Thermo-response of ion track pores in copolymer films of methacryloyl-L-alanine methyl ester and diethyleneglycol-bis-allylcarbonate

Masao Tamada*, Masaru Yoshida, Masaharu Asano and Hideki Omichi
Department of Material Development, Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Watanuki 1233, Takasaki, Gumma 370-12, Japan

and Ryiochi Kakakai
Department of Chemistry, Faculty of Engineering, Gumma University, Kiryu, Gumma 376, Japan

and Reimar Spohr and Johann Vetter
Gesellschaft für Schwerionenforschung, Planckstraße 1, Postfach 11 05 52, D-6100 Darmstadt 11, Germany
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Copolymer films (100 μm thick) were prepared by cast polymerization of methacryloyl-L-alanine methyl ester (MA-L-AlaOMe) and diethyleneglycol-bis-allylcarbonate (CR-39). The films swell in water at temperatures below 60°C. The degree of swelling increases with decreasing temperature down to 0°C. The swelling capacity of the films increases with increasing MA-L-AlaOMe content. The thermal response is reversible. Swelling and shrinkage have different time constants of ~24 h for swelling and ~10 min for shrinkage. The films were subject to an ion track etching process consisting of a heavy ion irradiation using gold ions of 11.4 MeV per nucleon specific energy followed by subsequent etching of the latent ion tracks in NaOH solution. The resulting porous membranes show a reversible change of the pore diameters of ~12% between 0°C and 60°C for a copolymer with 70 vol% MA-L-AlaOMe.

(Keywords: thermo-response; methacryloyl-L-alanine methyl ester; CR-39; particle track; copolymer film; cast polymerization)

INTRODUCTION

Much attention has been directed in recent years towards polymer hydrogels that undergo large volume changes due to external stimuli such as electric fields[1], temperature[2], illumination[3], pH[4] and various chemicals[5–7]. Such effects are similar to those observed in physiological, biological and chemical systems, and a variety of novel applications is expected from these hydrogels, including chemical valve membranes, artificial muscles, sensors, immobilized-enzyme reactors and controlled drug delivery systems.

New polymer hydrogels based on methacryloyl or acryloyl derivatives with pendant α-amino acid groups show a dramatic swelling in water at different temperatures[8–10]. The goal of the work reported here was to combine this swelling capability with the possibility of creating ion track pores known for the pure polymer of diethyleneglycol-bis-allylcarbonate (CR-39)[11–15]. For CR-39 the track areal density, the incident angle and the diameter of the produced pores can easily be adjusted as follows. The areal density of track pores corresponds directly to the number of incident ions per unit area. The angle of the tracks to the surface normal of the film is controlled by the incident angle of the impinging ions. And, finally, the track pore diameter is defined by the duration of the etch time.

The combination of methacryloyl-L-alanine methyl ester (MA-L-AlaOMe) and CR-39 is interesting because the pendant L-alanine methyl ester residue acts as a hydrogel with a reversible thermal response and – in contrast – the CR-39 component acts as a track recording material forming cylindrical pores after ion irradiation and chemical etching.

In the present paper we deal with the thermal response of various copolymer films of MA-L-AlaOMe and CR-39, their chemical etching, and the thermal response of the pore diameters of ion tracks created and etched in these films.

MATERIALS AND METHODS

Chemicals

MA-L-AlaOMe was synthesized according to published recipes[10]. CR-39 was supplied from PPG Industries-

*To whom correspondence should be addressed

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Asia/Pacific Ltd (Tokyo, Japan). The polymerization catalyst benzoylperoxide (BPO) was supplied from Wako Pure Chemical Industries Ltd (Osaka, Japan). The ion track etchant, NaOH (analysis grade), was supplied from Merck (Darmstadt, Germany).

Polymerization

The copolymer films of MA-L-AlaOMe and CR-39 were fabricated by cast polymerization. A mixture of MA-L-AlaOMe and CR-39, containing 3% BPO as catalyst, was poured into a cast consisting of two glass plates (90 mm × 120 mm × 3 mm) separated by a 100 μm thick polyethylene terephthalate spacer. The inner surfaces of the glass plates were coated with a detachment agent (KF-99, Shin-Etsu Chemical Co. Ltd, Tokyo, Japan) at a temperature of 200°C over 1 h. The mixture in the cast was polymerized at 75°C for 24 h. After polymerization the film could be detached from the glass plates. The composition of the copolymer film is expressed here by the volume percentage of MA-L-AlaOMe. The density of the copolymer film at 25°C was calculated from its weight and volume for a disc with a diameter of 25 mm and thickness of 90.9 μm. Its weight was measured with an electronic microbalance (4503 MP6 electron microbalance, Sartorius, Göttingen, Germany).

Irradiation

A film with 70 vol% MA-L-AlaOMe was cut into 40 mm × 40 mm squares and attached to glass plates (50 mm × 50 mm × 1 mm). The copolymer films on the glass plates were irradiated under vacuum conditions[16] at the UNILAC heavy ion accelerator of GSI Darmstadt by gold ions of 11.4 MeV per nucleon at a fluence of 5×10^5 ions cm^{-2}. The incident angle of the ions was 0° with respect to the surface normal.

Chemical etching

The unirradiated copolymer films were etched with 5 N NaOH solution at 70°C without stirring. The bulk etch rate was estimated from the decrease of the film thickness. The thickness of the coopolymer films was measured with a digital thickness gauge (Metro 1010 digital thickness gauge, Johannes Heidenhain, Traunreuth, Germany). The irradiated film with 70 vol% MA-L-AlaOMe was etched for 7 min in 5 N NaOH solution at 70°C without stirring. The surface of the etched copolymer film was observed with a scanning electron microscope (PW 6700/10 D746 Philips) after the reversible thermal response experiment. The distribution of pore diameters was obtained by measuring the diameter on photographs taken with an optical microscope (Image Shearing Readout Unit, Vickers Instrument, A. Vickers Ltd, York, UK). The area for counting the number of pores was 100 μm^2.

Thermal response

In the swelling experiments, the copolymer films (20 mm × 20 mm) were soaked in deionized water at 0°C. The films were weighed after 24 h when the equilibrium of swelling was reached. For testing the reversibility of swelling a film with 70 vol% MA-L-AlaOMe was alternately soaked for 24 h in deionized water at 0 and 60°C and weighed after reaching thermal equilibrium. The swelling ratio of the films is defined by:

$$\text{swelling ratio } [\%] = 100\ (W - W_0)/W_0$$

where W is the weight of the film after swelling and W_0 is the weight of the dry film.

The thermal response of the etched track diameters was observed for one selected pore. The diameter of a surface pore in the copolymer film was measured with an optical microscope.

RESULTS AND DISCUSSION

Thermal response

The effect of temperature on swelling was observed in water. Films with 0, 30, 50, 60 and 70 vol% MA-L-AlaOMe were soaked for 24 h in water at temperatures of 0, 20, 40, 60 and 80°C, until the water uptake of the film attained equilibrium. The corresponding swelling ratios were determined from the weight. *Figure 1* shows the effect of temperature on swelling. The swelling ratio of all films remained constant between 60°C and 80°C. At a temperature of 40°C all copolymers exhibited swelling while the polymer film of pure CR-39 maintained its initial swelling ratio. The swelling of copolymer films further increased with decreasing temperature below 40°C and attained its maximum at 0°C. This temperature dependence is similar to that of another copolymer hydrogel composed of 80 vol% MA-L-AlaOMe and 20 vol% 2-hydroxypropylmethacrylate, although this copolymer has a much larger swelling ratio of 2500% at 0°C and 30% at 60°C (ref 10). The much lower swelling of the films described in this report seems to be due to the highly crosslinked structure of the bifunctional monomer CR-39. The swelling capacity of the copolymers increases with increasing content of MA-L-AlaOMe. As it appears MA-L-AlaOMe seems responsible for the observed thermal response.

The time response of swelling and shrinkage was investigated using a film with 70 vol% MA-L-AlaOMe. The film was first soaked for 30 h in water at 0°C and immediately afterwards immersed in water at 60°C. *Figure 2* shows the thermal response of swelling. The swelling of the film reaches its half-maximum value after 5 h and requires ~24 h to reach thermal equilibrium. The film, however, shrinks within 10 min when it is immersed in water at 60°C. Therefore shrinkage is 140 times faster than swelling. At 60°C the remaining swelling ratio is only ~3%.

The reversibility of swelling is an essential requirement for future uses in actuators and sensors. To examine this, the film with 70 vol% MA-L-AlaOMe was alternately

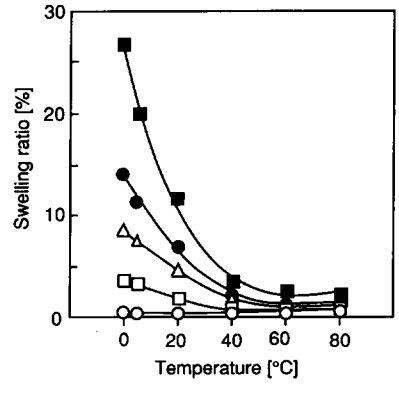

Figure 1 Swelling ratio of various copolymer films in the equilibrium state as a function of temperature. Percentage of MA-L-AlaOMe: 0 (○); 30 (□); 50 (△); 60 (●); 70 vol% (■)

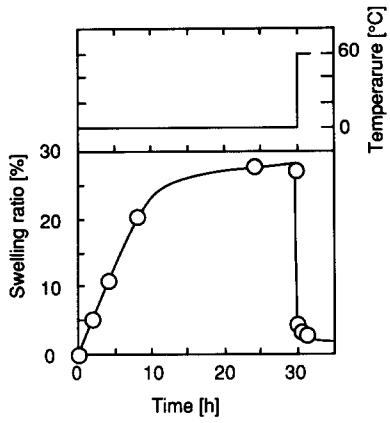

Figure 2 Thermal response of swelling for a film with 70 vol% MA-L-AlOMe

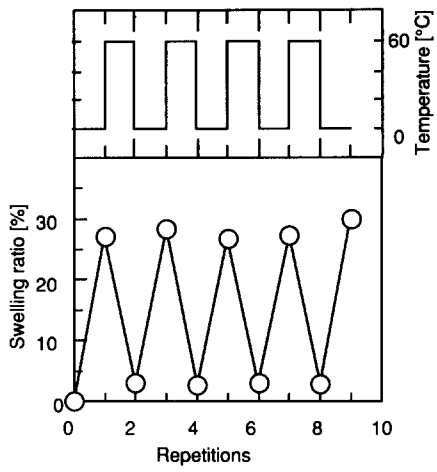

Figure 3 Cyclic response of swelling and shrinkage for a film with 70 vol% MA-L-AlaOMe

soaked in water at 0 and 60°C until equilibrium was reached. *Figure 3* shows the cyclic behaviour of swelling. The film swells at 0°C and shrinks at 60°C reversibly. The reversibility holds with the exception of the initial state. Thus the film appears to be a first step towards obtaining a repeatable actuator. The average swelling ratio was 27.9% at 0°C and 2.9% at 60°C.

Chemical etching

To investigate the effect of MA-L-AlaOMe on the bulk etch rate, unirradiated films with 0, 20, 40, 50, 60 and 70 vol% MA-L-AlaOMe were etched in 5 N NaOH at a temperature of 70°C. *Figure 4* shows the bulk etch rate of the films. The bulk etch rate increased with increasing MA-L-AlaOMe content. A linear relationship between the logarithm of the bulk etch rate and MA-L-AlaOMe content exists. The bulk etch rate of the film with 70 vol% MA-L-AlaOMe was about 100 times higher than that of pure CR-39.

A major factor determining the shape of etched tracks is the track etch ratio V_t/V_b, where V_t is the track etch rate and V_b is the bulk etch rate. To obtain cylindrical pores the track etch ratio[17] should be of the order of 100. Hence the increasing bulk etch rate with increasing MA-L-AlaOMe content is by itself unfavourable for producing cylindrical pores. A similar phenomenon has been reported for the copolymer of CR-39 with maleic anhydride[18] and bis-allyl urethane[19].

For creating ion track pores, the film with 70 vol% MA-L-AlaOMe was irradiated with gold ions of 11.4 MeV per nucleon and etched for 7 min in 5 N NaOH at 70°C. *Figure 5* shows the surface of the film observed with a scanning electron microscope. The etched tracks are circular pores. The contour of the pores is a well defined circle and the unirradiated surface is very smooth.

Figure 6 shows the size distribution of the pore diameters. The total number of counted pores was 56 on a surface of 100 μm^2. The resulting areal density of tracks is 5.6×10^5 ions cm^{-2} corresponding nicely to the predicted ion dose of 5×10^5 ions cm^{-2}.

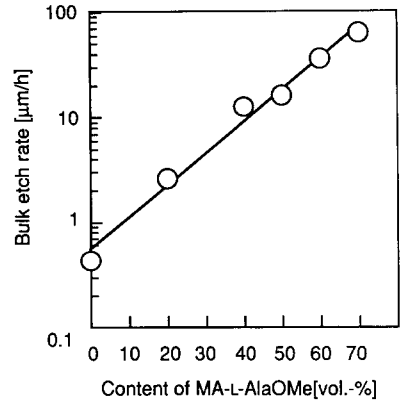

Figure 4 Effect of MA-L-AlaOMe on the bulk etch rate in 5 N NaOH at 70°C

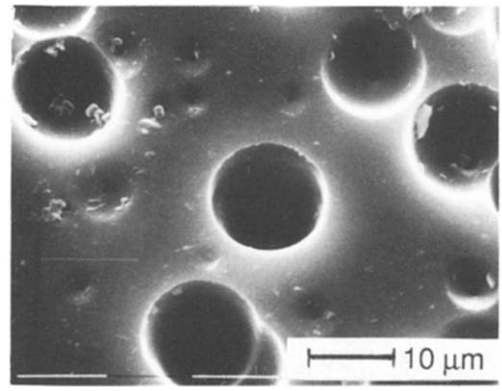

Figure 5 Surface pores in an ion irradiated and etched film with 70 vol% MA-L-AlaOMe observed by SEM. The irradiated film was etched for 7 min in 5 N NaOH at 70°C

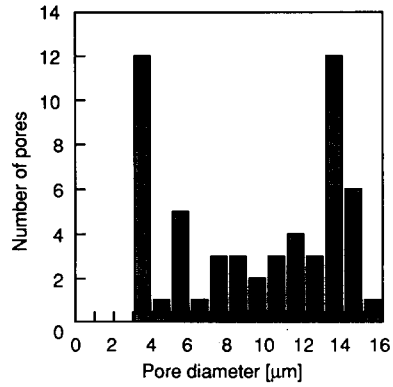

Figure 6 Pore diameter distribution in the etched copolymer film with 70 vol% MA-L-AlaOMe. The film was irradiated with gold ions (5×10^5 ions cm^{-2}) and etched for 7 min in 5 N NaOH at 70°C

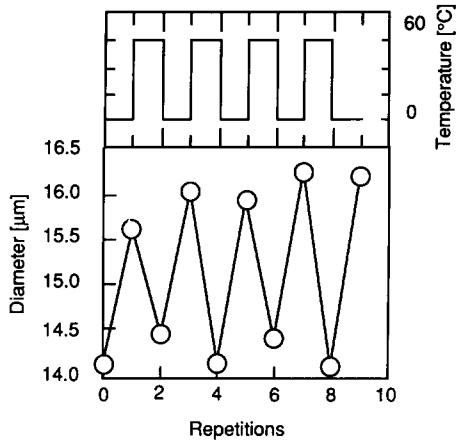

Figure 7 Thermal response of pore diameter in an etched film with 70 vol% Ma-L-AlaOMe. The irradiated film was etched for 7 min in 5 N NaOH at 70°C

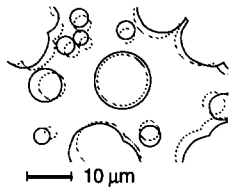

Figure 8 Pore geometry of swollen and shrunken state. The irradiated film with 70 vol% MA-L-AlaOMe was etched for 7 min in 5 N NaOH solution at 70°C. Solid lines are contours of pores in the swollen state and broken lines are those in the shrunken state. The area of observation was the same as that in *Figure 5*

The distribution of track diameters has peaks at 3 and 13 μm. The pores with 3 μm diameter are more shallow than those with 13 μm diameters and are probably due to an ion beam contamination by lighter ions. Light ions should have a smaller electronic stopping rate and thus lead to a strongly reduced track etch rate[20]. Further experiments are necessary to improve the pore size distribution.

Thermal response of ion track pores

The etched film with 70 vol% MA-L-AlaOMe was soaked in water at 0 and 60°C alternately and the diameter of one selected pore was measured after each thermal cycle. The pore located in the centre of *Figure 5* was used for this experiment. *Figure 7* shows the thermal response of its diameter. The diameter exhibits a reversible response, corresponding to the swelling response of the unirradiated film. The average diameter in the swollen state was 16.0 μm and in the shrunken state 14.3 μm except for the initial dry state of the freshly polymerized film. In comparison to the dry state (pore diameter 14.2 μm) the pore diameter increased by 1.1% in the shrunken state and by 13.1% in the swollen state. As a result, the cyclic size difference was 12.0%. In the case of swelling as shown in *Figure 3*, the dry film values were 2.9% below the shrunken state, 27.9% below the swollen state, and there was 25.0% difference between the shrunken and swollen states. The swelling ratio is defined by weight and thus must be corrected by the specific weight of the film. The density of the film with 70 vol% MA-L-AlaOMe is 1.26 g cm^{-3}. Thus these swelling ratio values of 2.9, 27.9 and 25% correspond to 3.7, 35.2 and 31.5% volume change, respectively (assuming the density of water = 1 g cm^{-3}). The change of volume in the film is a three-dimensional phenomenon. Therefore the one-third power of the volume change corresponds to the diameter change. The ratios of the one-third power of values ($1.037^{1/3}$, $1.352^{1/3}$, $1.315^{1/3}$) for the volume change to those (1.011, 1.131, 1.12) for the diameter change were 1.0, 0.98 and 0.98. Thus, the observed diameter changes correspond well to the observed volume changes. This also means that the increased volume of the film in the swollen state corresponds directly to the absorbed water. From this finding it is obvious that the diameter change of any pore size can be predicted from the swelling ratio of the unirradiated film.

Figure 8 compares the geometry of swollen pores with the geometry of shrunken pores whereby both geometries are centred about the central pore. The whole film swells and shrinks isotonically[21].

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