Arcada Working Papers 11/2014
ISSN 2342-3064
ISBN 978-952-5260-53-3

Track-etched ultrafiltration polymer membranes produced by light ion irradiation*

Stewart Makkonen-Craig[i], Ksenia Yashina[ii], Mikael Paronen[iii]

Abstract

Ultrafiltration (UF) membranes are central to filtration systems used extensively in industrial and communal water treatment processes and also in desalination pre-treatment. We have aimed to develop a new class of UF membranes with improved separation performance and efficiency, so to reduce substantially operational energy consumption and reliably remove targeted pollutants. A suitable alternative to conventional UF membranes are controlled micro- and nanostructured porous track etch membranes that could optimize the efficiency of UF modules tailored to specific separation processes. We developed a new approach to the ion irradiation and etching of polymers resulting in viable track etching using only ultralight ions. SEM imaging has confirmed the presence of etched pores consistent with other reported track etch membranes. This breakthrough in developing a new production method significantly reduces investment production costs because it only requires a common type of small accelerator than has low running costs, frequently available beamtime and capacity for high membrane production volume.

Keywords: Energy Saving, Flat Sheet Membrane, Nanostructure Morphology, Pore Size Distribution, Water Treatment, Ultrafiltration

1 INTRODUCTION

Track-etch membranes (TEMs) offer distinct advantages over conventional polymer membranes due to their well-defined pore structures and monodisperse pore size distributions (Apel, Spohr 2001). Their pore sizes and pore densities are independently

* This work was supported financially by Fonden för Teknisk Undervisning och Forskning.
[i] (a) Department of Energy and Materials Technology, Arcada University of Applied Sciences, Helsinki, Finland, (b) Laboratory of Radiochemistry, University of Helsinki, Finland [makkonst@arcada.fi]
[ii] Department of Energy and Materials Technology, Arcada University of Applied Sciences, Helsinki, Finland [yashinak@arcada.fi]
[iii] Department of Energy and Materials Technology, Arcada University of Applied Sciences, Helsinki, Finland [paronem@arcada.fi]

controlled parameters during the production process (Figure 1), and can cover a wide range from a few nm to a tens of μm and $1–10^{10}$ cm^{-2}, respectively (Lalia et al. 2013), with membrane thicknesses of 5−50 μm. Furthermore, they are amenable to surface functionalization to improve chemical selectivity or permit stimuli-response (Ulbricht 2006, Cuscito et al. 2007, Geismann, Yaroshchuk & Ulbricht 2007, Friebe, Ulbricht 2007, Friebe, Ulbricht 2009, He et al. 2009, Kuroki et al. 2010).

TEMs are utilized in many niche applications from industrial and biomedical separations processes to nanotemplating (Belkova et al. 2009, Ferain, Legras 2009, Xavier et al. 2008, Koshikawa, Usui & Maekawa 2009, Hanot, Ferain 2009). However, their conventional production is too expensive for uptake in large-scale industrial and small-scale domestic water treatment. Therefore it is desirable to establish low-cost manufacturing methods to promote research and development of applications in membrane technology (Wanichapicharta et al. 2000, Apel 2003). The key initial manufacturing stage is ion irradiation of the polymer film at nuclear reactors or large accelerator facilities than incur large costs and lead times (Apel 2003). It is this stage that alone incurs costs prohibitive to nearly all industrial UF system consumers. Irradiation instead by light ions significantly reduces investment production costs because it only requires a common type of small accelerator than has low running costs, frequently available beamtime and capacity for high membrane production volume. The literature suggests that continuous etchable tracks are the preserve of energetic heavy ions (Trautmann 1995, Trautmann, Bouffard & Spohr 1996, Musket 2006). However, our experience with light ion irradiation of polymer films and concerns about inconsistencies in track threshold data (Fink 2004), led us to investigate the possibility of surpassing reported limits of track etchability with light ions.

The lower linear energy transfer (LET) thresholds for creating continuous etchable latent ion tracks in polymer films suited to perform as membranes are reported as 720-900 eV nm^{-1} for polycarbonate (PC), polyimide (PI) and polyethylene terephthalate (PET) (Musket 2006, Apel, Fink 2004). Such dense radiolytic damage necessitates irradiation with medium to heavy ions. We have adopted a modified approach to the ion irradiation and etching of polymers resulting in a significant lowering of the LET threshold for viable track etch membrane production. Combining a new ion irradiation method with a new etching technique, it is possible to yield track etch membranes from polymer films irradiated with ultralight ions that impart only 40 eV nm^{-1}. The physical and chemical mechanisms responsible in this development are under investigation.

2 EXPERIMENTAL METHODS AND RESULTS

2.1 Choice of polymer film

The criteria for a suitable film include chemical and mechanical stability (for robustness as an eventual membrane), availability as a thin film, sensitivity towards ion irradiation and chemically selective etching of ion tracks. Three polymers have dominated the TEM field: PC, PI and PET, with many other polymers finding niche applications (Apel, Spohr 2001, Fink 2004).

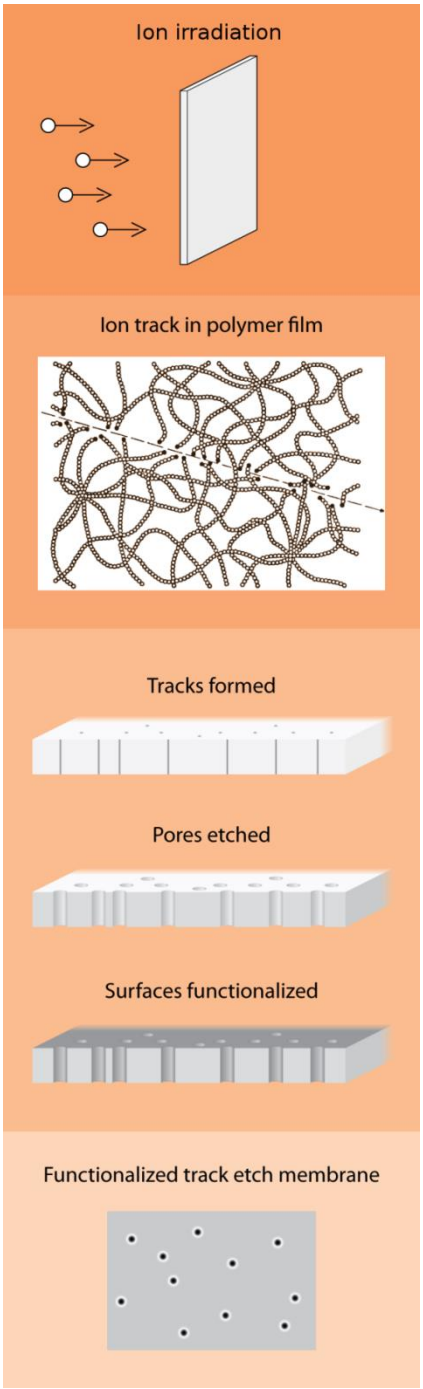


Figure 1. Principles of the functional track etch membrane fabrication process. A thin raw polymer film is exposed to high energy ions at an accelerator or nuclear reactor facility to create tracks along their trajectories (linear paths of radiolytic damage). Tracks are chemically more sensitive than their surrounding polymer matrix to chemical solvents. Thus the tracks can be preferentially etched away leaving discrete narrow linear pores.

Pore diameters can be controlled precisely by carefully selection of the etching conditions. It is the well-defined pore size and the narrow pore size distribution that make track etch membranes very attractive for separation processes.

To enhance separation selectivity the surface chemistry of these pores typically needs to be modified by integrating specific chemical functionalities. This is achieved, for example, by exposing the pores and/or planar surfaces to reactive chemicals that impart the desired functional groups.

We have not used PI and PET because of their unattainably high etching thresholds (900 eV nm^{-1}), i.e. the minimum radiolytic damage needed to yield a fully etchable track. Instead we have worked predominantly with polyarylate (PAR, product of polycondensation of phenolphthaleine and terephthalic acid) as an alternative to the conventional PC due the high temperature and tear resistance of PAR. The etching threshold is unknown for PAR, but we assume it to be equivalent or higher to that of PC (250 eV nm^{-1}). PAR has been used previously by other groups as starting material in TEM experiments (Apel, Titova & Tretyakova 1986, Zagurskii, Grebinskaya & Lavrentovich 1986, Cornelius et al. 2007).

Our starting material was a commercial 8 µm-thick PAR film (Aryphan, LOFO, Germany) that has robust mechanical properties and withstands temperatures up to 175°C. It is resistant to most acids and salts, but less so to alkalis and organic solvents. Importantly it has low water absorption, max. 0.25%, and thus is dimensionally stable.

2.2 Ion irradiations

PAR films were irradiated with deuteron ions from a small, fixed-energy biomedical cyclotron (Cyclone 10/5, IBA, Belgium) that was designed primarily for routine production of positron-emitting radionuclides used in radiopharmacy. Adaption to polymer film irradiations included construction of an external beamline, target system and associated optics (Figure 2).

Figure 2. Ion irradiation facility: 5 MeV deuterons were extracted from the cyclotron into an external beamline through a dipole switching magnet and to a target chamber with rolling film holder (right) all under a high vacuum.

To attain maximum efficacy, PAR films were irradiated at the highest possible LET from deuterons by selecting the optimum deuteron energy, i.e. sufficiently high energy to ensure full transmission through the film, but low enough energy to impart as much energy as possible. Deuteron ion energy was attenuated from the initial 5 MeV by transmission through 103 µm-thick aluminium foil (Goodfellow, UK) down to 1.4 MeV estimated from Monte Carlo simulations using SRIM (Ziegler, Ziegler & Biersack 2010). Figure 3 illustrates the estimated LET of deuterons in PAR. In combination with beamline optics the attenuating foil also served to scatter the beam homogenously over the target film, thus avoiding the need for beam rastering and its problematic localized heating.

Deuteron ion fluence was not accurately defined as a Faraday cup has not yet been installed in the external beamline and the degree of secondary electron emissions were unknown.

2.3 Chemical etching using reported methods

Chemical etching (dissolution) of latent ion tracks in polymers is a well-developed and reported technique (Apel et al. 2009, Apel et al. 2001, Apel et al. 2006, Trofimov et al. 2009, Spohr 2001, Sertova et al. 2009, Rohani et al. 2009) and the various methods are

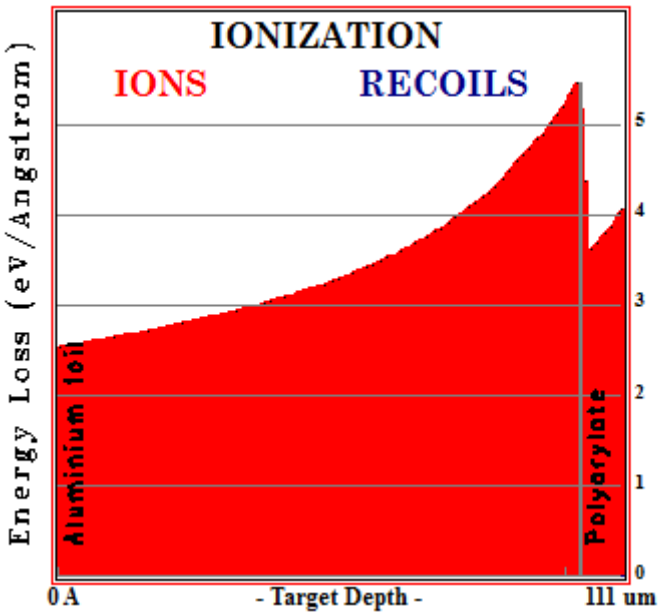


Figure 3. SRIM Monte Carlo simulation (Ziegler, Ziegler & Biersack 2010) *illustrating LET as a function track distance, which correlates to the ion energy as it slows down within the attenuating foil and polymer target material (the two are in reality separated by a high vacuum). The mean LET in PAR is approximately 38 eV nm^{-1}.*

summarized elsewhere (Fink 2004, Fischer, Spohr 1983). Careful control of etching conditions determines both pore diameter and shape. Exposure to ultraviolet light is often applied as a post-irradiation, pre-etching process to enhance oxidation of radiolytic species in the ion tracks and so to enhance the aspect ratios of etched pores (Belkova et al. 2009, Vilensky et al. 2003, Agarwal, Kalsi 2010, Zhu et al. 2004). Chemical treatment with appropriate solvents and etchants determines the penetration into and dissolution of the ion tracks. The bulk polymer is also inevitably etched, so controlling etching specificity influences strongly pore geometry (Fink 2004, Apel et al. 2009, Apel et al. 2006, Trofimov et al. 2009, Spohr 2001, Sertova et al. 2009, Rohani et al. 2009, Zhu et al. 2004, Ferain, Legras & Hanot 2001, Apel 2001).

Less conventional methods have also been applied in research to enhance etching selectivity. Such methods include heating by ultrasound (Pandey, Kalsi & Iyer 1998) or microwave radiation (Tripathy et al. 2010), addition of organic solvents (Lück et al. 1990, Chavan et al. 2014), plasma treatment (Dmitriev et al. 2000) and electrolysis (Cornelius et al. 2007, El-Samman, Hussein & Hassan 2010, Kumar, Kumar & Chakarvarti 2003).

The novelty of using PAR means that the literature on etching this polymer is scarce (Fink 2004). We made a considerable effort to screen different etchants and etching methods for our deuteron-irradiated PAR films. All of the methods above (except for plasma treatment) and unusual various combinations of them were investigated. However, none yielded continuous pores, even when etching conditions were pushed to the extremes where the significant structural damage was imparted to the bulk polymer.

2.4 Chemical etching using our novel method

Real progress was finally achieved by enhancing the etching process using a physical method applied elsewhere but in a completely different manner, in combination with a novel ion irradiation protocol. Our new combined method is a trade secret and currently subject to IPR assessment.

The first experiments yielded shallow pits in deuteron irradiated PAR film, then refinement of the method increased pit aspect ratio until we attained breakthrough with pores (Figure 4). Earlier successful etchings yielded few pores (Figure 5A), which hampered sample analysis and membrane function. Ion irradiation simulations and experiments led us towards a paradigm shift that, with an experimental modification, resulted in a substantial increase in the number of pores (Figure 5B). The implications are that pore density is now high enough for effective sample analysis and comparable with commercially-produced membranes and so viable as a functioning membrane. Definitive evidence for pores in our membranes was attained by SEM imaging of membrane internal cross-sections (Figure 6). Etching optimisation is also necessary to reach desirable pore dimensions.

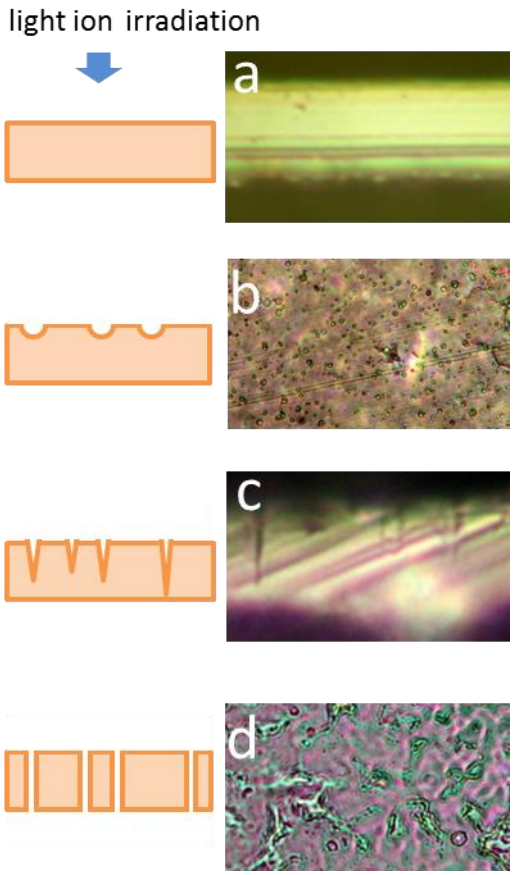
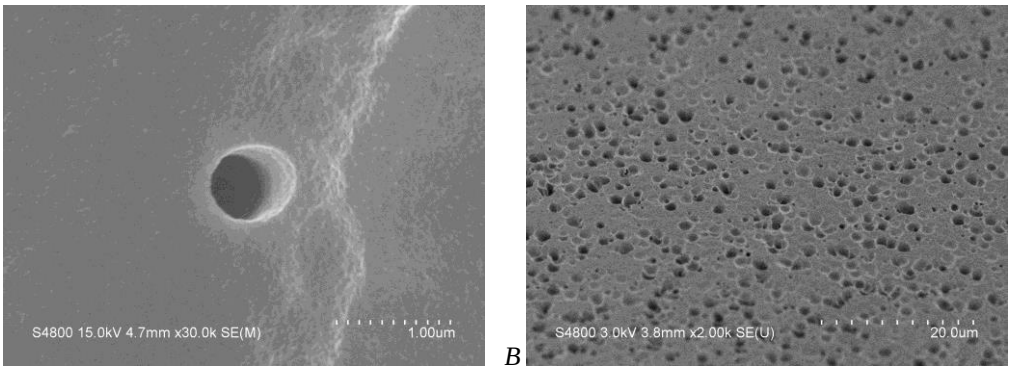
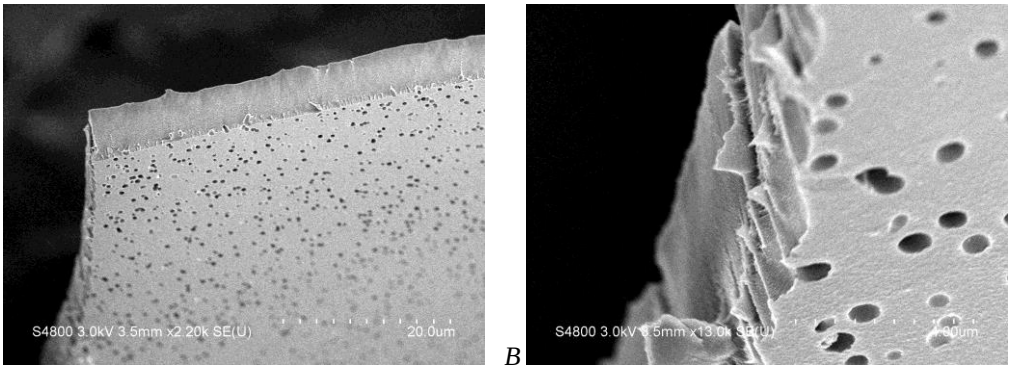


Figure 4. (a) Cross-section of PAR film processed using conventional etching technology showing no structures, (b) pitted surface attained from initial experiment with our new etching technology, (c) cross-section of deeper pits from early optimization, (d) bright spots through surface of first pores achieved.



A *B*

Figure 5. (A) SEM image of a single track etched pore entrance in an earlier low pore density deuteron-irradiated PAR sample. (B) SEM image of same type of membrane sample but with increased pore density.



A *B*

Figure 6. SEM images of outer surface and cross-sectional surface of one of our deuteron-irradiated PAR track etched membranes confirming the presence of etched pores consistent with other reported TEMs.

Optimization of etching parameters has reduced long etching times to manageable lengths: from 6 h down to 30 min. This development significantly increases our processing capacity, i.e. the rate at which we can test experimental parameters, and the commercial attractiveness of our new etching process for industrial membrane production. Optimizing of parameters continues in the attempt to attain higher pore aspect ratios, while analysis of the membranes is pursues in order to elucidate the new etching mechanism.

Initial etching experiments employed conventional laboratory apparatus that limited sample size and would be incompatible with industrial-scale production. The novelty of our etching method meant that no suitable large-scale apparatus existed, and so we designed our own. While currently continuing to work at the laboratory scale we designed etching apparatus that could be later scaled up. Materials were evaluated for chemical and physical compatibility, and after testing several prototypes we now have a working, scalable etching system. Membranes are now produced at sizes suitable for conventional testing and can be evaluated for homogeneity on the cm scale.

2.5 Pilot filtration trial

In a recent pilot investigation on the efficacy of our membranes to remove bio-organic content from raw water, we sampled water from a tributary to Vantaanjoki river (Helsinki, Finland) and performed microbiological testing of its filtrate (Figure 7). The results were very positive, i.e. a significant reduction in bacterial content, although the identities of the organic content were unknown and so served only for demonstration. Complete exclusion of bacteria can be achieved by further optimizing the membrane production process.

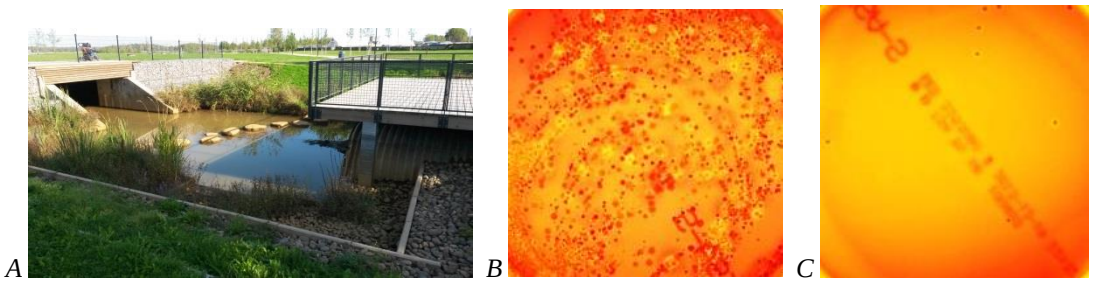


Figure 7. (A) Vantaanjoki river tributary sampling site. (B) Agar plate microbiological assay of raw water from sample site showing visibly a large number of bacterial colonies. (C) Agar plate microbiological assay of raw water from sample site filtered with one of our membranes showing almost complete removal of bacteria.

3 CONCLUSIONS

The paradigm that producing continuous etchable tracks are the preserve of irradiation by energetic heavy ions would appear to remain valid when using reported etching methods. Light ions used by our group impart a comparatively small amount of energy and are, with good reason, perceived as insufficient. However, we made a radical shift to develop a completely novel production technology that combines a new irradiation protocol and a new etching technique to produce a new class of polymer ultrafiltration (UF) membranes. The economic implications are such that only a small, light ion accelerator is needed, thus reducing production costs and making polymer track etch membranes competitive where they could be of most industrial and societal benefit, i.e. as ultrafiltration membranes in water treatment.

This project has evolved recently from the fundamental scientific proof-of-concept stage to validation of the novel technology in the laboratory. We continue to optimize the production technique to improve etching selectivity, processing rate and scalability. Our near-term desire is to progress to validation and demonstration of our technology in the relevant environments in order to build industrial collaborations, to acquire external funding for scaling-up production and prototype development, and to continue exploring basic science to elucidate and promote the mechanisms responsible for positive results and lead to further innovations.

The initial motivation for this project was to develop a membrane production method that would be acceptable to industry in terms of outlay cost, and reduce substantially their energy consumption and release of environmentally harmful effluents. Our membranes have potential in several fields of separation technology, and for demonstration we have chosen to focus primarily on the selective removal from water of two important classes of compounds: bacteria and natural organic material (NOM).

REFERENCES

Agarwal, C. & Kalsi, P.C. 2010, "UV-irradiation effects on polyester nuclear track detector ", *Radiation Physics and Chemistry,* vol. 79, no. 8, pp. 844 <last_page> 847.

Apel, P. 2003, "Swift ion effects in polymers: industrial applications", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* vol. 208, pp. 11-20.

Apel, P. 2001, "Track etching technique in membrane technology", *Radiation Measurements,* vol. 34, no. 1-6, pp. 559-566.

Apel, P. & Spohr, R. 2001, , *Introduction to ion track etching in polymers*. Available: http://www.ion-tracks.de/introduction1/.

Apel, P.Y., Akimenko, A.P., Blonskaya, I.V., Cornelius, T., Neumann, R., Schwartz, K., Spohr, R. & Trautmann, C. 2006, "Etching of nanopores in polycarbonate irradiated with swift heavy ions at 15 K", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* vol. 245, no. 1, pp. 284-287.

Apel, P.Y., Blonskaya, I.V., Oganessian, V.R., Orelovitch, O.L. & Trautmann, C. 2001, "Morphology of latent and etched heavy ion tracks in radiation resistant polymers polyimide and poly(ethylene naphthalate)", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* vol. 185, no. 1-4, pp. 216-221.

Apel, P.Y., Blonskaya, I.V., Orelovitch, O.L. & Dmitriev, S.N. 2009, "Diode-like ion-track asymmetric nanopores: Some alternative methods of fabrication", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* vol. 267, no. 6, pp. 1023-1027.

Apel, P.Y. & Fink, D. 2004, "Ion-track etching" in *Transport processes in ion-irradiated polymers*, ed. D. Fink, Springer, , pp. 151.

Apel, P.Y., Titova, S. & Tretyakova, S. 1986, "A study of etching of heavy ion particles in polyarylate", *JINR Communications,* vol. 18-86-788, pp. 1.

Belkova, A.A., Sergeeva, A.I., Apel, P.Y. & Beklemishev, M.K. 2009, "Diffusion of aniline through a polyethylene terephthalate track-etched membrane", *Journal of Membrane Science,* vol. 330, no. 1-2, pp. 145-155.

Chavan, V., Agarwal, C., Pandey, A.K., Nair, J.P., Surendran, P., Kalsi, P.C. & Goswami, A. 2014, "Controlled development of pores in polyethylene terepthalate sheet by room temperature chemical etching method", *Journal of Membrane Science,* vol. 471, no. 0, pp. 185-191.

Cornelius, T.W., Apel, P.Y., Schiedt, B., Trautmann, C., Toimil-Molares, M.E., Karim, S. & Neumann, R. 2007, "Investigation of nanopore evolution in ion track-etched polycarbonate membranes", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* vol. 265, no. 2, pp. 553-557.

Cuscito, O., Clochard, M.-., Esnouf, S., Betz, N. & Lairez, D. 2007, "Nanoporous β-PVDF membranes with selectively functionalized pores", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* vol. 265, no. 1, pp. 309-313.

Dmitriev, S.N., Kravets, L.I., Sleptsov, V.V., Elinson, V.M., Potryasai, V.V. & Orelovich, O.L. 2000, "A high-frequency plasma-discharge effect on poly(ethylene) terephthalate films exposed to heavy ions", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* vol. 171, no. 4, pp. 448-454.

El-Samman, H., Hussein, A. & Hassan, S. 2010, "Pore growth in heavy ion-irradiated PET foils using a constructed ECE unit", *Journal of Radioanalytical and Nuclear Chemistry,* vol. 285, no. 2, pp. 259-262.

Ferain, E. & Legras, R. 2009, "Templates for engineered nano-objects for use in microwave, electronic devices and biomedical sensing application", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* vol. 267, no. 6, pp. 1028-1031.

Ferain, E., Legras, R. & Hanot, H. 2001, *Method for creating pores and microporous film*.

Fink, D. (ed) 2004, *Transport processes in ion-irradiated polymers*, Springer.

Fischer, B.E. & Spohr, R. 1983, "Production and use of nuclear tracks: imprinting structure on solids", *Reviews of Modern Physics,* vol. 55, no. 4, pp. 907-948.

Friebe, A. & Ulbricht, M. 2009, "Cylindrical Pores Responding to Two Different Stimuli via Surface-Initiated Atom Transfer Radical Polymerization for Synthesis of Grafted Diblock Copolymers", *Macromolecules,* vol. 42, no. 6, pp. 1838-1848.

Friebe, A. & Ulbricht, M. 2007, "Controlled Pore Functionalization of Poly(ethylene terephthalate) Track-Etched Membranes via Surface-Initiated Atom Transfer Radical Polymerization", *Langmuir,* vol. 23, no. 20, pp. 10316-10322.

Geismann, C., Yaroshchuk, A. & Ulbricht, M. 2007, "Permeability and Electrokinetic Characterization of Poly(ethylene terephthalate) Capillary Pore Membranes with Grafted Temperature-Responsive Polymers", *Langmuir,* vol. 23, no. 1, pp. 76-83.

Hanot, H. & Ferain, E. 2009, "Industrial applications of ion track technology", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* vol. 267, no. 6, pp. 1019-1022.

He, D., Sun, W., Schrader, T. & Ulbricht, M. 2009, "Protein adsorbers from surface-grafted copolymers with selective binding sites ", *Journal of Materials Chemistry,* vol. 19, no. 2, pp. 253.

Koshikawa, H., Usui, H. & Maekawa, Y. 2009, "Thermally stable and anisotropically conducting membranes consisting of sub-micron copper wires in polyimide ion track membranes", *Journal of Membrane Science,* vol. 327, no. 1-2, pp. 182-187.

Kumar, S., Kumar, S. & Chakarvarti, S.K. 2003, "Design of a multifoil electrolytically controlled etching cell", *Radiation Measurements,* vol. 36, no. 1–6, pp. 165-167.

Kuroki, H., Ohashi, H., Ito, T., Tamaki, T. & Yamaguchi, T. 2010, "Isolation and analysis of a grafted polymer onto a straight cylindrical pore in a thermal-responsive gating membrane and elucidation of its permeation behavior", *Journal of Membrane Science,* vol. 352, no. 1-2, pp. 22-31.

Lalia, B.S., Kochkodan, V., Hashaikeh, R. & Hilal, N. 2013, "A review on membrane fabrication: Structure, properties and performance relationship", *Desalination,* vol. 326, no. 0, pp. 77-95.

Lück, H.B., Matthes, H., Gemende, B., Heinrich, B., Pfestorf, W., Seidel, W. & Turuc, S. 1990, "Production of particle-track membranes by means of a 5 MV tandem accelerator", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* vol. 50, no. 1–4, pp. 395-400.

Musket, R.G. 2006, "Extending ion-track lithography to the low-energy ion regime ", *Journal of Applied Physics,* vol. 99, no. 11, pp. 114314.

Pandey, A.K., Kalsi, P.C. & Iyer, R.H. 1998, "Effects of high intensity ultrasound in chemical etching of particle tracks in solid state nuclear track detectors", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* vol. 134, no. 3–4, pp. 393-399.

Rohani, R., Yamaki, T., Koshikawa, H., Takahashi, S., Hasegawa, S., Asano, M., Maekawa, Y., Voss, K., Trautmann, C. & Neumann, R. 2009, "Enhancement of etch rate for preparation of nano-sized ion-track membranes of poly(vinylidene fluoride): Effect of pretreatment and high-LET beam irradiation", *Nuclear*

Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, vol. 267, no. 3, pp. 554-557.

Sertova, N., Balanzat, E., Toulemonde, M. & Trautmann, C. 2009, "Investigation of initial stage of chemical etching of ion tracks in polycarbonate", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, vol. 267, no. 6, pp. 1039-1044.

Spohr, R. 2001, *Etch hints for polymers with high track-etch-rate*, European Research Training Network EuNITT.

Trautmann, C. 1995, "Observation and chemical treatment of heavy-ion tracks in polymers ", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, vol. 105, no. 1-4, pp. 81.

Trautmann, C., Bouffard, S. & Spohr, R. 1996, "Etching threshold for ion tracks in polyimide ", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, vol. 116, no. 1-4, pp. 429.

Tripathy, S.P., Kolekar, R.V., Sunil, C., Sarkar, P.K., Dwivedi, K.K. & Sharma, D.N. 2010, "Microwave-induced chemical etching (MCE): A fast etching technique for the solid polymeric track detectors (SPTD)", *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, vol. 612, no. 2, pp. 421-426.

Trofimov, D.A., Shkinev, V.M., Spivakov, B.Y. & Schué, F. 2009, "Improvement of pore geometry and performances of poly(ethylene terephthalate) track membranes by a protective layer method using plasma-induced graft polymerization of 1H,1H,2H-perfluoro-1-octene monomer", *Journal of Membrane Science*, vol. 326, no. 2, pp. 265-269.

Ulbricht, M. 2006, "Advanced functional polymer membranes", *Polymer*, vol. 47, no. 7, pp. 2217-2262.

Vilensky, A.I., Zagorski, D.L., Kabanov, V.Y. & Mchedlishvili, B.V. 2003, "UV- and γ-sensitization of latent tracks in polyethylene terephthalate", *Radiation Measurements*, vol. 36, no. 1-6, pp. 131-135.

Wanichapicharta, P., Chittrakarna, T., Sujaritturakarna, W. & Coster, H.G.L. 2000, "Production of nuclear-track etched membranes", *Science Asia*, vol. 26, pp. 175-179.

Xavier, S., Mátéfi-Tempfli, S., Ferain, E., Purcell, S., Enouz-Védrenne, S., Gangloff, L., Minoux, E., Hudanski, L., Vincent, P., Schnell, J., Pribat, D., Piraux, L. & Legagneux, P. 2008, *Stable field emission from arrays of vertically aligned free-standing metallic nanowires*.

Zagurskii, V.V., Grebinskaya, L.N. & Lavrentovich, Y.I. 1986, "Influence of track effects upon chemical etching of polyarylate", *Soviet Atomic Energy,* vol. 60, pp. 257.

Zhu, Z., Maekawa, Y., Koshikawa, H., Suzuki, Y., Yonezawa, N. & Yoshida, M. 2004, "Role of UV light illumination and DMF soaking in production of PET ion track membranes ", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* vol. 217, no. 3, pp. 449.

Ziegler, J.F., Ziegler, M.D. & Biersack, J.P. 2010, "SRIM – The stopping and range of ions in matter (2010) ", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* vol. 268, no. 11-12, pp. 1818.