

TEMPERATURE RESPONSIVE TRACK MEMBRANES

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1. INTRODUCTION

Particle track membranes (PTM) have a narrow size distribution of pores of cylindrical shapes. This characteristic makes PTM enable to differentiate particles of similar dimensions precisely. 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 carried out inside living organisms under various inner and outer conditions. One of the possible approaches to realize such a sophisticated membrane is combining PTM with a polymer of a different characteristic responding to these environmental conditions by means of chemically bonding the polymer to the pore wall.

Hydrogels are known to possess the

ability to change their volumes when environmental stimuli such as temperature, pH, electric fields are imposed [2,3]. These changes are accompanied by the absorption and desorption of water by the gels. There is a critical temperature called "lower critical solution temperature LCST" at which an abrupt change in volume of the gels occurs [4]. The theoretical treatment of the changes has been studied [5]. Even the applications of these changes have been tried to realize artificial muscles, biosensors, etc.[6].

The present report intends to show the possibility of synthesizing such membranes by combining PTM with the hydrogel. One of the conveniences of applying hydrogels as the polymer to modify PTM is the ease of changing the properties by choosing the appropriate chemical structure of the repeating unit of the polymer gels. In the present study, the hydrogel that was obtained by the polymerization of an acryloyl or methacryloyl monomer containing amino acid groups in its repeating unit was used. The reason to choose such a hydrogel containing amino acids is based on the fact that specific characteristics of living organisms responding to environmental

conditions are highly dependent on the presence of various types of amino acids in the forms of proteins, enzymes, etc.

2. AMINO ACID CONTAINING HYDROGELS

The acryloyl or methacryloyl monomer containing amino acid unit was synthesized as follows: methyl ester of amino acid hydrochloride was dissolved in chloroform containing triethylamine. Acrylic or methacrylic acid was added to the solution diluted with tetrahydrofuran. Then, dicyclohexyl-carbodiimide was added to the solution kept at a low temperature with agitation. The precipitate of dicyclohexylurea was removed by filtration to give a raw material of amino acid containing acryloyl or methacryloyl monomer. The polymerization of the purified monomer was carried out by irradiating the monomer solution with gamma rays from cobalt-60 at room temperature [7]. The polymer obtained with a small dose (less than 100kGy) was dissolved in water at low temperature. Above LCST, however, it precipitated from the water solution. This change was followed by the decrease in transmittance of visible light at 500 nm in the case of acryloyl-L-proline methyl

Fig. 1. Change in transmittance at 500 nm of aqueous solution of the polymer gel of acryloyl-L-proline methyl ester

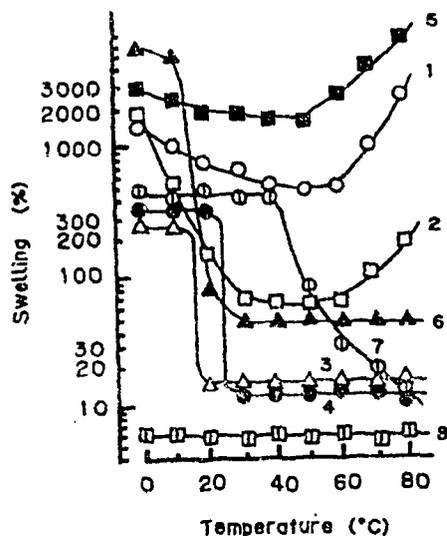
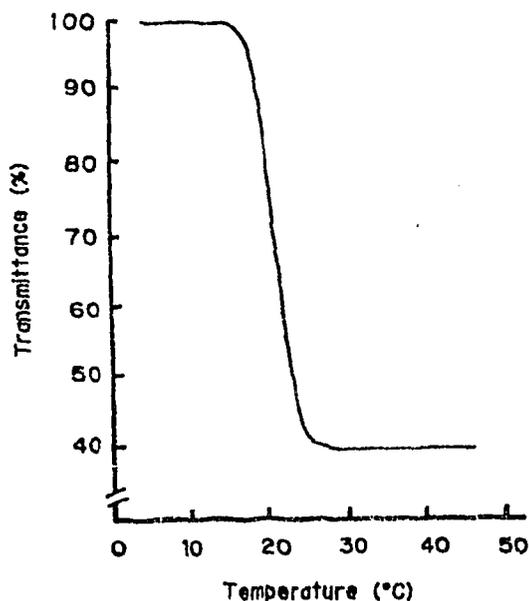


Fig. 2. Degree of swelling of methacryloyl amino acid containing polymer gels treated for 24h at each temperature after preswelling at 0°C for 3 weeks: methyl esters of (1)glycine, (2)alanine, (3)valine, (4)isoleucine and (5)alanine, (6)alanine ethyl ester, (7)alanine butyl ester, (8) alanine benzyl ester

ester as shown in Fig.1 for example and by the evolution of an endothermic peak in the DSC curve due to the phase transition [8]. It was observed that the polymer size reversibly changed according to the temperature change. This monomer was copolymerized with a small amount of such a crosslinkable monomer as polyethylene glycol dimethacrylate under a similar procedure mentioned above. The copolymer obtained was no more soluble in water. A large amount of water was absorbed by the copolymer below LCST. Above LCST, on the other hand, the water was released from the copolymer. This change can be followed by the weight measurement of the copolymer. The water uptake thus obtained is indicated as the degree of swelling of the copolymer in Fig.2. The degree of swelling depends on what kind of amino acid group and two adjacent alkyl groups are included in the monomer unit. The balance between a hydrophilic group and a hydrophobic group and that between two different hydrophobic groups are responsible to this change. The change in swelling with the change in temperature was reversible.

3. PREPARATION OF THERMO-RESPONSIVE MEMBRANES

The commercially available CR-39 is known as a polymer with a high sensitivity to the irradiation of heavy ions. It is possible to produce cylindrical pores by the irradiation of heavy ions of high energy and the following chemical etching with an alkali solution. For synthesizing a membrane of porous structure with a function responding to temperature change, CR-39 was selected as a raw material. Two processes as shown in Fig.3 were tried. In Process 1, diethyleneglycol-bis-allylcarbonate, the monomer unit of CR-39, and the amino acid containing monomer were catalytically copolymerized. Then, the copolymer film was irradiated by such heavy ion beams as Au of the energy ca. 10MeV/u and subject to the following chemical etching with 6N NaOH solution at 60° for 6 h. In Process 2 the homopolymer film of diethyleneglycol-bis-allylcarbonate which was preliminarily irradiated with heavy ion beams and etched with the alkali solution was used as a raw material for the further chemical modification procedure. The amino acid containing acryloyl monomer was graft polymerized onto the porous membrane either by the method of radiation-induced polymerization or photo-induced polymerization [9-11].

4. CHARACTERISTICS OF THERMO-RESPONSIVE MEMBRANES

The copolymer film which was irradiated with heavy ion beams was chemically etched. Fig.4 shows the comparison of etching speed between the

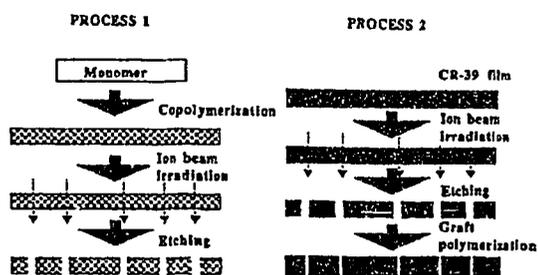


Fig.3. Preparation of thermo-responsive membranes

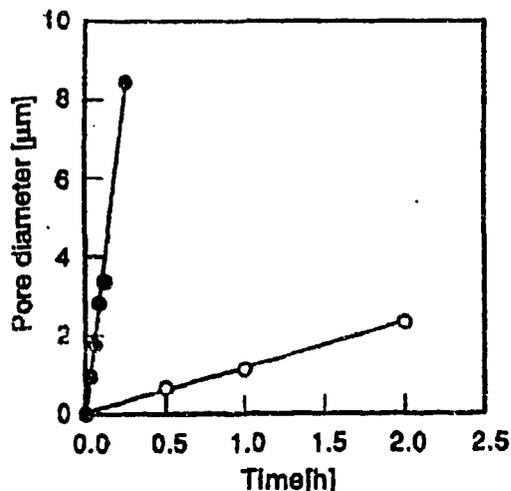


Fig. 4. Pore diameter and etching time with 6N NaOH solution at 60°C

copolymer and CR-39. In both cases, the pore diameter changes linearly with the etching time. The growth rates of pore diameter obtained from the slopes are 33.6 and 1.1 $\mu\text{m}/\text{h}$ for the copolymer film and CR-39, respectively. The necessary etching time to obtain the same pore diameter is, therefore reduced by a factor of ca. 1/30 by copolymerizing amino acid containing monomer. The cross-sectional view of the pore observed by the scanning electron microscopy indicated that the copolymer film possessed cylindrical

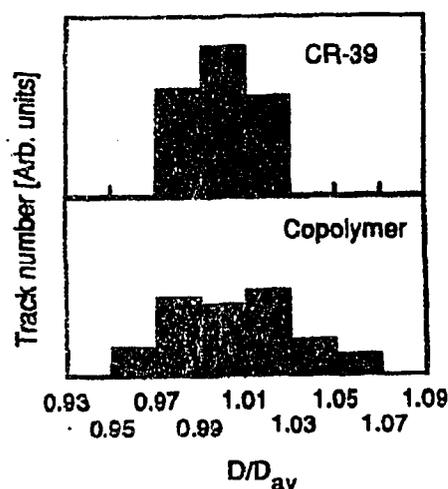


Fig. 5. Distribution of pore diameter expressed by D/D_{av} for CR-39 and copolymer film containing methacryloyl L-alanine methyl ester

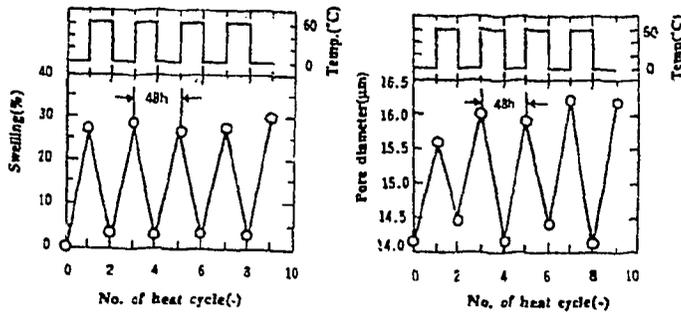


Fig. 6. Effect of heat cycle on changes in degree of swelling and pore diameter

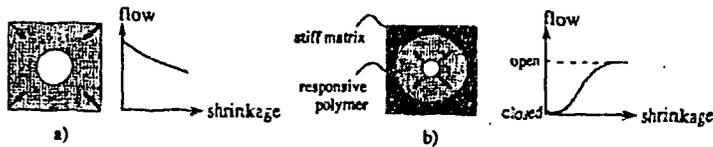


Fig. 7. Dynamic ranges of flow through (a) copolymer membrane and (b) graft polymer membrane

pores when the sensitivity expressed by V_t/V_b-1 was sufficiently large. The pore size distributions are shown in Fig.5. Comparing the pore size distributions of CR-39 and copolymer, that of the copolymer was a little broader. One of the reasons of the expanded distribution may be attributed to the mixing of the radiation sensitive component of CR-39 with the amino acid containing hydrogel layer in the copolymer.

The porous membranes obtained by Process 1 and Process 2 were dipped in water. Fig.6 shows that the water uptake of the copolymer membrane changes between 0% and 30% when the stepwise change in temperature of the outside water is repeated between 0°C and 60°C. Along with this cyclic change, the pore size changes reversibly. The maximum and minimum pore size were ca. 16 μm and 14 μm , respectively. The time constant of the thermo-response of pore size change was not equal between the two steps of increasing and decreasing temperature. That is, the former was ca.10 min while the latter was 24 h. A complete closure of the pore was observed with the graft membrane. The maximum pore diameter was 1.2 μm . The possibility to realize such an on-off characteristic with this membrane is based

on the fact that the layer of the thermo-responsive hydrogel is localized on the surface of pore. Then, only the pore region is able to respond to the stimulus from outside. The response time in this case, however, depend on the amount of the hydrogel layer. The smaller the amount of the hydrogel is, the quicker is the response.

The combination of such a thermo-responsive pore structure makes it possible to apply the membrane to such field as control of a micro flow through the pore by changing temperature, pH, electric field, etc. Schematic changes in flux with these two type of porous membranes are shown in Fig.7. In the case of the membrane obtained in Process 1, the flow can be changed within a certain range. The presence of the maximum and the minimum of the flow in this case is due to the residual pore size even at the temperature providing the utmost shrinking. With the membrane obtained in Process 2, on the other hand the gate is controlled from the complete shut off state to the maximum open state. In near future this technique will be applied to the realization of distinguishing one molecule from the other of similar size with different chemical affinity by introducing a hydrogel component which

has a specific affinity to a certain molecule.

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