

# Study of Oxygen-Permeable Polyurethane Ionomer. II

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**ABSTRACT:** Oxygen-permeable polyurethane ionomers with dimethyldimethoxysilane or dimethyldimethoxysilane have been successfully synthesized at our lab, and their ionomer structures have been proven by infrared spectra. In our previous paper,<sup>1</sup> it was found that the amount of oxygen permeated through the film made by a dimethyldichlorosilane polyurethane ionomer increased with increasing the concentration of dimethyldichlorosilane. Presently, our experimental results also indicate that use of dimethyldimethoxysilane or dimethyldiethoxysilane in preparing polyurethane ionomers does substantially raise the amount of oxygen diffusing into the films made by these ionomers. These results suggest that use of dimethyldichlorosilane, dimethyldimethoxysilane, or dimethyldiethoxysilane, with strong hydrophilic property, in making polyurethane ionomer will give better oxygen permeability of siloxane-based polyurethane ionomers. It is interesting to point out that both tensile strength and the elongation of a siloxane-based polyurethane ionomer film become weaker as the concentration of dimethyldimethoxysilane or dimethyldiethoxysilane increases. This may be the result of intramolecular interaction of ionomer molecules, coupled with the reduction of the formation of hydrogen bonding between ionomer-ionomer molecules and between ionomer-water molecules. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1932–1938, 2000

## INTRODUCTION

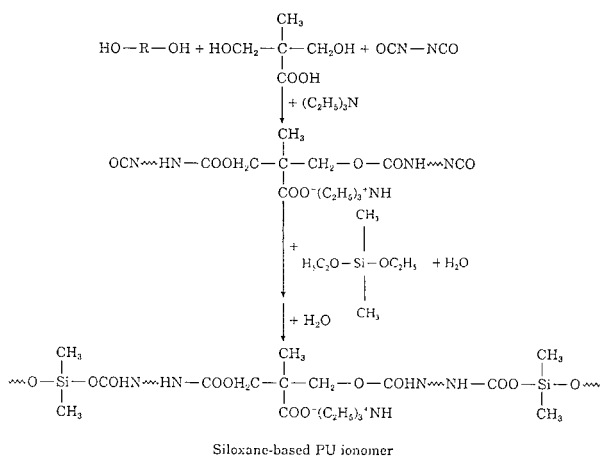
In the previous paper,<sup>1</sup> we dealt with the effect of dimethyldichlorosilane on the permeability of oxygen in the film made by a siloxane-based polyurethane ionomer. Our experimental results clearly indicated that the use of dimethyldichlorosilane in preparing polyurethane ionomer did substantially raise the amount of oxygen diffusing into the film made by this ionomer. Theoretically, although the siloxanes have unique properties such as a high degree of resistance to oxidation, weather, and water, the use of different

types of siloxanes, due to the differences in their structure in preparing siloxane-based polyurethane ionomer, is likely to be able to improve the permeability of oxygen and other physical properties for this ionomer's film. For this reason, we further investigated the effect of dimethyldimethoxysilane (DMDMS) and dimethyldiethoxysilane (DMDES), respectively, on the permeability of oxygen to the film of siloxane-based polyurethane ionomer. The reaction of toluene diisocyanate with dimethyldimethoxysilane or dimethyldiethoxysilane, polyester (made by the reaction of adipic acid with 1,6-hexandiol and diethylene glycol), dimethylol propionic acid (DMPA), and other additives to form possible structure of a siloxane-based polyurethane ionomer is given below:

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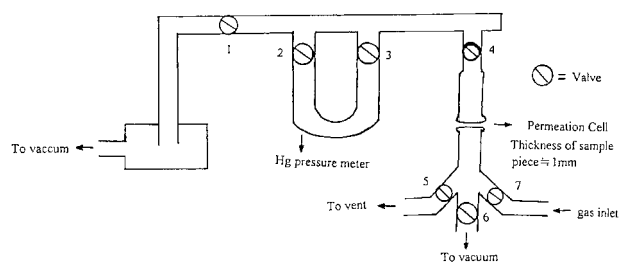
## EXPERIMENTAL

### Materials

Toluene diisocyanate (TDI), triethylamine, diethylenetriamine, and acetone were obtained from Merck Co. (Darmstadt, Germany). DMPA and N, N-dimethylacetamide were supplied by Alcolac Industrial Chemicals (USA) and J.T. Baker Chemicals (Phillipsburg, NJ), respectively. Polypropylene glycol (mol wt  $\approx$  700), 1,4 butanediol, and polytetramethylene glycol (mol wt  $\approx$  2000) were received from Tai Chin Chemical Industry Co, Ltd. (Kaohsiung, Taiwan). DMDMS and DMDES were supplied by Shin-Etsu Chemical Co., Ltd. (Chiyoda-ku, Tokyo, Japan). All these chemicals were used without further purification.

### Method

A 0.025 equivalent of 1,4-butane diol, 0.06 equivalent of DMPA, 0.008 equivalent of PPG (polypropylene glycol), and 0.018 equivalent of PTMEG (polytetramethylene glycol) were charged into a 1000-mL four-necked pyrex glass flask equipped with a stirrer, thermometer, and condenser. In the above flask a 0.1573 equivalent of toluene diisocyanate was subsequently added and reacted at 80–85°C for about 2 h to form a NCO-terminated polyurethane (PU) prepolymer. A 0.034 equivalent of triethylamine was then reacted with this NCO-terminated PU prepolymer in 80g acetone to form a quaternized NCO-terminated PU prepolymer.<sup>2–8</sup> This quaternized NCO-terminated PU prepolymer further reacted with hydrolytes of dimethyldimethoxysilane (0.01 equivalent)



Scheme 1

or dimethyldiethoxysilane (0.01 equivalent), and 170 g water was then added to form the siloxane-based PU ionomers with approximately 17.5% solids. After removing the acetone by blowing the siloxane-based PU ionomer solution out in vacuo, this ionomer aqueous solution with 17.5% solids was poured into a polypropylene dish to 1 mm dish thickness and dried in an oven at 60°C. This film was cast to be a dumbbell shape with a narrow width of 10 mm  $\pm$  0.5, a narrow length of 60 mm  $\pm$  0.5 and a total length of 150 mm was used for tensile and elongation testing by an Instron (GT-7010-A2, Gottech Testing Machines INC.). The oxygen permeation testing of this film, with an area of  $4\pi$  and a thickness of 1 mm, was done by using the apparatus similar to the Yanaco Gas Permeability Analyzer Model GTR-10, shown in Scheme 1.

An oxygen gas having a high partial pressure is allowed to diffuse into the one side of siloxane-based PU ionomer film at a constant time of 24 h, whereas the other side of this film is placed under low partial pressure or vacuum. During the measurements, the valves labeled 1, 2, and 6 are closed but valves 5 and 7 are open. The gas permeability coefficient can be obtained from the following equation<sup>9,10</sup>:

$$P = V_r L / A \Delta p$$

where  $p$  is the gas permeability coefficient;  $V_r$  the volume flux of gas permeability at the standard condition;  $L$  the thickness of the film;  $A$  the cross area of gas permeability and  $\Delta p$  the difference in pressure between two sides of the film. The experimental errors for the above measurements were estimated to be within  $\pm 0.5\%$ .

## RESULTS AND DISCUSSIONS

The infrared (IR) spectra for TDI, DMDES, hydrolyte of DMDES, and siloxane-based PU iono-

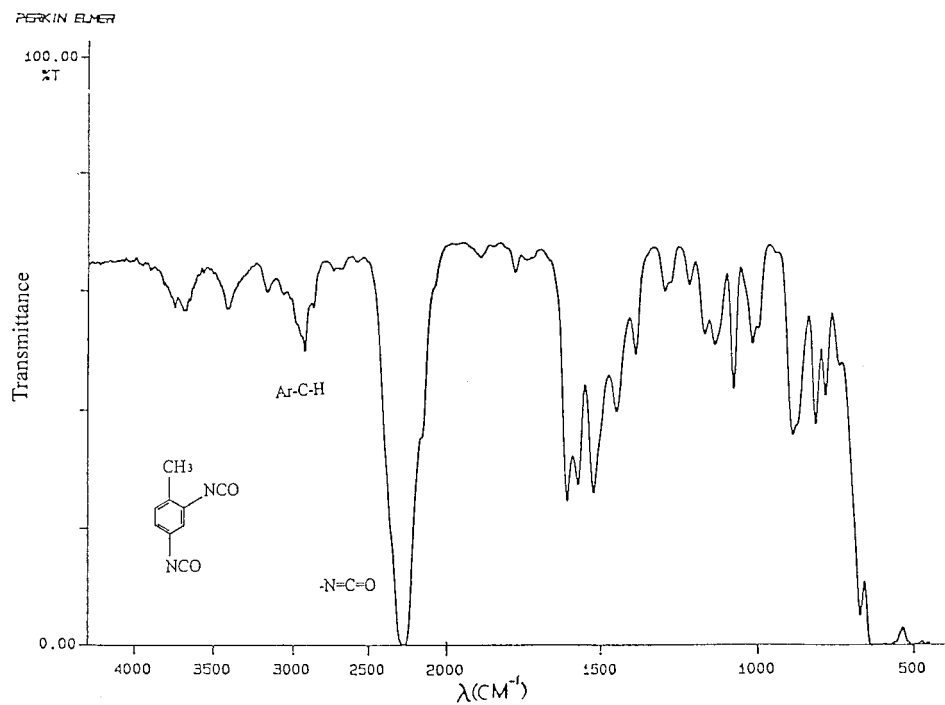


Figure 1 Spectra of TDI at  $25 \pm 0.05^\circ\text{C}$ .

mer are shown in Figures 1–4. An analysis of Figures 2 and 3 clearly reveals that the hydrolyte spectra of DMDDES show the strong absorbance

peak at around  $3500\text{ cm}^{-1}$  (OH), and absorbance peaks at  $1030\text{ cm}^{-1}$  (Si—OH) and  $1275\text{ cm}^{-1}$  (Si=CH). These spectra demonstrate that the

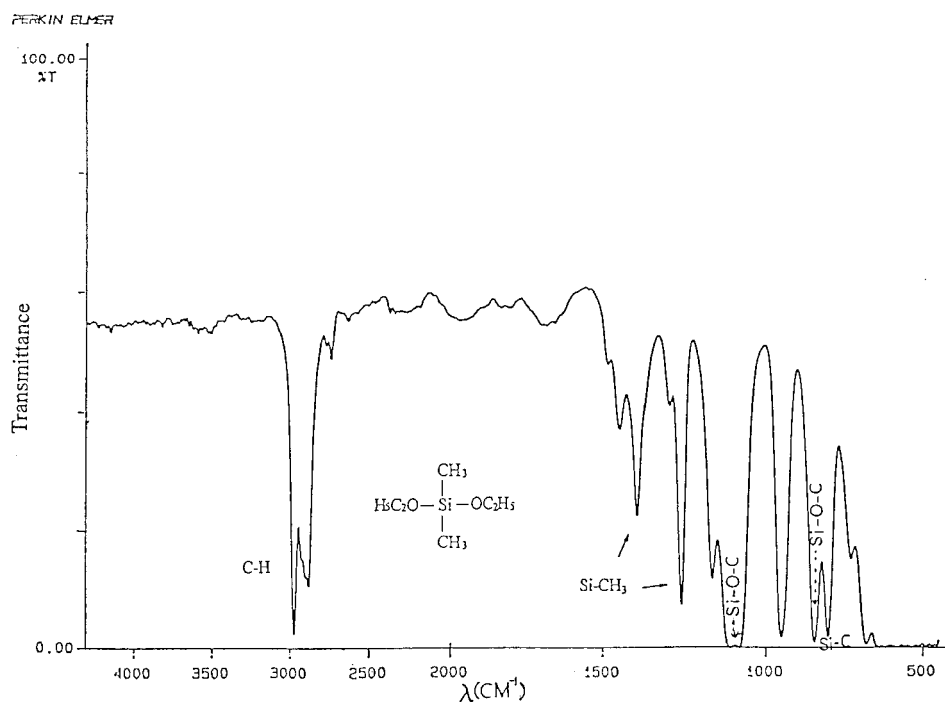
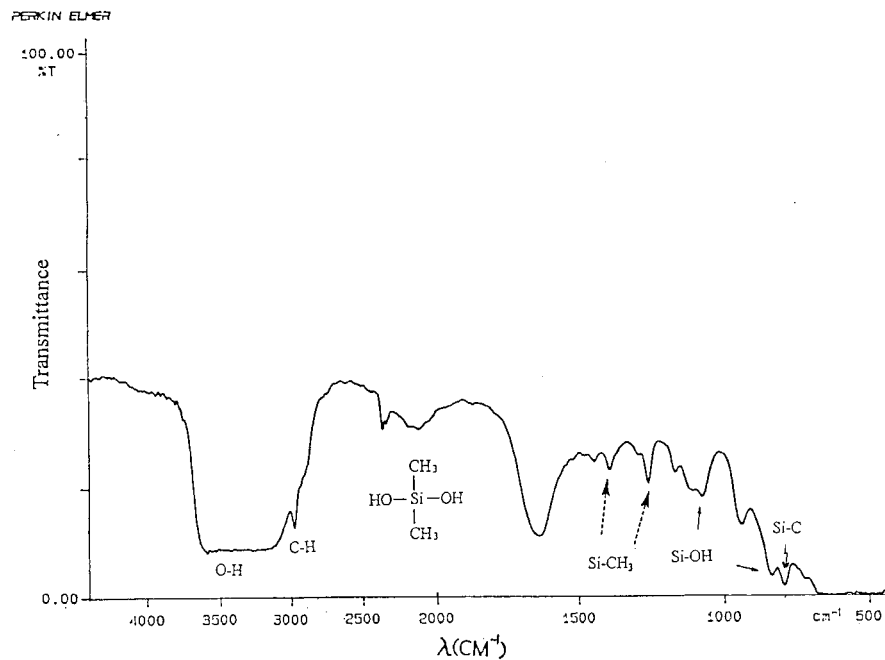


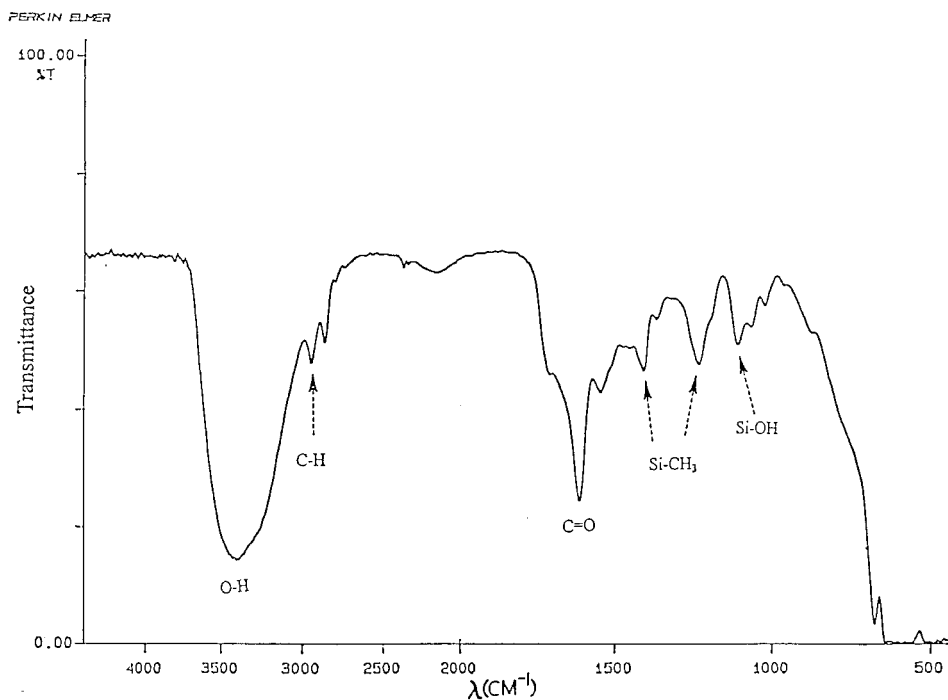
Figure 2 Spectra of DMDDES at  $25 \pm 0.05^\circ\text{C}$ .



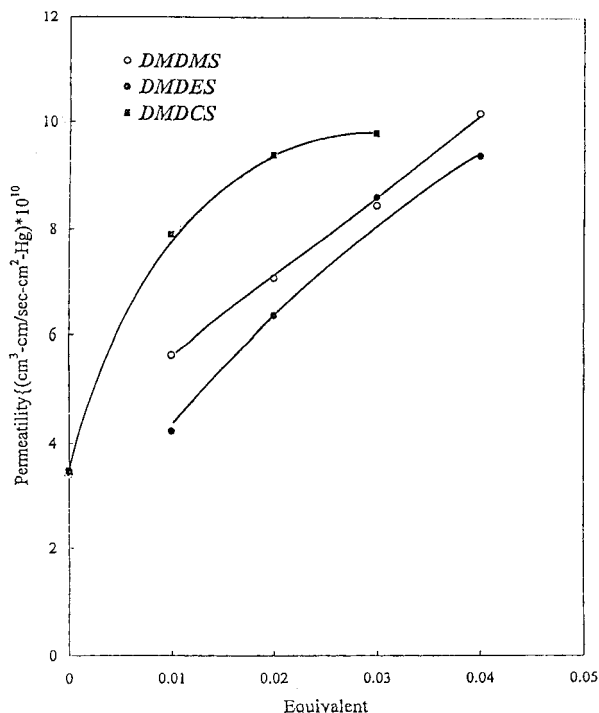
**Figure 3** Spectra of the hydrolyte of DMDDES at  $25 \pm 0.05^\circ\text{C}$ .

DMDDES is hydrolyzed. The reaction of TDI with polyester, DMPA, DMDDES, and other additives to form a siloxane-based PU ionomer with DMDDES

is illustrated by the formation of the absorbance peaks at around  $1725\text{ cm}^{-1}$  (C=O),  $1030\text{ cm}^{-1}$  (Si-OH),  $1275\text{ cm}^{-1}$  (Si-CH), and  $3300\text{--}3500$



**Figure 4** Spectra of the DMDDES-based PU ionomer at  $25 \pm 0.05^\circ\text{C}$ .



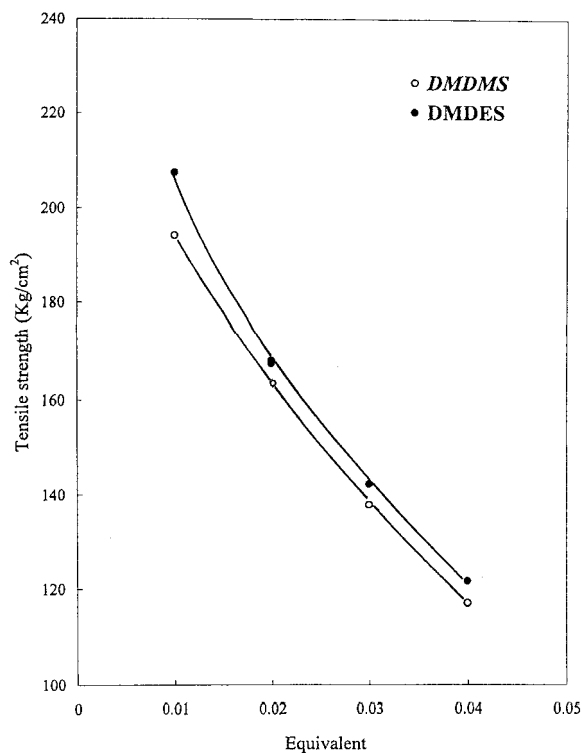
**Figure 5** Plot of the oxygen permeability of the film as a function of the equivalent of dimethyldichlorosilane (DMDCS), dimethyldimethoxysilane (DMDMS), and dimethyldiethoxysilane (DMEDES), respectively, at  $25 \pm 0.05^\circ\text{C}$ .

$\text{cm}^{-1}$  (OH), and by the almost disappearance of the absorbance peak at around  $2275 \text{ cm}^{-1}$  (NCO), shown in Figure 4 in comparison to those of Figures 1–3. These results suggest that the reaction of TDI with DMEDES, polyester, DMPA, and other additives does form siloxane-based PU ionomer.

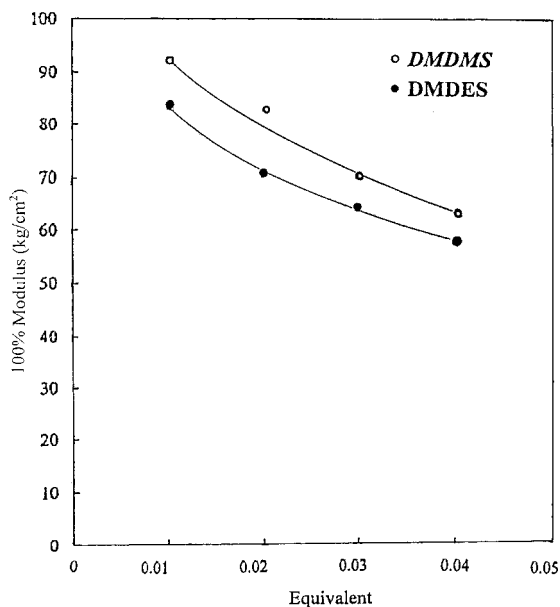
The oxygen permeability of the film made by different siloxane-based PU ionomers as a function of the equivalent of DMDMS or DMEDES linked to the backbone of the PU ionomer molecule is given in Figure 5. Figure 5 clearly indicates that the amount of oxygen permeated through the film increases with increasing the concentration of DMDMS or DMEDES. This may be attributed to more porosity formed. The amount of oxygen permeated through the film made by DMDMS-based PU ionomer is greater than that of DMEDES-based PU ionomer. In general, the extent of the hydrolyzation of siloxane compound depends on the hydrophilic property of this compound. Because the hydrophilic property is stronger for  $\text{CH}_3\text{O}$  of DMDMS than for  $\text{C}_2\text{H}_5\text{O}$  of DMEDES, more hydrolytes of DMDMS are

formed. These hydrolytes of DMDMS readily react with TDI in the presence of other additives to form siloxane-based PU ionomer with more porosities. This explains why PU ionomer with DMDCS has better oxygen permeability. In addition, our earlier work investigated the effect of the dimethyldichlorosilane<sup>1</sup> on the amount of oxygen permeated through the film made by dimethyldichlorosilane-based PU ionomer. The results of oxygen permeability for dimethyldichlorosilane-based PU ionomer are greater than that of DMDCS- or DMEDES-based PU ionomer. Thus, we can draw a conclusion that PU ionomer with the strong hydrophilic part of siloxanes does, indeed, have high oxygen permeability.

The tensile strength and the modulus property of self-cured films for both dimethyldimethoxy and dimethyldiethoxy silane-based PU ionomer molecules are seen to decrease with increasing the concentration of DMDMS or DMEDES, as shown in Figures 6 and 7. This is possibly due to increased hydrophobic chains of DMDMS or DM-



**Figure 6** Plot of the tensile strength vs. the equivalent of dimethyldichlorosilane, dimethyldimethoxysilane (DMDMS), and dimethyldiethoxysilane (DMEDES), respectively, used to prepare siloxane-based PU ionomer at  $25 \pm 0.05^\circ\text{C}$ .



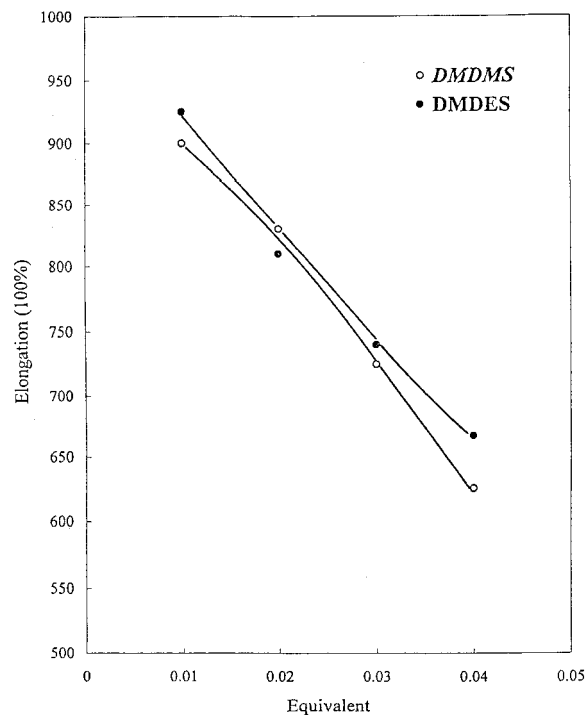
**Figure 7** Plot of 100% modulus vs. the equivalent of dimethyldiethoxysilane (DMEDES) and dimethyldimethoxy (DMDMS), respectively, used to prepare siloxane-based PU ionomer at  $25 \pm 0.05^\circ\text{C}$ .

DES attached to the backbone of PU ionomer molecule resulting in preventing the formation of the hydrogen bonding and in weakening the capability of cross-linking of PU ionomer molecule. Thus, the tensile strength for both DMDMS- and DMEDES-based PU ionomer films appreciably decreases as the concentration of DMDMS or DMEDES increases. On the other hand, the elongation of dry film made by DMDMS- or DMEDES-based PU ionomer molecule at the breaking point appears to decrease with an increase in the concentration of DMDMS or DMEDES, shown in Figure 8. Increased chain of DMDMS or DMEDES linked to the backbone of PU ionomer molecule may greatly reduce the interaction between ionomer ionomer molecules (i.e., intermolecular interaction) and the formation of hydrogen bonding between ionomer molecule-water molecule and between ionomer-ionomer molecules. This may be the reason to explain why the elongation of DMDMS- or DMEDES-based PU ionomer film becomes lower as the concentration of DMDMS or DMEDES increases.

## CONCLUSION

Oxygen-permeable PU ionomers successfully synthesized at our lab are demonstrated to be a

DMDMS- or DMEDES-based PU ionomer by IR spectra. In our previous paper, it was found that the amount of oxygen permeated through the film made by a dimethyldichlorosilane-based PU ionomer increased with increasing the concentration of dimethyldichlorosilane. At present, our experimental results also indicate that use of DMDMS or DMEDES in PU ionomer molecules does, indeed, substantially raise the amount of oxygen permeated through the film made by these ionomers. More importantly, our experimental results suggest that use of dimethyldichlorosilane, DMDMS, or DMEDES in PU ionomer molecules, with strong hydrophilic property, will give rise to better oxygen permeability of siloxane-based PU ionomer films. For the tensile strength of self-cured films of DMDMS- or DMEDES-based PU ionomer, it is interesting to find out that both films become weaker as the concentration of DMDMS or DMEDES increases. This may be the result of intramolecular interaction of ionomer molecules, coupled with reducing the formation of hydrogen bonding between ionomer-water molecules.



**Figure 8** Plot of the elongation vs. the equivalent of dimethyldichlorosilane, dimethyldimethoxysilane (DMDMS), and dimethyldiethoxysilane (DMEDES), respectively, used to prepare siloxane-based PU ionomer at  $25 \pm 0.05^\circ\text{C}$ .

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