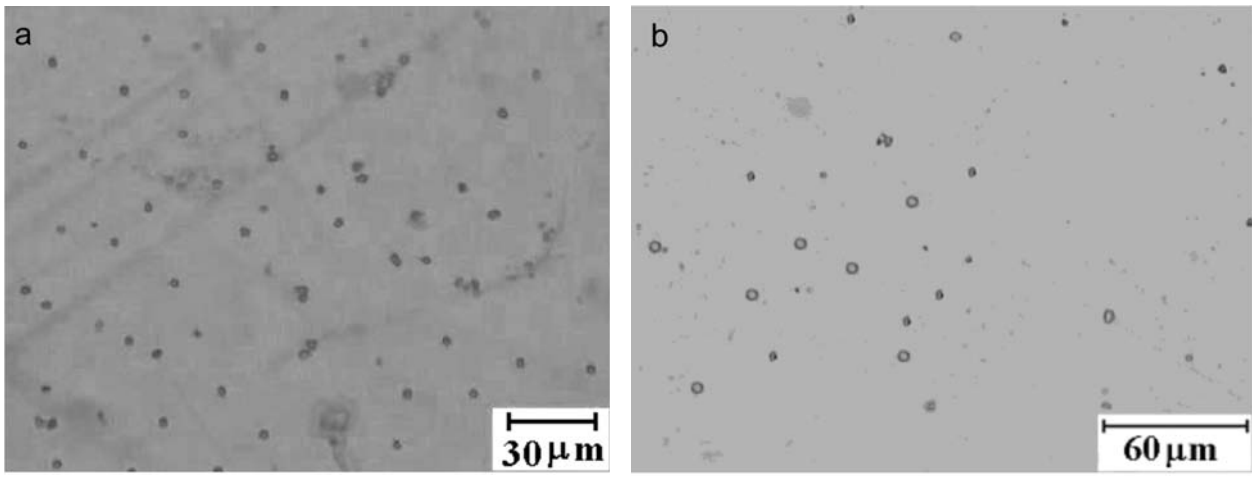

Fig. 3. OM images of the PC films surface etched in 4 N solution at 50°C during (a) 30 min; (b) 1 h.

ing a height of 5 mm was used to collimate the alpha particles emitted from an ^{241}Am source with an activity of 1 μCi (37 kBq) (Fig. 1). PC films were cut to pieces to cover the collimator internal diameter. Then, the films were placed perpendicularly to the alpha particle directions. Therefore, the latent tracks (not slanted) were created in the film. Therefore, according to the collimator geometry, the source activity and irradiation time (1 min), the projectile density of alpha particles on the film was obtained to be ~10^5 cm^{-2}.

Chemical etching procedure

The irradiated samples were etched in NaOH with normality of 2–7 N, an etching time of 1–120 min and an etching temperature of 30–80°C. During track etching, the damaged zone transforms into a detectable track [2]. The formed alkaline sediment on the film surface during the etching procedure was cleaned in distilled water using an ultrasonic system of FRITSCH Laborette 17 model and dried in an oven with an ambient temperature of 30°C for 10 min.

Imaging apparatus

The film samples were examined via an optical microscope (OM) OLYMPUS PMG3, made in Japan, and a scanning electron microscope (SEM), XL-30 model, made by Phillips Company, Holland.

Results and discussion

Figures 3 and 4 show the pores images created by alpha particles, which were taken by the OM and the SEM systems. The pores sizes were measured by the mentioned apparatus and the average value for each film was calculated.

The microscopic photographs of the track-etched membrane sample fractures are given in Fig. 5, as well. The picture shows the homogeneity of inside diameter of pores in the PC film. Variations of pore diameters against the etching time for normalities of the etching solutions at a constant temperature of 50°C were measured and the results are shown in Fig. 6a. It can be clearly seen that by increasing the etching time, the pore diameter increases, whereas further increasing of the etching time causes a decrease in the pore size and finally followed by an almost invariable value. In fact, there are two phenomena of etching and annealing (due to passage of time) at a fix temperature, which behave in reverse manners. At low etching times the etching process is dominant, while at higher etching times the annealing process is dominant. The pore size increases due to etching, while the annealing process decreases the pore size [2]. Therefore, one could expect to obtain a maximum value over the time. Figure 6b shows the precise behavior of low diameter pores with different scales. It is possible to prepare the PC track-etched membrane with lower pore sizes, however, the small pore observation requires HRSEM.

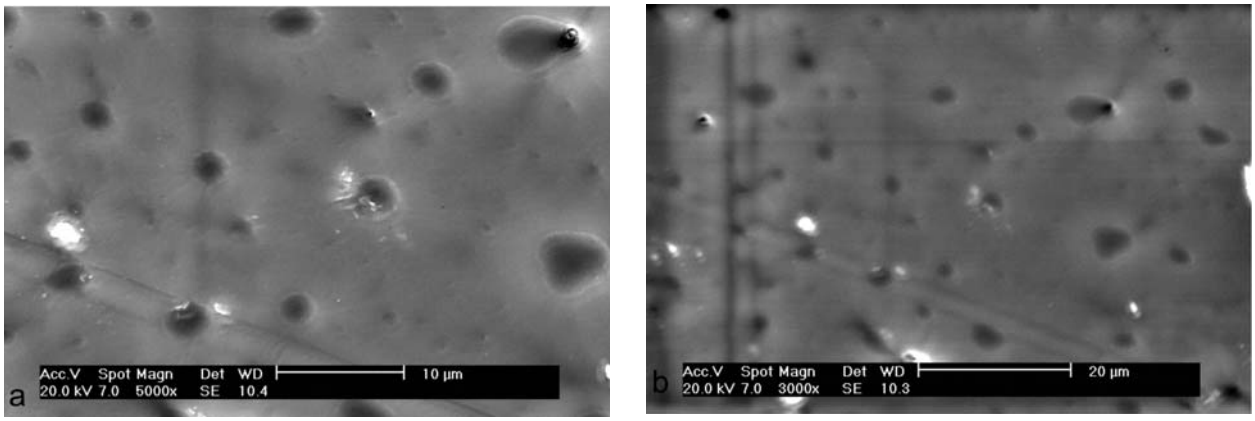

Fig. 4. SEM images of PC films surface etched in 10 min at 40°C with etching concentration 6 N (a and b).

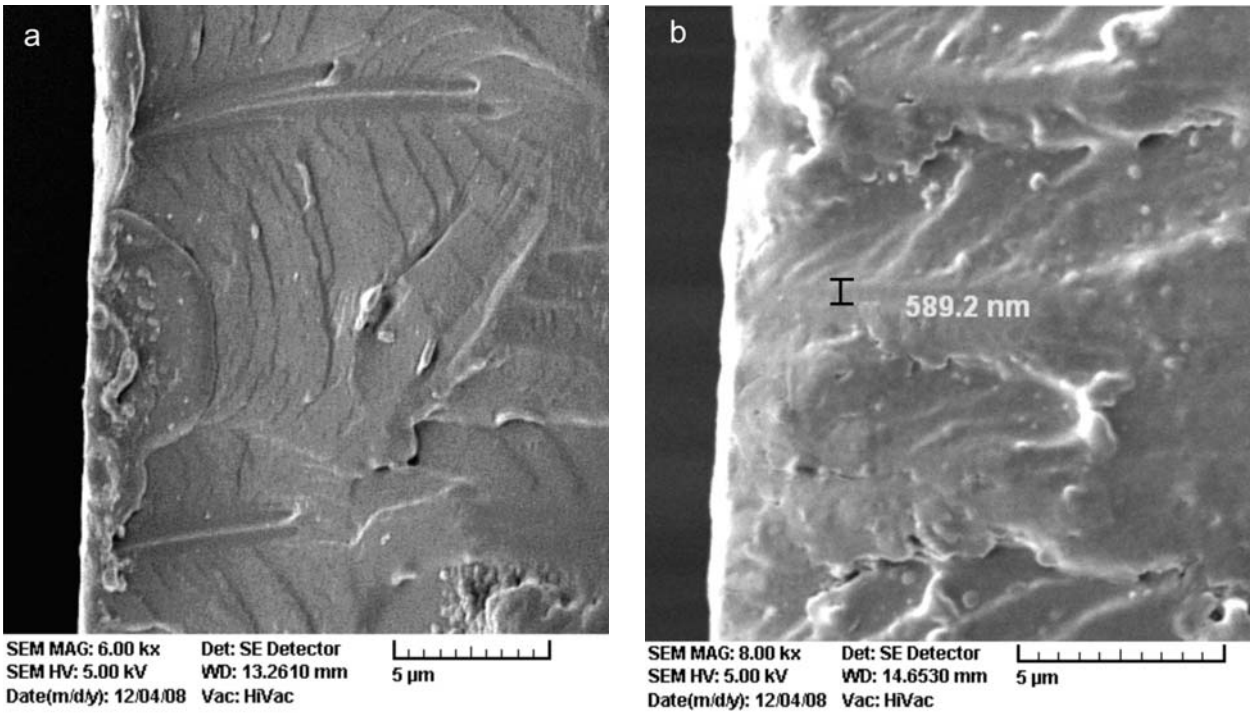

Fig. 5. SEM images of PC track-etched membrane sample fractures of the PC films etched in 1 min at 50°C with etching concentration of 7 N (a and b).

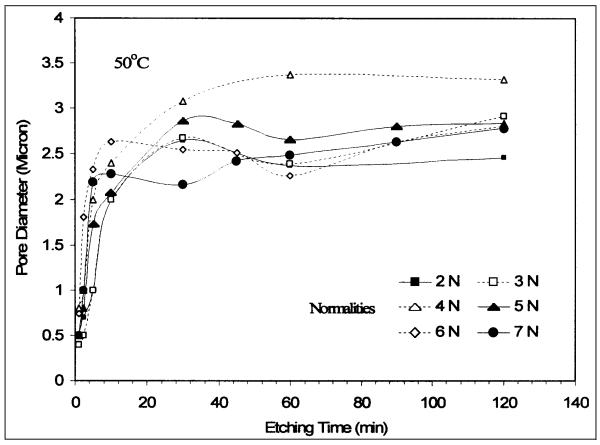

Fig. 6a. Variation of pore diameters against the etching time for normalities of the etching solutions at 50°C.

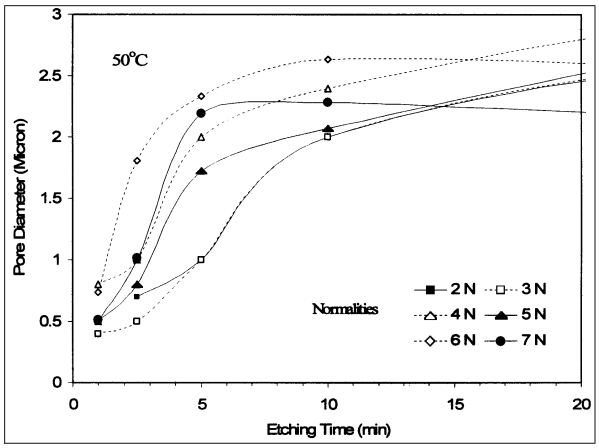

Fig. 6b. Variation of pore diameters against the etching time for normalities of the etching solutions at 50°C (different scales).

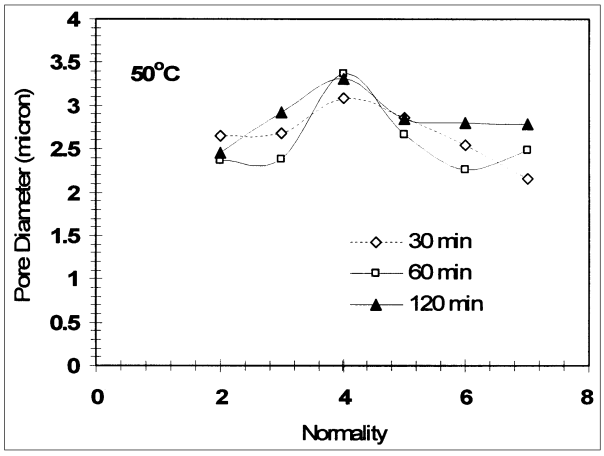

Fig. 7. Variation of pore diameters as a function of etching solution concentrations at 50°C.

The variation of a pore diameter against the solution concentration at 50°C was also investigated and the results are demonstrated in Fig. 7. The maximum pore size was obtained utilizing 4 N etching solution. Figure 8 shows the variation of the pore size vs. etching process temperature for different etching times of 15, 30, 45, and 60 min in a 5 N solvent concentration. The curve associated with an etching time of 30 min, is comprised of higher pore size curves associated with other etching times and are in agreement with those obtained in Fig. 6. The results also show that the pore sizes do not vary considerably due to increasing temperature and they seem to decrease at 80°C. This could be due to an increase in polymer chain mobility that is caused by rising temperature. However, in the author's view, the variations are not very considerable due to the range of uncertainty level, which here is estimated as 30%. In other words, in the applied temperature range it was

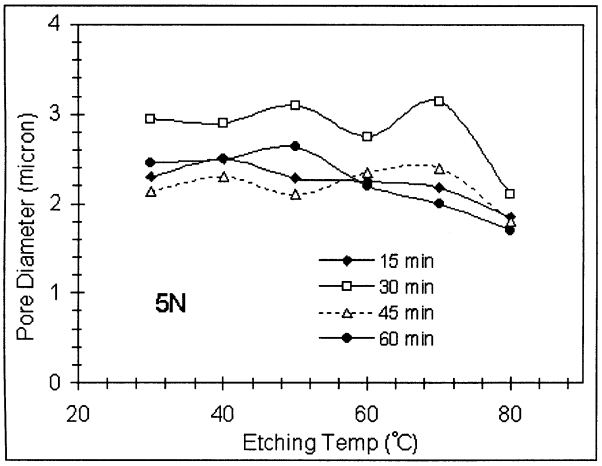

Fig. 8. Variation of pore diameters via etching temperature (etching solution concentrations is 5 N).

not expected to see the pore size variation due to the limitation of the sample thickness in our experiments, where, temperature raising would decrease the pore size due to the mentioned annealing process effect [4].

Conclusion

Increasing the etching time up to a definite value causes the pore diameters to increase. For the most cases, the pore diameters will decrease by further increasing the etching time, as well. At longer etching time, the pore diameters tend to be approximately invariable over time.

It also seems that after 1 h of etching time at the same temperature, the two processes of etching and annealing reach an equilibrium status. Therefore, to create a maximum pore diameter in the PC film, the normality of the etching solution could be chosen as 4 N at the etching time of 30 min. The pore size does not vary considerably due to increasing the temperature up to about 80°C. Uncertainty of about 30% was obtained via the standard deviation calculation of the pore size measurement. It can also be concluded that controlling the pore diameters will be possible by changing the etching parameters like time, temperature and etchant solution concentration.

References

1. De'jardin P, Vasina EN, Berezkin VV, Sobolev VD, Volkov VI (2005) Streaming potential in cylindrical pores of poly(ethylene terephthalate) track-etched membranes: variation of apparent zeta potential with pore radius. Langmuir 21;10:4680–4685
2. Durrani SA, Bull RK (1985) Solid state nuclear track detection. Pergamon Press, Oxford
3. Ferain E, Legras R (2001) Pore shape control in nanoporous particle track etched membrane. Nucl Instrum Methods Phys Res B 174;1/2:116–122
4. Fischer BE, Spohr R (1983) Production and use of nuclear tracks: imprinting structure on solids. Rev Modern Phys 55;4:907–948
5. Ho JPY, Yip CWY, Koo VSY, Nikezic D, Yu KN (2002) Measurement of bulk etch rate of LR115 detector with atomic force microscopy. Radiat Meas 35:571–573
6. Nikezic D, Yu KM (2004) Formation and growth of tracks in unclear track materials. Mater Sci Eng R 46:51–123
7. Rzepka S, Neidhart B (2000) Transport processes through track-etch membrane filters in a reagent delivery cell. Fresenius J Anal Chem 366;4:336–340
8. Suzuki Y, Yamaki T, Koshikawa H *et al*. (2007) Preparation of ion-track membranes of poly(p-phenylene terephthalamide): control of pore shape by irradiation with different ion beams. Nucl Instrum Methods Phys Res B 260:693–695
9. Varobiev ED, Ovchinnikov VV, Shestakov VD (1989) Some peculiarities of use of the polymeric nuclear track membranes in clean rooms. JINR Report 18:89–529
10. Vater P (1988) Production and applications of nuclear track microfilters. Radiat Meas 15:1/4:743–749
11. Yamazaki IM, Paterson R, Geraldo LP (1996) A new generation of track etched membranes for microfiltration and ultrafiltration. J Membr Sci Part I 118;2:239–245