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Section 13. Radiation chemistry in quantum beam–material system

Application of ion beams to synthesis of environmentally responsive track membranes

H. Omichi [a,*], M. Yoshida [a], M. Asano [a], N. Nagaoka [b], H. Kubota [b], R. Katakai [b], R. Spohr [c]

[a] *Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute (JAERI), 1233 Watanuki, Takasaki, Gunma 370-12, Japan*

[b] *Faculty of Engineering, Gunma University, 1-5-1 Tenjin, Kiryu, Gunma 376, Japan*

[c] *Gesellschaft für Schwerionenforschung mbH (GSI), Planckstr. 1, D-64291 Darmstadt, Germany*

Abstract

Ion beams with an energy of 10 MeV/n were used for producing porous membranes of poly(ethylene terephthalate) and poly(diethyleneglycol-bis-allylcarbonate) films. The condition to obtain cylindrical pores was explained by the relation between the relative etching rate and restricted energy transfer from ion beams to polymer films. The porous membranes were chemically modified either by copolymerizing or by grafting such hydrogel monomers as *N*-isopropylacrylamide and acryloyl-L-proline methyl ester. The obtained membranes changed pore size in response to the change in environmental conditions such as temperature. The change was followed by electron microscopy. A cyclic change in conductivity of potassium ion through the membrane of a single pore was observed when the temperature of the dialysis cell containing a 0.1 M KCl solution was cycled between two temperatures. The selectivity of organic ion passing through the membrane drastically changed at the phase transition temperature of the attached hydrogel layer.

1. Introduction

When high energy ion beams are irradiated onto polymer films, areas of decomposed polymer chains are produced along the ion's trajectory. The chemical etching of the areas with a concentrated alkali or acid produces holes in the cross-section of the films. This technique has been applied to manufacturing particle track membranes (PTMs) possessing cylindrical pores of a uniform pore size. Because PTMs offer distinct advantages over conventional filters, which usually consist of bonded fibers or porous foams, PTMs have been applied to such fields as precise separation of biological cells, filtering polluted air streams, stabilizing beverages, etc.

It is possible to classify membrane filters into two categories: passive membranes and active membranes. The passive membranes transmit components of a solution by applying an external force in the form of a gradient in pressure, voltage, temperature or concentration. The membrane itself does not change chemically or physically. Active membranes, on the other hand, work against concentration gradients whereby a modification of membrane structure occurs by consuming energy. The latter membranes are still in the region of biology, typically exist as cell membranes. PTMs are thought, at the present stage, passive membranes acting as barriers to the flow of matter, electrical charge or heat between two compartments. If PTMs are modified to possess an ability to change their physical or chemical structures according to such environmental factors as temperature, pH, electric field, etc., in other words, if they have a special character called 'intelligent materials' [1], they will approach biological cell membranes. It will be one of the ultimate goals for PTMs to develop such sophisticated characters. One idea to realize this goal is to modify the pore structure of the PTM with the aid of a polymer which changes its physical and/or chemical properties responding to these environmental conditions.

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[*] Corresponding author. Tel.: +81-273 469 216; fax: +81-273 469 690; e-mail: omichi@taka.jaeri.go.jp.

Hydrogels are known to change their volume when environmental stimuli are imposed. In the case of temperature effect, for example, there is a phase transition temperature at which an abrupt change in volume of the gel occurs. The present study intends to synthesize an environmentally responsive PTM with the ability of changing the pore size according to temperature change by combining PTM with environmentally responsive hydrogels.

2. Experimental

100 μm thick films of poly(diethyleneglycol-bis-allylcarbonate), CR-39, and its copolymers composed with a hydrogel-forming monomer at different ratios were used for the study on ion track formation in polymer films and on the microscopic observation of pore structure. For the purpose of transportation study of organic materials and conductivity measurement, a commercially available poly(ethylene terephthalate), PET (Hostaphan RN19, Höchst Diafoil GmbH), 19 μm thick film was used.

As for hydrogel-forming materials, two types of monomer were used. One was *N*-isopropylacrylamide (NIPAAm) and the other was acryloyl-L-proline methyl ester (A-ProOMe). The phase transition temperatures of the polymers made of these monomers are 32°C and 14°C, respectively.

Heavy ion beams such as ^{197}Au, ^{208}Pb, ^{209}Bi and ^{238}U from UNILAC (Universal Linear Accelerator), GSI, and ^{1}H, ^{4}He, $^{1}2C$, ^{20}Ne, ^{40}Ar, ^{84}Kr and ^{129}Xe from an AVF cyclotron of TIARA (Takasaki Ion Accelerators for Advanced Radiation Application), JAERI, were used to produce PTMs from polymer films. The energy was changed from 10 MeV/n of ^{1}H to 11.6 MeV/n of ^{238}U. The fluence was mainly 10^6 ions/cm^2. A single ion hit system of GSI was used to prepare a membrane possessing only one hole in the film. The irradiated films were etched with 5–6 M NaOH aqueous solution at 40–60°C for 1–5 h.

Two processes were carried out to produce modified PTMs with hydrogel components. In process I copolymer films composed of CR-39 monomer and A-ProOMe were irradiated by ion beams and chemically etched. In process II CR-39 or PET films were irradiated and etched at first followed by chemical modification with hydrogel monomers. Radiation-induced grafting technique was applied to bonding hydrogel layers to the wall of pores of PTMs. The porous membranes of CR-39 or PET were irradiated by γ-rays under N_2 atmosphere at room temperature. The irradiation dose was 30 kGy. Then the films were immersed in a 10 wt% aqueous solution of monomer for starting the grafting of hydrogel to porous membranes at 60°C. The yield of grafting was estimated from the weight increase of the films after the reaction. The pore size of the grafted films was estimated from the observation of electron microscopy of freeze-dried films.

The dialysis cell was filled with a 0.1 M KCl solution for the conductivity measurement through a single hit PET membrane modified with NIPAAm as a diaphragm. The applied voltage was 125 mV at a frequency of 6 Hz. The temperature of the water bath was cyclically changed between 24°C and 34°C. Another type of cell was used for the permeation of organic molecules. The membrane was inserted as a diaphragm in the cell filled with a standard buffer solution (Hepes of 5 mM adjusted to pH 7.5) containing a radio-tracer labeled molecule such as choline chloride. The permeation was measured as a function of temperature of the solution.

3. Results and discussion

3.1. Preparation of PTM

In order to select heavy ion beams for making membranes with cylindrical pores, CR-39 films were irradiated with ^{40}Ar and ^{208}Pb of 11.6 MeV/n and etched with 6 M NaOH solution at 60°C for 1 h. The reason to use CR-39 is due to the fact that this polymer is known as a highly sensitive polymer to ion beams with an excellent sensitivity to etching agents.

Fig. 1 shows the pores produced in the cross-section of CR-39 films observed by electron microscopy. While ^{208}Pb irradiation produced cylindrical pores in the perpendicular direction to the surface, a conic shape basin not penetrating to the opposite side of the membrane surface was observed in the case of ^{40}Ar. This difference is based on the mechanism of etching of the region called latent track. On the molecular level the track etching is determined by the number of reactive sites in the form of chain ends or functional groups, by the so-called 'free volume' in the vicinity of the reactive site which is accessible to the

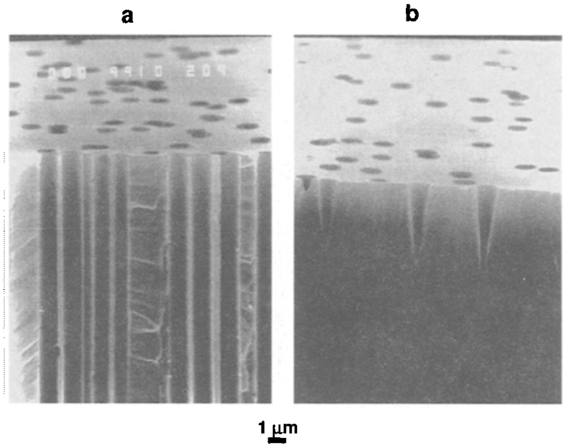

Fig. 1. Cross-sectional view of CR-39 PTM observed by electron microscopy: (a) irradiated with 11.6 MeV/n ^{208}Pb, (b) 11.5 MeV/n ^{40}Ar. Both films were etched in an 6 M NaOH solution at 60°C for 1 h.

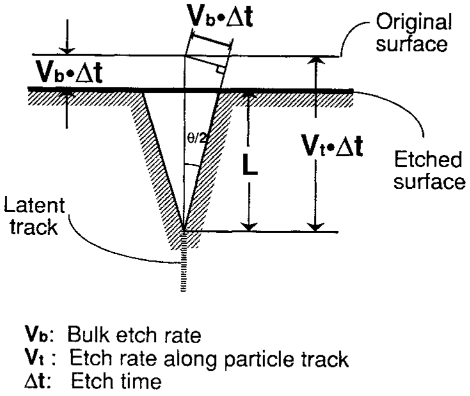

Fig. 2. Illustration of etch pit. The etching proceeds along the ion trajectory at a rate v_t while the unirradiated zone is etched at a rate v_b.

etchant during its approach to the reactive site, by the reaction rate of the chemical reaction, and by the required degradation of the polymer before it can be ultimately dissolved [2]. The observed etch pit is the result of accumulating these factors.

The practical factor to decide the shape of pore is the ratio of track etching rate v_t in the direction along the ion trajectory to the bulk etching rate v_b in the unirradiated zone [3]. It is often observed that even the unirradiated zone is partly dissolved by etchant materials. Eq. (1) gives a relative etching rate:

$$Q = (v_t/v_b) - 1. \tag{1}$$

The vertical angle of the cone θ as schematically shown in Fig. 2 is provided by Eq. (2):

$$\theta/2 = \sin^{-1}(v_b/v_t). \tag{2}$$

It is easily understood that the pore becomes virtually cylindrical when Q is sufficiently large.

The condition to produce cylindrical pores in polymer films has not been sufficiently exemplified. It is commonly understood that heavier ions are preferable for making pores cylindrical. The process of producing pores in polymer films is composed of two steps: physical energy transfer from ion beams to polymer films and chemical etching of the damaged zone. The first physical step has been discussed by the scientists who deal with dielectric track detectors. It was first introduced in 1964 to describe an experimental experience that in dielectric solids irradiated with nuclear particles of different ionizing power, in certain experimental conditions, there were no etched pits observable under an optical microscope [4]. For a quantitative treatment of this concept, a first approach was to associate the threshold with a proper energy loss of the particle. Later on, new models were proposed along the trajectories of various ions. These models have led to new quantities as a possible quantitative measure of the registration threshold, namely to those related to a critical value of the parameters: primary ionization [5], restricted energy loss, REL, and energy dose of delta-rays [6].

An empirical relation between Q and REL for many plastic materials was obtained by Somogyi et al. [3]. They observed that Q was roughly proportional to $(\mathrm{REL})^3$ for many plastic materials like cellulose acetate, polycarbonate and poly(ethylene terephthalate). Their observation is, however, limited to a rather narrow range of a lower energy because of the purpose to check the possibility to produce etchable tracks by the ion beam irradiation.

In order to obtain a condition to produce cylindrical pores, the survey at higher energy region is necessary. We studied a wide REL region by changing ion species from proton to uranium. The value of REL was calculated by [7]

$$(\mathrm{d}E/\mathrm{d}x)_{\omega<\omega_0} = (2\pi n Z_1^2 e^4/mc^2\beta^2)\{\ln(2mc^2\beta^2\gamma^2\omega_0/I^2) - \beta^2 - 2(C/Z_2) - \delta\}, \tag{3}$$

where n is the electron density of the polymer, Z_1 is the effective charge of the ion, β is the relative velocity of the ion, γ is $1/(1-\beta^2)^{1/2}$, I is the mean ionization potential of the polymer and C/Z_2 and δ are shell and density-effect correction factors, respectively. It is assumed that the delta-ray or secondary electron whose energy is below ω_0 participates in the formation of the noted track. In the case of CR-39 the average atomic charge Z_2, ionization potential I and cut-off energy ω_0 are estimated as 3.95, 70.2 eV and 200 eV, respectively [8]. Under the present irradiation condition both C/Z_2 (~ 0.01) and δ (~ 0) are negligibly small.

Fig. 3 shows that the logarithmic plot between Q and REL for CR-39 and its copolymers with A-ProOMe is not

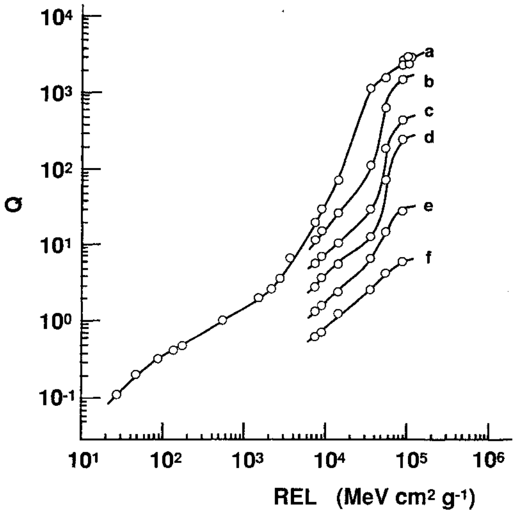

Fig. 3. The relation between Q and REL in the case of CR-39 and its copolymers with A-ProOMe composed in different ratios: (a) CR-39, (b) CR-39/A-ProOMe = 90/10, (c) 80/20, (d) 70/30, (e) 50/50, (f) 30/70.

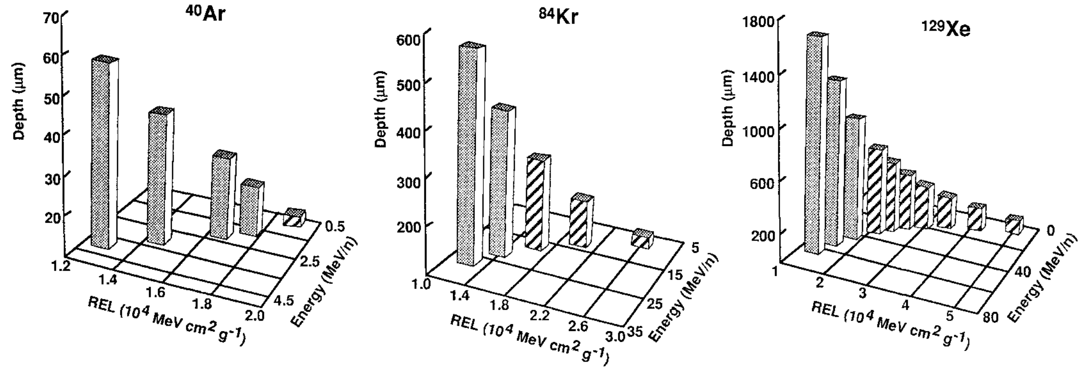

Fig. 4. Three-dimensional plots of REL and energy of ^{40}Ar, ^{84}Kr and ^{129}Xe versus their depth in CR-39. The hatched bars indicate the region to provide cylindrical pores.

exemplified by a single straight line which was reported by Somogyi et al. [3]. It is noted that the slope in the region below a certain REL value ($\sim 10^3$ MeV cm^2 g^{-1}) is smaller than that in the region above this REL. From the results in Fig. 3 the condition to provide the cylindrical pore was estimated. In the present study it was assumed that the pore shape was virtually cylindrical when Q was above 100, referring to the cone angle θ estimated from Eq. (1). This condition was obtained when REL of ^{84}Kr, ^{129}Xe, ^{197}Au, ^{208}Pb, ^{209}Bi and ^{238}U was above 10^4 MeV cm^2 g^{-1}. In the case of lighter ions like ^{1}H, ^{4}He, ^{12}C, etc., either double conical basins with no interaction with each other or pores of trapezium shape in the cross-section were produced. In the case of copolymers composed of the CR-39 monomer and A-ProOMe composed of A-ProOMe for more than 50 wt%, there was no REL region to provide the condition where Q was above 100.

The relation among REL, the energy of the ions and the penetration depth of these ions was obtained. The depth was calculated by a Monte Carlo simulation code, TRIM [9]. Fig. 4 shows an example of a three-dimensional plot of these values in the case of irradiating ^{40}Ar, ^{84}Kr and ^{129}Xe which are available from the cyclotron of TIARA. The hatched bars indicate the condition to provide cylindrical pores for CR-39 films. It is clearly observed that ion beams of higher energy with a smaller REL value deeply penetrate into polymer films while the pore shape deviates from cylinder. From a practical point of view, it is preferable to use such heavy ions as ^{129}Xe to produce cylindrical pores in the films with sufficient thickness.

3.2. Characteristics of environmentally responsive PTM

The grafting of A-ProOMe was carried out on CR-39 PTM which was made by the irradiation of 11.4 MeV/n ^{197}Au and etching with a 6 M NaOH solution for 1 h at 60°C. A phenomenon of complete on–off of pores produced in PTM was first observed by using the radiation-induced grafting of hydrogel layer to the wall of pores. The electron micrographs in Fig. 5 show that the pores of the PTM obtained by grafting 8 wt% of A-ProOMe and freeze-dried at 0°C are all closed while they are clearly open at 40°C. Because the phase transition temperature of poly(A-ProOMe) hydrogel is 14°C, the hydrogel layer attached to the pore wall absorbs water and swells below this temperature while the layer expels water and shrinks above this temperature. The picture at 0°C indicates that the pore is occupied by the swollen hydrogel layer containing a great deal of water.

The change in pore size was observed in the case of CR-39 copolymer with A-ProOMe composed of an equal amount of these monomers. Fig. 6 shows that the pore size of the copolymer PTM changes between 1.5 µm and 3.5 µm when the temperature of the water bath in which the PTM is immersed is changed between 0°C and 30°C at 24 h intervals. It is clearly observed that the pore changes its diameter in accordance with the change in temperature. The result in this figure also indicates that the changing rate of pore size when the temperature is increased is much faster than that when the temperature is lowered. Probably, this difference is due to the characteristic of the used hydrogel. The volume increase of poly(A-ProOMe) hydro-

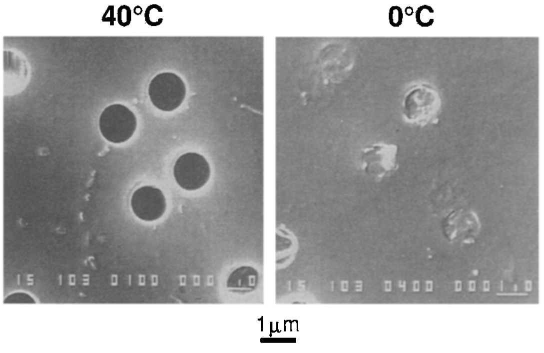

Fig. 5. Scanning electron micrographs of chemically modified CR-39 PTM with poly(A-ProOMe). The films were freeze-dried at 40°C and 0°C.

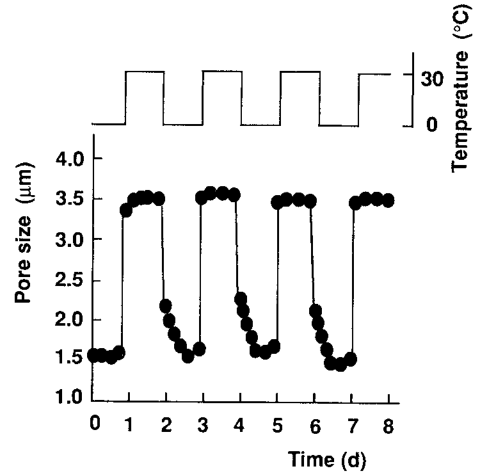

Fig. 6. Change in pore size of copolymer PTM composed of CR-39 and A-ProOMe in 50/50 wt-ratio. The temperature of the water bath containing the film was cyclically changed between 0°C and 30°C at 24 h intervals.

gel is not so rapid when compared with the volume shrinking because of the energetic process of expanding molecular structure in order to accommodate a big amount of water.

According to this temperature change in pore size, it is possible to control the flow of ions in a solution. Fig. 7 shows the change in current through the membrane when the temperature of the 0.1 M KCl solution is cyclically changed between 24°C and 34°C under the supply of voltage. In this case a single pored PTM grafted with NIPAAm at the yield of 8 wt% was used as a diaphragm. The conductivity at different temperature was compensated by the next equation:

$$k = k_{20}\{1 + a(T-20) + b(T-20)^2\}, \qquad (4)$$

where k_{20} is the electric conductivity at 20°C, and a and b are constants, respectively [10]. The phase transition temperature of this hydrogel, poly(NIPAAm), is 32°C. Although the change in current was rather slow, a good reproducibility of pore size at both temperatures was obtained. It is noted, however, that the complete closure of pores in order to prevent the transportation of potassium ions was not observed under the present condition. This is probably based on the fact that the hydrogel layer of poly(NIPAAm) swollen with water permits the transportation of such small ionic species as potassium even if the pore is completely occupied with the hydrogel layer.

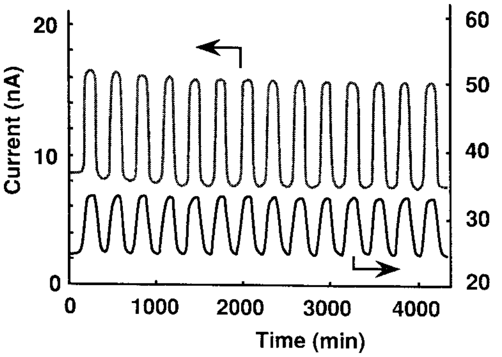

Fig. 7. Cyclic change in current through a thermo-responsive PTM made of single pored PET. The membrane was used as a diaphragm of a dialysis cell containing a 0.1 M KCl solution. The temperature was changed between 24°C and 34°C.

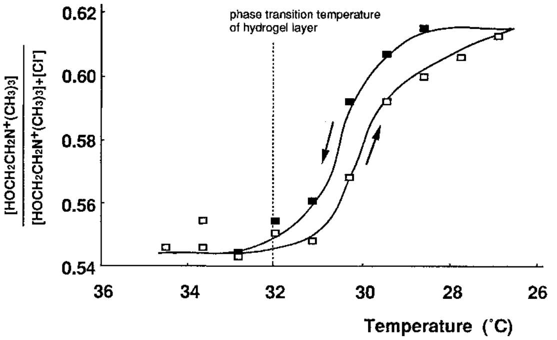

Fig. 8. The selectivity of permeation between choline positive ions and chlorine negative ions through a thermo-responsive PTM of PET. The fluence of the ion beams was 10^6 ions/cm^2. The arrows indicate the directions of temperature change.

It is expected that the permeation through the pores of the modified PTM is more precisely controlled by temperature with the increase in size of passing molecules. Choline chloride with a molecular weight of 140 was labeled by tritium for the positive part and by ^{36}Cl for the negative part. The permeability of choline$^+$ and chlorine$^-$ was determined from the radioactivity in the collected fractions. Fig. 8 shows the change in selectivity of positive ion when the temperature is decreased from 36°C to 26°C and vice versa. When the pore is open at higher temperature regions, the selectivity of the positive ion is close to 0.5, which means that both positive and negative ions freely pass through the open pore. With a decrease in temperature, the selectivity of positive ions becomes larger. It is remarkable that the selectivity changes abruptly when the temperature approaches the phase transition temperature of the attached hydrogel layer (in this case 32°C). Although the true reason for this selectivity change is not known, it is probable that the narrowing of the pore size brought about by gel swelling forces the contact between the hydrogel layer and the passing ions, which may change the balance between positive and negative ions. Another point is the presence of hysteresis of the change. The abrupt change occurred at a lower temperature by cooling down when it was compared with the change by heating up. This is another example to indicate the characteristic of the hydrogel.

4. Conclusions

Ion beams with an energy of 10 MeV/n were used for producing porous membranes of PET and CR-39 films. The condition to obtain cylindrical pores was explained by the relation between relative etching rate Q and restricted energy transfer from ion beams to polymer films REL. The porous membranes modified either by copolymerizing or by grafting hydrogel-forming monomers changed pore size in response to the change in temperature. A cyclic change in the conductivity of potassium ions through the membrane of a single pore was observed when the temperature of the dialysis cell was cycled between two temperatures. The selectivity of an organic ion passing through the membrane changed at the phase transition temperature of the attached hydrogel layer.

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