

SYNTHESIS OF TEMPERATURE-RESPONSIVE PARTICLE TRACK MEMBRANES WITH A LINAC

H. Omichi¹⁾, M. Yoshida¹⁾, M. Asano¹⁾, M. Tamada¹⁾, R. Katakai²⁾, Ch. Trautmann³⁾, J. Vetter³⁾, and R. Spohr³⁾

1)Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment, 1233 Watanuki-machi, Takasaki, Gunma 370-12, Japan

2)Faculty of Engineering, Gunma University, Tenjin-cho, Kiryu, Gunma 376, Japan

3)Gesellschaft für Schwerionenforschung mbH, Postfach 11 05 52, D-6100, Darmstadt, Germany

Abstract

A copolymer film made of diethyleneglycol-bisallylcarbonate (CR-39) and an amino acid-containing monomer called acryloyl-L-proline methyl ester (A-ProOMe) was irradiated by ion beams of Lead from UNILAC heavy ion accelerator of GSI and subject to the chemical etching with an alkali solution. The pore structure obtained in the particle track membrane (PTM) was observed by electron microscopy. The cyclic change in temperature of water in which the PTM was immersed induced a hysteresis loop of pore diameter change.

Introduction

PTM has a narrow size distribution of pores of cylindrical shapes. This characteristic enables PTM to precisely differentiate particles of similar dimensions. PTM has been applied to separating biological cells, filtering polluted air streams, stabilizing beverages, etc. [1]. The pore size of PTM, however, is unequivocally decided by the irradiation conditions of heavy ion beams and the following chemical etching. If PTM is provided with a flexibility of pore size which changes depending on the changes in such environmental conditions as pH, temperature, electric field, etc., the application of PTM would be expanded. It might be possible to control a micro flow through the membrane which is realized in living organisms under various inner and outer conditions. One of the possible approaches to synthesize such a sophisticated membrane is combining PTM with a polymer of characteristics responding to these environmental conditions.

Hydrogels are known to possess the ability to change their volumes when environmental stimuli are imposed [2, 3]. These changes are accompanied by the absorption and desorption of water by the hydrogels. The theoretical treatment of the changes has been studied [4]. Even the applications of these changes have been tried to realize artificial muscles, biosensors, etc. [5].

The present report intends to show the possibility of synthesizing such membranes by means of ion beam irradiation from a linac onto a copolymer film composed of a radiation-sensitive component and a stimuli-sensitive component. One of the conveniences of applying hydrogels as the stimuli-sensitive component is the ease of choosing an appropriate chemical structure. In the present study, an acryloyl monomer containing amino acid groups in its repeating unit was used.

Experimental

Film preparation

The monomer of CR-39 supplied by PPG Industries-Asia was used without a further purification. A-ProOMe was synthesized and purified according to the previous papers [6-7]. The copolymer film was prepared by a cast polymerization of the mixture of monomers with a catalyst. The thickness of the film was adjusted by the spacer installed into two glass plates containing the monomer solution.

Irradiation and Chemical Etching

The copolymer film of the size 4 cm x 4 cm was fixed on a glass plate and was irradiated in vacuum with 1×10^7 Pb ions/cm² of 11.4 MeV/u at the UNILAC of GSI. A special inlet system for irradiating multiple samples was used. The irradiated film was cut into small pieces and was etched with NaOH solution of 6 N at 60°C for prescribed periods.

Observation of Pore Structure

The pore structure was observed with an electron microscope. The cross-section of the pore was obtained by breaking the PTM. In order to observe the change in pore diameter with temperature, the PTM was immersed in water at 0°C for overnight, then the temperature was raised to 80°C and maintained for 1 day. This procedure was repeated 4 times.

Results and Discussion

The energy of the projectile ion is transferred to electrons of target atoms. The electronic collision-cascade leads to the formation of a track core of ca. 10 nm in diameter along the ion path [8]. Then, the electronic energy decay produces such intermediates as ionic and excited species, radicals, which may recombine or react within a volume much larger than the ion track, due to the diffusion effects. These intermediates are finally stabilized as crosslinking of chemical bonds or scission products. In the case of the copolymer of CR-39 and A-ProOMe, the component of CR-39 is radiation sensitive, while that of A-ProOMe is crosslinkable. The resultant copolymer would, therefore, be partly scissioned by the ion beam irradiation depending on the

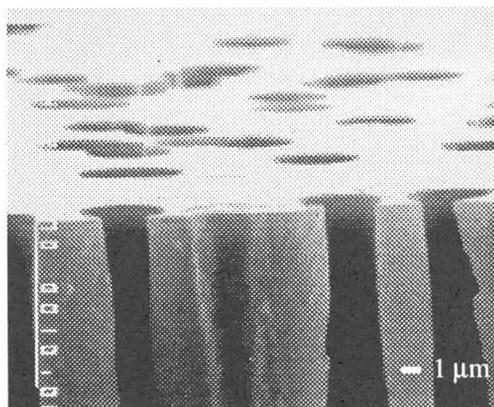


Fig. 1 Electron micrograph of the PTM containing 70 % of A-ProOMe

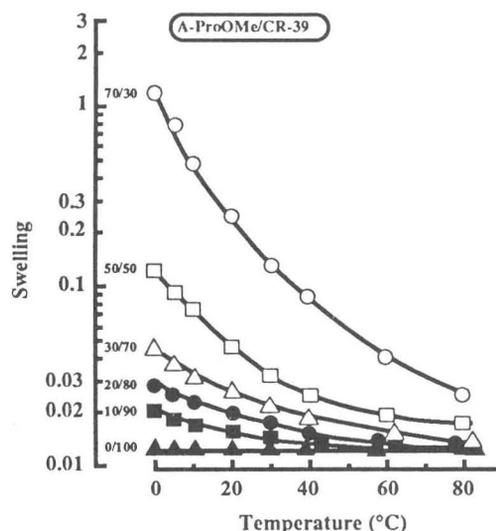


Fig. 3 Effect of copolymer content on swelling of films

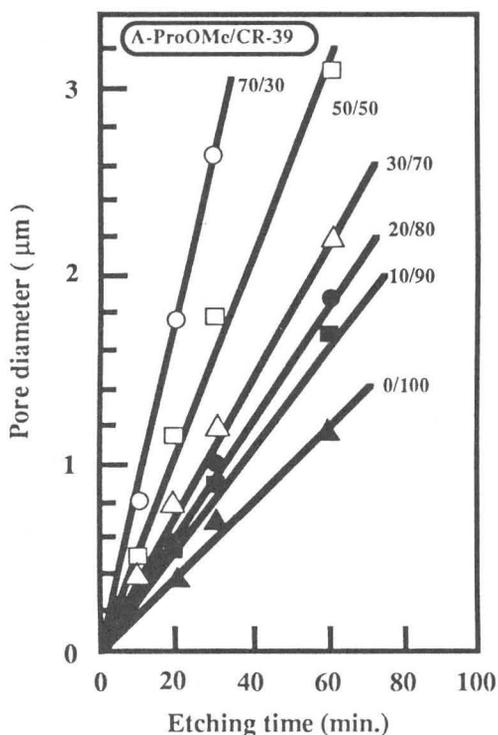


Fig. 2 Effect of copolymer content on pore diameter of PTM

composition. The scission products are composed of molecules possessing molecular weight lower than that of the original polymer. Then, some gaseous compounds of these products diffuse out of the track. A little heavier products are dissolved in the solution when the irradiated polymer film is immersed in the etchant solution. The layer of decomposition outside the track is gradually introduced by the hydrolysis of the polymer. Finally, empty cylindrical pores of several μm in diameter are produced.

Fig. 1 shows the electron micrograph of the pore structure of the membrane containing 70 % of A-ProOMe. The surface of PTM seems to be homogeneous and smooth. Cylindrical pores of similar sizes are observed. The average pore size is ca. $2 \mu\text{m}$ under the present condition. Some of the pores are overlapped with neighboring pores.

The pore size was controlled by the copolymer composition and the etching time. Fig. 2 shows how widely the pore size is changed by these conditions. The increase in pore size has a linear relationship with etching time irrespective of the copolymer composition. By increasing the content of A-ProOMe in the copolymer the increase in pore size is drastically accelerated. The PTM containing 70 % of A-ProOMe gave deformed pore shape because of the excessive etching.

The acceleration of etching by adding A-ProOMe is related with the hydrophilic property of the copolymer. Fig. 3 shows the swelling ratio in water of the copolymer films before irradiation at different temperatures. The higher the content of the hydrogel component A-ProOMe is, the larger the difference in swelling ratio is between high and low temperatures. On the other hand, the swelling of the polymer film containing only CR-39 does not change with temperature. This is reasonable because of the hydrophobic property of CR-39 polymer. When the copolymer film has such a hydrophilic characteristics, PTM ob-

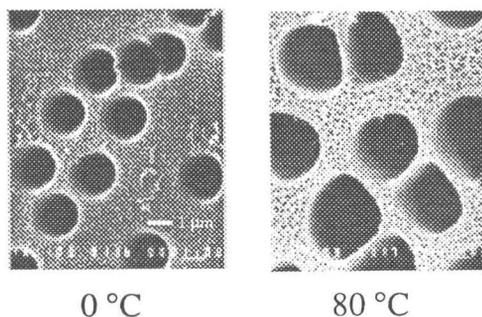


Fig. 4 Electron micrograph of PTM at 0°C and 80°C

tained from the copolymer film easily absorbs the alkali solution. This is based on the fact that the etching procedure is composed of the swelling of the membrane, dissolution of the irradiated part with the solution and the removal of the etch products from the reaction zone. The deformed pore shape of the PTM at a higher content of AProOMe is probably due to the abrupt etching reaction and the rapid diffusion of etched products through the drain.

Fig. 4 shows the change in pore structure between 0°C and 80°C. The pore diameter of ca. 2 μm was doubled with the rise of temperature. At the same time, the original circular shape of the pore was deformed. These changes are caused by the shrinking of the hydrogel component as shown in Fig. 3. The heterogeneous shrinking is probably due to the inhomogeneity in the thickness of the undissolved part between neighboring pores. The micro structure of the undissolved part at 80°C indicates the presence of the entanglement of polymer chains, which is quite different from the rigid structure at 0°C.

The PTM was repeatedly immersed in water kept at 0°C and at 80°C. Fig. 5 shows the change in pore diameter during the heat cycle between these two temperature regions. The pore size precisely changed between 1.8 μm and 2.6 μm. The enlargement of the pore was almost instantaneous although its shrinkage was rather slow. This change is controlled by the content of the hydrogel component. The smaller the content of the hydrogel is, the quicker the change is. On the other hand, the range in pore diameter change decreases with the decrease in the hydrogel content.

Conclusions

1. PTM was obtained with a linac from a copolymer containing a radiation-sensitive component and a stimuli-responsive hydrogel component.
2. The pore diameter was changed by temperature, which was attributed to the volume change of the hydrogel component.
3. This change was recycled between two different temperatures among which a phase transition temperature of the hydrogel existed.

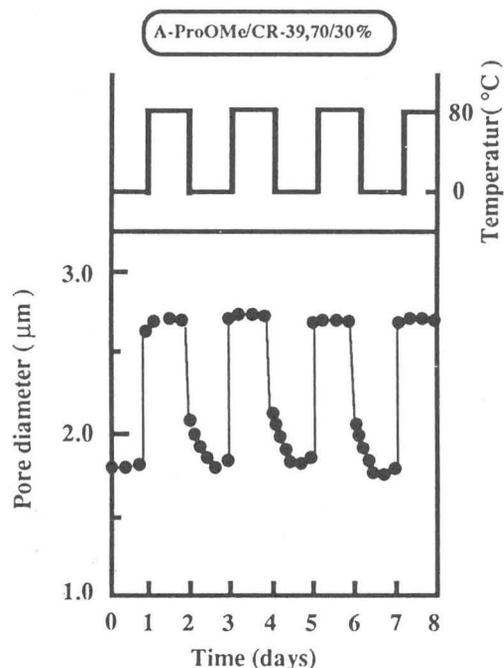


Fig. 5 Change in pore diameter between 0°C and 80°C

References

- [1] Proceedings of the 2nd Meeting "Particle Track Membranes and Their Applications", 1991, Poland.
- [2] D. J. Hemker, V. Garza, and C. W. Frank, *Macromolecules*, **23**, 4411 (1990).
- [3] S. Beltran, H. H. Hooper, W. Harvey, H. W. Blanch, and J. M. Prausnitz, *J. Chem. Phys.*, **92**, 2061 (1990).
- [4] T. Tanaka, I. Nishino, S. T. Sun, and S. V. Nishino, *Science*, **218**, 467 (1982).
- [5] Y. Osada, *J. Intell. Mater. Syst. and Struct.*, **4**, 50 (1993).
- [6] M. Yoshida, M. Tamada, M. Kumakura, and R. Katakai, *Radiat. Phys. Chem.*, **38**, 7 (1991).
- [7] M. Tamada, M. Yoshida, M. Asano, H. Omichi, R. Katakai, R. Spohr, and J. Vetter, *Polymer*, **33**, 3169 (1992).
- [8] R. Spohr, "Ion Tracks and Microtechnology-Principles and Applications", pp. 110, Vieweg, 1990.