

# Porous Polydimethylsiloxane Membranes Treated with Aminopropyltrimethoxysilane

TAKAOMI KOBAYASHI,\* HITOSHI SAITOH, and NOBUYUKI FUJII

Nagaoka University of Technology, Department of Chemistry, Kamitomioka, Nagaoka, Niigata, 940-21, Japan

## SYNOPSIS

Polydimethylsiloxane (PDMS) membranes were made by catalytic hydrosilylation of a siloxane compound having a vinyl group and an SiH group in the presence of 1,4-dioxane. By washing it with water many pores were formed in the membrane. Then, the pore size of the membrane was controlled by treatment of aminopropyltrimethoxysilane (APTMS) solution. When increasing the APTMS concentration, the pore size of the membrane was reduced by the formation of APTMS oligomer on the surface of the membrane. The characteristics of the membrane was examined by IR, ATR-IR, and SEM techniques. Also, the permeation properties of dextrans and polystyrene latexes through the treated membrane were examined by the ultrafiltration method. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Polydimethylsiloxane (PDMS) containing an unsaturated vinyl group and that having an SiH group facilitate vulcanization in the presence of a catalyst (usually a platinum derivative).<sup>1</sup> The vulcanizate is applied to rubber synthesis<sup>1,2</sup> and various fields of industry use.<sup>3</sup> In the field of membrane technology, there are a large number of reports on permeation of gas mixtures through PDMS membrane having nonporous structure.<sup>4,5</sup> However, little is known concerning the study of porous PDMS membrane. As new materials for membrane technology, we previously developed PDMS vulcanizate having pores formed by hydrogen foams during hydrosilylation cure.<sup>6</sup> It was difficult to prepare the thin membrane having various pore sizes by this method, because the pore formation sensitively depends on the conditions of hydrogen generation during the cure such as cure time, cure temperature, and membrane thickness.

In the present work we prepared PDMS membrane having many pores by hydrosilylation cure in the presence of 1,4-dioxane. Then the pore size of the PDMS membrane was controlled by treatment

with a silane coupling agent. The characteristics of the membrane treated with the silane coupling agent and ultrafiltration property of dextrans for polystyrene latexes and dextrans was examined.

## EXPERIMENTAL

### Materials

PDMS having vinyl content of 0.28 mmol/g was prepared according to the literature.<sup>6,7</sup> In order to obtain proper mechanical strength of PDMS membrane cured by hydrosilylation in accordance with the equation (Scheme 1), we employed vinyl-type PDMS having Q resin structure, quadrifunctional siloxane SiO<sub>2</sub> (Scheme 2), designated by conventional silicone nomenclature.<sup>2</sup> Hydrosilyl type PDMS, poly(methylhydrogen siloxane) containing 16 mmol/g of SiH group, was prepared from 1,3,5,7-tetramethylcyclotetrasiloxane.<sup>8</sup> Table I shows the content of the silicone compound for hydrosilylation. The amount of the catalyst in the compound is 20 ppm of Pt based on total PDMS. SiO<sub>2</sub> fusing filler having silanol groups (Aerosil 380; relative surface area: 380 m<sup>2</sup>/g, average diameter: 12 nm, density: 50 g/L) was compounded with vinyl-type PDMS before mixing of hydrosilyl-type PDMS. The physical properties of the cured PDMS with 2.5-mm

\* To whom correspondence should be addressed.

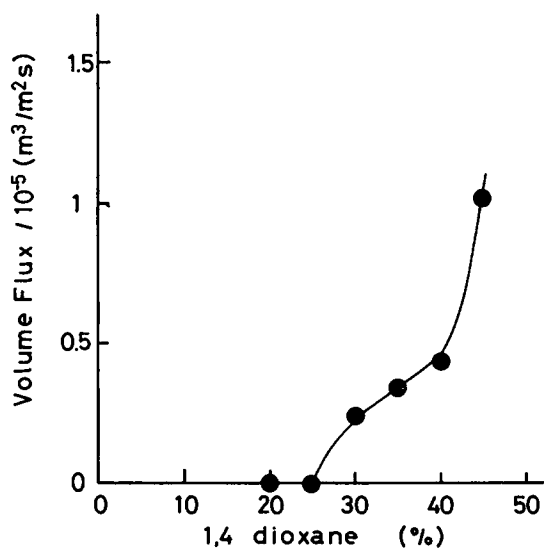


## RESULTS AND DISCUSSION

### Membrane Formations and Silane Coupling Treatments

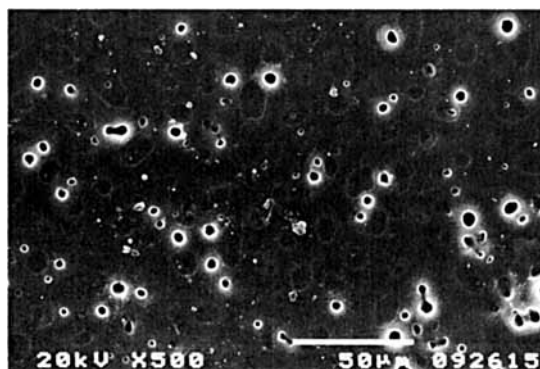
In order to check the pore formation in the membrane, water was permeated through the membranes by use of the ultrafiltration cell under hydraulic pressure of 7.5 kPa. Figure 1 shows volume flux of water for PDMS membranes prepared from PDMS compounds containing various amounts of 1,4-dioxane. The values of the volume flux become zero at lower than 25 wt % of 1,4-dioxane content. Then, the amount of water permeated through the membrane increased with an increase of 1,4-dioxane content.

Figure 2 show photographs of SEM for (a) surface and (b) cross section of the porous membrane prepared from the PDMS compound containing 45 wt % 1,4-dioxane. In the photograph of the surface, there are many pores in the range of about 1–5- $\mu\text{m}$  diameter. The photograph shows the cross section of the membrane having about 120- $\mu\text{m}$  thickness. It is noted that there are many fine grooves crossing through the membrane. In contrast with the porous membrane, PDMS membrane prepared without 1,4-dioxane had homogeneous cross section and no fine grooves. In addition, the pores were not observed on the surface of the membrane. In the absence of 1,4-dioxane nonporous membrane was formed. This suggests that the presence of 1,4-dioxane is important in the pore formation.

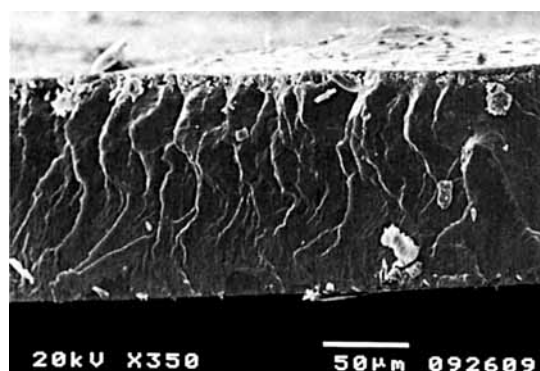


**Figure 1** Volume flux of water permeated through PDMS membranes prepared from silicone compounds having various amounts of 1,4-dioxane.

a)



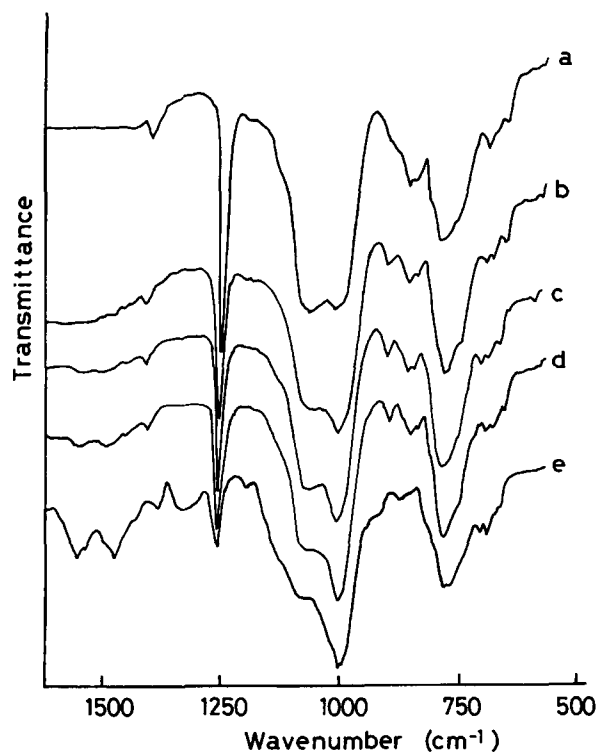
b)



**Figure 2** SEM of (a) surface and (b) cross section of PDMS membrane prepared from the compound containing 45 wt % 1,4-dioxane.

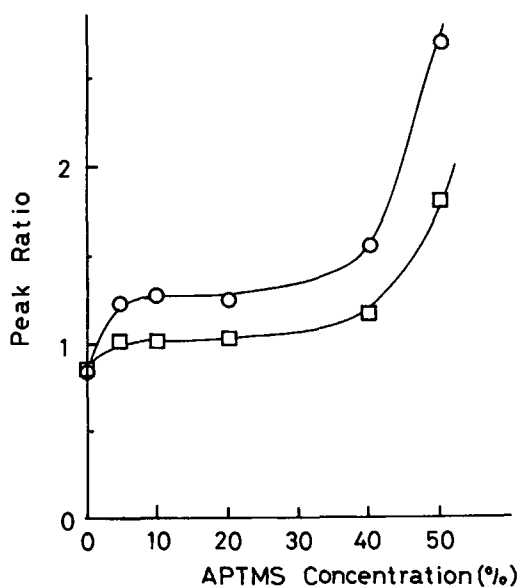
In attempt to control the pore size of the membrane, treatment of the membrane with a silane coupling agent<sup>14</sup> such as APTMS was carried out. It was well known<sup>15,16</sup> that APTMS is hydrolyzed in acidic solution to obtain the silane triols. The silane triols condense to a siloxane network. The oligomers of the coupling agent precipitate on the substrate and then react with the OH group on the surface (Scheme 3).

The treatment of PDMS membranes with APTMS was followed by taking IR and ATR-IR spectra of the treated membrane. In IR spectra of PDMS membranes before and after the APTMS treatment, the peaks at about 2180 and 3000  $\text{cm}^{-1}$ , assigned to the SiH group of poly(methylhydrogensiloxane) and asymmetric CH stretching for Si—CH<sub>3</sub> group of PDMS<sup>17</sup> are observed. Further, the spectrum of the PDMS membrane without the APTMS treatment has a broad peak in the 3300–3500  $\text{cm}^{-1}$  region, assigned to Si—OH group of fus-

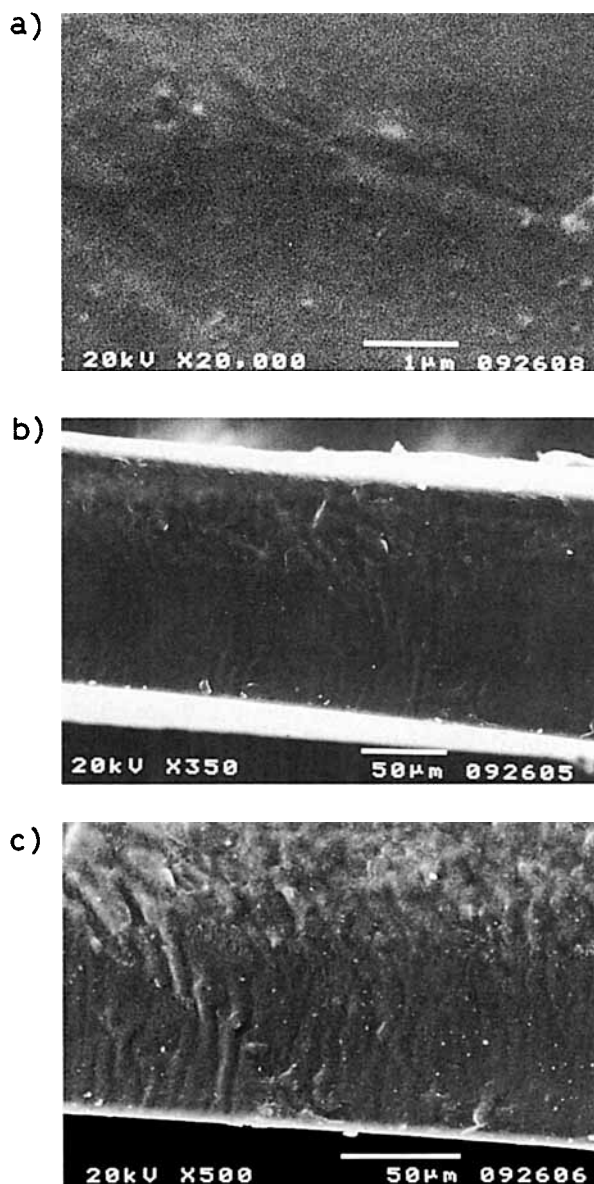


**Figure 3** ATR-IR spectra of PDMS membranes treated with (a) 0, (b) 5, (c) 10, (d) 40, and (e) 50 wt % of APTMS solutions.

ing filler, but the broad peak disappeared in the spectrum for the treated membrane. This indicates that APTMS reacts with the Si—OH site on the



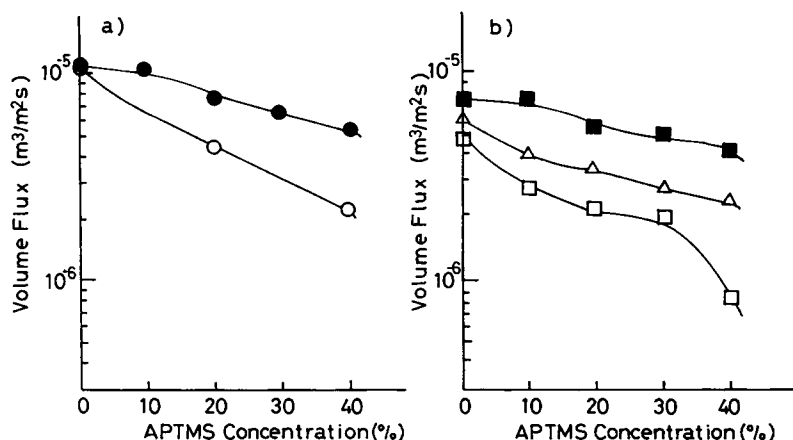
**Figure 4** Peak ratios of (○) 1000 or (□) 1130  $\text{cm}^{-1}$  to 1270  $\text{cm}^{-1}$  in ATR-IR spectra of PDMS membranes treated with various APTMS solutions.



**Figure 5** SEM photographs of (a) surface and (b) and (c) cross section of the PDMS membrane treated with 50 wt % of APTMS solution.

fusing filler in the membrane. The amino group of APTMS has absorption in about the 3000  $\text{cm}^{-1}$  region.<sup>16</sup> However, the peak of the amino group of APTMS bound to the surface overlaps with the strong peak of the asymmetric CH stretching of PDMS in the spectrum.

Figure 3 shows ATR-IR spectra of PDMS membranes treated with various APTMS solutions. The spectra of PDMS membranes have characteristic peaks assigned to Si—O—Si symmetric, asymmetric stretching, and Si—CH<sub>3</sub> stretching at about 800, 1000–1130, and 1270  $\text{cm}^{-1}$ , respectively.<sup>17</sup> Es-



**Figure 6** Volume flux of latex and dextrans (D, DA) for PDMS membranes treated with various APTMS solutions. (a) water (●) and 5 ppm aqueous solution of latex having 0.19- $\mu\text{m}$  diameter (○). (b) DA at (■) pH 11 and (□) pH 4 and (△) D at pH 4. The molecular weight DA and D is  $5 \times 10^5$  and  $2 \times 10^6$ , respectively; 0.1 wt % aqueous solution was used for the experiments.

pecially the peak at  $1130\text{ cm}^{-1}$  is characteristic of the highly crosslinked siloxane such as the  $\text{SiO}_2$  units.<sup>17</sup> We reported that the treated PDMS membrane had the characteristic peak in  $1000\text{ cm}^{-1}$  for the Si—O—Si group of the silane coupling agent bound to the surface of the substrate such as glass.<sup>10</sup> The intensity of the characteristic peak increased with an increase in APTMS concentration (Fig. 3). The appearance of the peak for the Si—O—Si groups in the spectrum of PDMS membrane implies that the coupling reaction proceeds on the surface with the forming siloxane chain (Scheme 3).

Figure 4 shows peak ratios of 1000 and 1130 to  $1270\text{ cm}^{-1}$  at various APTMS concentrations. With increasing APTMS concentration, the values of the peak ratio somewhat increased and then became constant in the range of 5–40 wt % APTMS concentrations. However, the values of the peak ratio markedly increased at the 50 wt % APTMS concentration. This suggests that the formation of the APTMS oligomer on the surface of the membrane is significantly accelerated in the concentration region between 40 and 50 wt %.

Figure 5 show SEM photographs of PDMS membrane treated with 50 wt % APTMS solution. As shown in Figure 2, the untreated PDMS membrane has a many pores on the surface and fine grooves in the cross section. But, as shown in Figure 5(b), the pores on the surface of the treated membrane was not observed at the magnification  $\times 20000$ . In addition, the fine grooves of the treated membrane are not clear relative to the cross section of the untreated membrane. These comparisons suggest that the pore

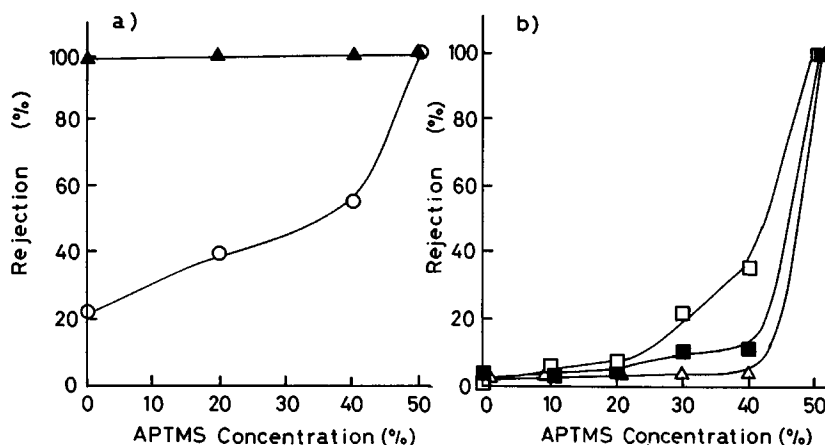
size in the membrane is reduced by the treatment of APTMS as a result of the formation of APTMS oligomer on the surface of the membrane.

#### Permeation Behavior of Solutes

In order to estimate the pore size of the membrane, we examined the permeability of polystyrene latexes and Ds. Here, the diameter of each latex used is 0.19 and  $1\ \mu\text{m}$ . In addition, D and DA having  $2 \times 10^6$  and  $5 \times 10^5$  molecular weight was used, respectively. Figure 6 shows volume flux of water and aqueous solution of the latex or the D. The value of the volume flux decreased for the membrane treated with APTMS. This results from the decrease of the pore size of the membrane treated with APTMS solution. In the latex having  $1\text{-}\mu\text{m}$  diameter, the amount of the permeated solution through the membranes was extremely low because the latex particles clogged pores of the membrane.

Figure 7 shows plots of rejection of latex and Ds versus APTMS concentration. As the concentration of APTMS solution increased, the values of the rejection for each solute increased. In latex having  $1\text{-}\mu\text{m}$  diameter, however, the values of the rejection is almost 100% regardless of the APTMS concentration. Also, in the membrane treated with 50 wt % APTMS solution, the rejection of all solutes used was nearly 100%.

It is interesting to note that the rejection of DA at pH 4 is high compared with those of D and DA at pH 11. In the membrane treated with 30 and 40 wt % solutions, a notable difference between both



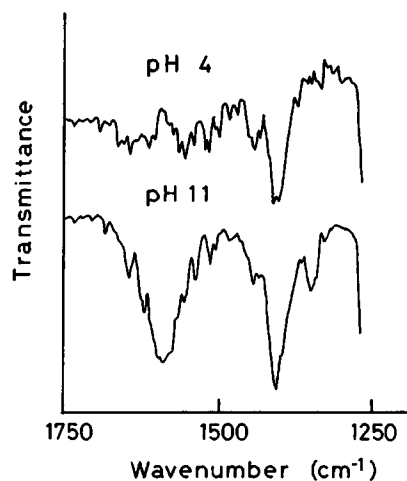
**Figure 7** Rejection of latexes and dextrans (D, DA) for PDMS membranes treated with various APTMS solutions. (a) latex having (▲) 1- $\mu\text{m}$  diameter and (○) 0.19- $\mu\text{m}$  diameter. (b) DA at (■) pH 11 and (■) pH 4 and (△) D at pH 4.

pH solutions of DA was observed. For the data of volume flux as shown in Figure 6(b), there is tendency that the volume flux of DA (pH 11), D (pH 4), and DA (pH 4) decreased in that order. As is well-known, values of volume flux in ultrafiltration of macromolecular solute solution influence the viscosity of the solution and the degree of rejection.<sup>18</sup> We measured reduced viscosity of 0.1 wt % of these solute solutions at 30°C. The values of the reduced viscosity ( $\text{cm}^3/\text{g}$ ) of the solution for DA at pH 4 and 11 and D at pH 4 were 2.1, 1.0, and 1.2, respectively. It was reported that DA having diethylamino groups positively charges at the acidic pH region; pK of the group is 8.5–8.9.<sup>19</sup> Accordingly, the molecular size of DA at pH 4 is apparently larger than that at pH 11 because of the expanding conformation of DA chains by electrostatic repulsion of positively charged diethylamino groups as is typical in polyelectrolytes.<sup>20</sup>

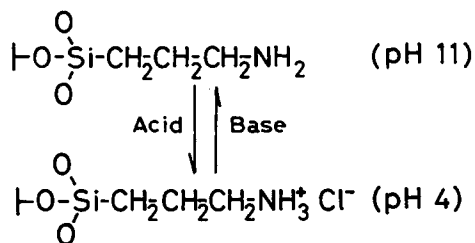
For the membrane treated with 40 wt % of APTMS solution, a significant pH dependency in the shape of ATR-IR spectra was observed. Figure 8 compares ATR spectra in the wavenumber range between 1300 and 1700  $\text{cm}^{-1}$  for the treated membrane. Before the measurement, the treated membranes were soaked in dilute aqueous solutions of HCl and NaOH at pH 4 and 11, respectively, and then dried *in vacuo*. The ATR-IR spectra of the treated membranes have a band at 1485  $\text{cm}^{-1}$  for the  $\text{CH}_2$  bending mode of the propyl chain of APTMS.<sup>16</sup> In the case of the membrane soaked in dilute NaOH solution at pH 11, the peak at about 1585  $\text{cm}^{-1}$  is attributed to bending of the amino group of APTMS,<sup>16,17</sup> while it disappeared at pH 4. In addition, weak bands at about 1575 and 1600  $\text{cm}^{-1}$

are assigned to the symmetric and asymmetric deformation modes of the  $\text{NH}_3^+$  group,<sup>16</sup> respectively. Accordingly, it seems that the pH change of the spectra resulted from the acid–base equilibrium (Scheme 4) of amino groups bound to the treated membrane.

From these data, the restricted permeation of DA at pH 4 is due to electrostatic repulsion between the cationic solute and positively charged membrane. Also, the contribution of mechanical sieve to the rejection of DA at pH 4 is included because of both the small pore size of the membrane and the large molecular size of DA at pH 4. On the other hand, at pH 11, the contribution of charge effect to the permeation of DA is small, because of a low protonation of the amino group and the diethylamino group



**Figure 8** ATR-IR spectra at pH 4 and 11 for PDMS membrane treated with 40 wt % APTMS solution.



Scheme 4

for APTMS bound to the membrane and DA, respectively.

## CONCLUSIONS

Porous PDMS membranes prepared by hydrosilylation cure in the presence of 1,4-dioxane were treated with APTMS at various concentrations in order to control the pore size. The properties of the treated membrane and permeation behavior of dextrans and latex beads were examined at pH 4 and 11.

The authors wish to express their thanks to Toshiba Silicone Co. Ltd., for supplying APTMS and for variable suggestions. We acknowledge the measurement of SEM photographs by Ryuji Satoh in the Department of Chemistry, Nagaoka University of Technology.

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Received February 17, 1993

Accepted June 14, 1993