Fabrication of Precursor Membrane with Reactive Groups via Plasma-Induced Graft Polymerization

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1. Introduction

The porous substrate having many nano to micron-sized pores inside is an essential material that is widely used in filtration [1], separator [2], substrate for pore-filling membrane [3], gating membrane [4], membrane chromatography [5], and so on. The convective mass transfer through the pores plays an important role for little pressure loss and energy conservation, using it in filtration or membrane chromatography purposes. Further modification of pore surface with functional molecules can broaden the application field of the porous material: ethylene glycol chain grafting onto pore surface can improve resistivity to protein adhesion, chelating agent grafting can add ion exchange property, and also membrane reactor can be achieved by catalytic agent grafting.

In order to extend the porous material while fully maintaining the inherent function, only the pore surface should be functionalized. The requirement is quite opposite to the case of pore-filling membrane, which requires high filling ratio of the pores. A promising and versatile strategy to achieve such requirement is to fabricate the precursor membrane having reactive groups on the pore surface uniformly throughout the membrane (Scheme 1). Subsequent reaction of the reactive groups with aminated molecule can easily yield functional porous substrate without losing its intrinsic property.

In order to fabricate such precursor membrane, plasma-induced graft polymerization technique (PIGP) is an appropriate methodology [3]. The plasma-induced vacuum ultraviolet (VUV) [6] has favorable features that can penetrate the substrate, modify only the pore surface and has little damage to the substrate. When ultraviolet [7] is used instead of plasma-induced VUV, the energy of the ray is too low to penetrate through opaque and thick substrate, and uniform modification throughout the membrane is difficult. On the other hand, if γ-ray [8] is used instead, the energy of the ray is so strong that it induces polymerization not...

Scheme 1. Strategy to fabricate functional porous substrate via precursor membrane with thin polyGMA layer.
only on the pore surface but also inside substrate polymer. Plasma-induced VUV has the intermediate and appropriate energy for the purpose.

In the present study, precursor membrane for various functional membranes was attempted to be fabricated by immobilizing very thin reactive group layer onto the pore surface of a porous substrate via PIGP. Glycidyl methacrylate (GMA) having epoxide group was chosen as a monomer reactive to amino group terminated functional molecules (Scheme 1).

2. Methodology

2.1. Materials
Porous polyethylene (PE) film was kindly supplied by Asahi Chemical Co. Ltd., Japan, and was used as porous substrate. The PE substrate has a thickness of 90 μm, maximum pore diameter of 200 nm, porosity of 50%, and 22.9 m²/g specific surface area measured by BET method. Ethanol, methanol, sodium dodecyl sulfate (SDS), and GMA were supplied by Wako Pure Chemicals, Japan, and were used as received.

2.2. Introduction of PolyGMA onto Membrane Pore Surface via Two PIGP Methods
Two methods of PIGP were used for fabricating polyGMA grafted membrane: one is peroxide method [9] and the other is free radical method [3]. In peroxide method, porous PE substrate was treated with an argon plasma with the pressure of 10 Pa and then was exposed to air for 60 s to generate peroxide groups on its pore surface. The substrate containing peroxide groups was immersed into extensively degassed (freeze-thawed) monomer solution. By holding the solution at 80 °C for designated time, the peroxide groups were broken to give active radical sites, and graft polymerization reaction proceeded from the initiator radicals. Resulting membrane was extensively washed with water and ethanol several times, and analyzed after drying.

On the other hand, in free radical PIGP method, the procedure was the same as that of the above peroxide method, except that exposure to air was not carried out and the reaction temperature was 30 °C. In the method, graft polymerization proceeds from radicals produced by direct hydrogen drawing from PE by plasma-induced VUV.

The grafting degree of polymer introduced by PIGP can be influenced by monomer concentration, polymerization time, and solvent. The low amount of polymerization was attempted to be attained by all the parameters. Note that a typical condition in the case of fabricating pore-filling membrane is as follows; water is used as solvent, 5 wt% monomer and 5 wt% SDS solution is used for the reaction. The reaction time is from 30 to 120 minutes.

In the present study, contrary to the classic condition, 30/70 vol/vol methanol/water mixed solution was used as solvent instead of pure water. Although it is known that the incorporation of organic solvent into water can lower the reaction rate in PIGP [3], further increase of methanol was not practical because freeze-thawing of the methanol-rich aqueous solution often cracks the solution bottle. The monomer concentration was set as 0.5 wt%, which is only one tenth of pore-filling condition. The reaction time was set as short as 15 minutes.

2.3. Gravimetric and Spectroscopic Analysis of PolyGMA Grafted Membrane
Filling ratio of the fabricated membrane is defined as the following equation.

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\text{Filling ratio} = \frac{\text{Volume of grafted polymer}}{\text{Pore volume of porous substrate}}
\]

As density of vinyl polymer does not vary so much, it is regarded as 1.0 [10] in the present study. In the porous PE substrate, surface area of outer surface is about 10^4 times smaller than that of pore surface, thus contribution of outer surface area was ignored.

FT-IR spectra of the porous substrate and the prepared membrane were observed with Nicolet MAGNA 550 (Thermo Scientific Japan).

The fabricated precursor membrane was cut into 20 μm thick pieces by microtome and the cross-section of the membrane was observed by infrared microscope unit (Nic-Plan microscope) at intervals of 10 μm (aperture size was set as 10 μm × 100 μm). As the porous substrate is 90 μm thick, the spectra were taken at ten points. The cross-sectional distribution of polyGMA in the substrate was evaluated by the ratio of the peak derived from GMA to that from PE.

3. Results and Discussion
In the peroxide method, the filling ratio of the fabricated membrane was 5.0 wt%. By dividing the amount by BET surface area of the material, number density of the monomeric GMA unit on the pore surface can be estimated, and it is amounted to 9.3 GMA units/nm² pore surface. When free
radical PIGP method was used, the filling ratio was as low as 0.6 wt%, amounted to 1.1 GMA units/nm², which could hardly affect pore size and inherent property of the porous substrate. As the grafting amount was small, FT-IR was used to ascertain the success of polyGMA grafting in Figure 1, in addition to gravimetric analysis. The stretching vibration adsorptions of carbonyl group and epoxide group derived from GMA were found in 1730 cm⁻¹ and 1260 cm⁻¹ respectively. The cross-sectional distribution of GMA group throughout the membrane fabricated by free radical PIGP method was assessed by infrared microscope and the result is shown in Figure 2. It is clearly shown that the GMA group is uniformly distributed throughout the membrane, which is suitable for precursor membrane. The precursor membrane could be modified by aminated functional molecules to fabricate further functional porous material (Scheme 1).

4. Conclusion
Precursor membrane having very thin functional layer on the pore surface of porous substrate was fabricated by conditioning plasma-induced graft polymerization. In order to reduce the amount of graft polyGMA, monomer concentration, reaction time, solvent were all reconditioned. As a result, porous substrate with 0.6 wt% polyGMA (1.1 GMA unit/nm² pore surface) on its pore surface was fabricated via free radical PIGP method. Uniform introduction of the reactive GMA was proven by infrared microscopy of the membrane cross-section. The precursor membrane will be used for fabricating further functional porous substrate by simply reacting with aminated functional molecules.

References