Selective Permeation of Cross-Linked Polyelectrolyte and Polyelectrolyte-Filled Nonwoven Membranes

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ABSTRACT: Selective permeation, driven by ionic attraction, is one of the most important properties of polyelectrolyte membranes. In this study, selective permeation behaviors of different polyelectrolytes, poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS), poly(styrene sulfonic acid) (PSS), and poly(methacrylic acid) (PMA), were studied via solution-diffusion mechanism. Among these three polyelectrolytes, PSS membranes showed the highest permeabilities for both water and dimethyl methylphophonate vapors due to their high diffusion coefficients caused by the high flexibility of PSS chains. It was also found that the cross-linking of polymer chains increased membrane permeabilities by weakening the physical network formed by ionic attraction. However, the type and cross-linking of polyelectrolytes did not have significant effect on the membrane selectivities. Nonwoven fabric was employed to control the selective permeation of polyelectrolyte membranes. It was found that filling the nonwoven fabric with polyelectrolytes led to composite membranes with reduced permeabilities and increased selectivities. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 227–233, 2012

Key words: membranes; crosslinking; diffusion

INTRODUCTION

Polyelectrolytes are polymers containing ionic groups, which can dissociate into charged moieties in the presence of polar solvents such as water. Polysulfonate and polyacrylic acid are examples of well-known polyelectrolytes. The presence of ionic groups such as sulfonic acid or carboxylic acid causes the high hydrophilic nature of polyelectrolytes, which leads to preferential permeation of water molecules. Therefore, polyelectrolyte membranes show selective permeation behavior, i.e., allowing the transport of water while blocking the permeation of organic molecules.

Selective permeation behavior is one of the important requirements for membrane-based separation processes, such as gas separation[1–3] and chemical protection applications.[4–6] To understand the permeation process of polyelectrolyte membranes, solution-diffusion mechanism has been used in the literature.[7–9] In this mechanism, permeation is determined by sorption, which is the amount of permeant dissolved in the membrane matrix, and diffusion, which is the rate for the permeant to diffuse through the membrane matrix. One of the important factors to determine sorption behavior is the interaction between the polymer chains and the permeant molecules. On the other hand, diffusion is determined by the activation energy of diffusion, which generally increases with increases in the size of permeant molecules and the stiffness of polymer chains.[10]

In this study, three different polyelectrolyte membranes were prepared and their selective permeation behaviors were investigated. The effect of polymer structure on membrane permeation and selectivity was studied via solution-diffusion mechanism. In addition, polyelectrolytes were filled into nonwoven fabric to obtain composite membranes with controllable permeation behavior.
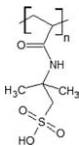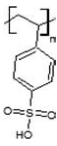
EXPERIMENTAL

Materials

Monomers, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), sodium 4-vinylbenzenesulfonate (NaVS) and methacrylic acid (MA), initiators, 2,2′-azobis(2-methylpropionitrile) (AIBN), and potassium peroxydisulfate (KPS), and crosslinking agents, ethylene glycol diacrylate (EGD) and divinyl benzene (DVB), were purchased from ς-Aldrich. The solvent, dimethylsulfoxide (DMSO), and the permeant, dimethyl methylphophonate (DMMP), were also obtained from ς-Aldrich. PP nonwoven was provided by FiberVisions®. The base weight, density,

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	PAMPS	PSS	PMA
Chemical structure			
Monomer	3 mol/L AMPS	1 mol/L NaVS	10 mol/L MA
Initiator	0.3 mol/L AIBN	0.1 mol/L AIBN	1 mol/L KPS
Cross-linker	0.3 mol/L EGD	0.1 mol/L DVB	1 mol/L EGD
Solvent	DMSO	DMSO	Water

and thickness of PP nonwoven are 2.2 dpf, 40 g/m^2, and 0.36 mm, respectively.

Preparation and characterization of membranes

Polyelectrolyte membranes, poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS), poly(styrene sulfonic acid) (PSS), and poly(methacrylic acid) (PMA), were synthesized and crosslinked via free radical polymerization. Table I shows the types and concentrations of monomers, initiators, crosslinkers, and solvents used for the synthesis of PAMPS, PSS, and PMA membranes. Monomers, initiators, and crosslinkers were first added to solvents (DMSO for PAMPS and PSS, and water for PMA) and stirred for 3 h at room temperature. The solutions were then placed between Teflon plates and heated. The heating time and temperature were 60°C and 6 h for PAMPS, 60°C and 12 h for PSS, and 90°C and 6 h for PMA, respectively. The as-prepared poly(sodium 4-vinylbenzenesulfonate) was protonated in 0.1M HCl for 12 h and washed with distilled water to form PSS membranes. Polyelectrolyte-filled nonwoven membranes were also prepared by soaking nonwovens in reacting solutions, followed by the same polymerization procedure.

All membrane samples were immersed in acetone to remove unreacted substances, followed by drying in vacuum at 60°C for 24 h. The glass transition temperatures (T_g) of crosslinked PAMPS, PSS, and PMA were observed using differential scanning calorimetry (DSC). To remove the thermal history, the heating thermograms were recorded twice for each sample at 20°C/min heating rate between −10 and 350°C on a PerkinElmer Diamond DSC and the second heating curve was evaluated. The T_g values of crosslinked PAMPS, PSS, and PMA were measured to be 190, 80, and 250°C, respectively. The morphology of polyelectrolyte and polyelectrolyte-filled nonwoven membranes was examined using Hitachi S-3200 Scanning Electron Microscope (SEM) after gold sputtering.

Permeation behavior measurements of membranes

The vapor permeabilities of polyelectrolyte membranes were measured using the modified method based on the American Society for Testing and Materials (ASTM) E96-95 procedure. Permeation cells were prepared by placing membranes between the open-top caps and glass vials, which were filled with permeants, and placed in an environment chamber (35°C and 10 RH %). The weights of permeation cells were recorded until the weight losses became constant. Vapor permeabilities (P, mol/m/s/mmHg) were then obtained by $P = \frac{\Delta G \cdot l}{t \cdot A \cdot \Delta P}$, where ΔG is the weight loss at the steady state, l the membrane thickness, t the time, A the membrane area exposed to vapor, and Δp the vapor pressure differential across the membranes. The selectivities (α), i.e., the ratios of water permeabilities over DMMP permeabilities, were calculated by $\alpha = \frac{P_{\text{water}}}{P_{\text{DMMP}}}$. Membranes were weighed before and after the permeation testing to evaluate the vapor sorption. Sorption coefficients (S, mol/m^3/mmHg), the concentrations of vapors in polymer matrix at equilibrium, were calculated using $S = \frac{G_s}{V \cdot \Delta P}$, where G_s is the weight of permeation absorbed in membranes, V the volume of membranes, and Δp the vapor pressure differential across the membranes.[8] The diffusion coefficients (D, m^2/s) of permeants across the membranes were calculated based on the membrane permeabilities and sorption coefficients using $P = D \cdot S$. Reproducibility of data was assessed by conducting the measurements on at least five specimens for each membrane.

RESULTS AND DISCUSSION

Vapor permeabilities and selectivities of polyelectrolyte membranes

Due to the presence of hydrophilic groups such as sulfonic acid or carboxyl acid, polyelectrolytes tend to be dissoluble in water. Many attempts have been reported to prevent the solubility of polyelectrolytes,

TABLE II
Permeation, Sorption and Diffusion Coefficients of PAMPS, PSS, and PMA Membranes

Permeant	Membrane	$P \times 10^8$ (mol/m/s/mmHg)	S (mol/m^3/mmHg)	$D \times 10^{11}$ (m^2/s)
Water	PAMPS	2.6	400	6.5
	PSS	3.5	320	10.9
	PMA	3.1	620	5.0
DMMP	PAMPS	0.21	230	0.9
	PSS	0.28	220	1.3
	PMA	0.27	370	0.7

including crosslinking, copolymerization, and blending.[11–14] In this work, all polyelectrolytes were crosslinked and the crosslinking degree, i.e., the molar percentage of crosslinker in monomer, is typically 10 mol %.

Two permeants, water and dimethyl methylphosphonate (DMMP), were used to observe the permeation behavior of polyelectrolyte membranes. DMMP is one of organophosphorus compounds and is often used as the simulant of nerve agent, Sarin (GB). The blocking of nerve agent is of critical importance for chemical and biological protection application. In this study, permeabilities of PAMPS, PSS, and PMA membranes were measured using these two permeants and the results are shown in Table II. Among these three polyelectrolyte membranes, PSS membrane has the highest permeabilities for both water and DMMP.

To understand the permeation behavior of polyelectrolyte membranes, their sorption and diffusion coefficients were also measured and are shown in Table II. PSS membrane shows the lowest sorption coefficients for both water and DMMP although it has the highest permeabilities. This may be due to the presence of hydrophobic benzene rings in PSS. From Table II, it is also seen that PSS membrane has the highest water and DMMP diffusion coefficients, which are probably the main reason for PSS membrane to have the highest permeabilities among all three membranes. Diffusion is highly influenced by polymer chain flexibility. The T_g of PSS (80°C) is lower than those of PAMPS (190°C) and PMA (250°C), indicating that the PSS chains are more flexible than PAMPS and PMA chains. Therefore, the high chain flexibility of PSS may cause the high diffusion coefficients and eventually the high permeabilities of PSS membrane, as shown Table II.

Figure 1 shows selectivities of water over DMMP for PAMPS, PSS, and PMA membranes. All three polyelectrolyte membranes show preferential permeation of water compared to DMMP. Both sulfonic acid and carboxylic acid form hydrophilic regions through ionic attraction and hydrogen bonding, which lead to high water sorption of polyelectrolyte membranes (Table II). In addition, DMMP has larger molecular size than water and the diffusion process is affected by the size of the permeant.[10,15] The penetration of the larger molecule, DMMP, takes a longer diffusion time, which results in lower DMMP diffusion than water diffusion, as shown in Table II. Therefore, the high selectivities of polyelectrolyte membranes are the consequence of high water sorption and diffusion. However, three polyelectrolyte membranes show similar selectivities, which are not significantly affected by the chain flexibility of polyelectrolytes. More study is needed to completely understand the mechanism.

Effect of crosslinking degree

Crosslinking of polyelectrolytes is an important route for the formation of three-dimensional chemical network by connecting linear polymer chains through covalent bonding. The main goal of crosslinking is to modify polymer properties, such as chemical stability, chain stiffness, and crystallinity.[16] In addition, crosslinking often improves the mechanical properties and thermal properties of polymers.[17] In this research, crosslinking was employed to prevent the water solubility of polyelectrolytes and adjust their permeation behavior.
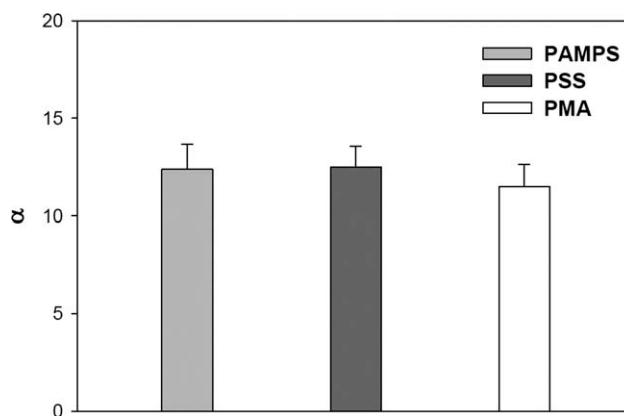

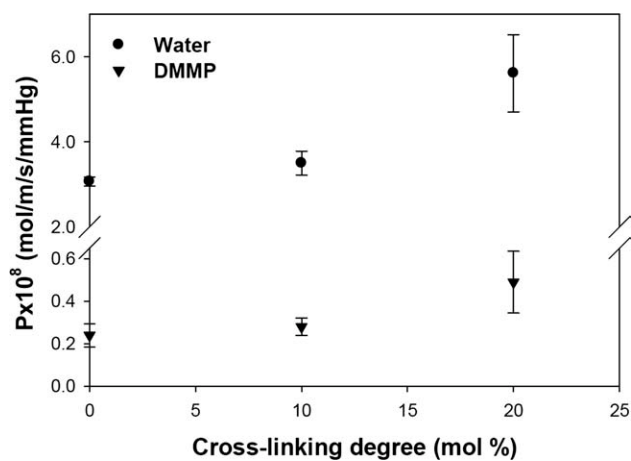**Figure 1** Selectivities of PAMPS, PSS, and PMA membranes.

Figure 2 Permeabilities of PSS membranes as a function of crosslinking degree.
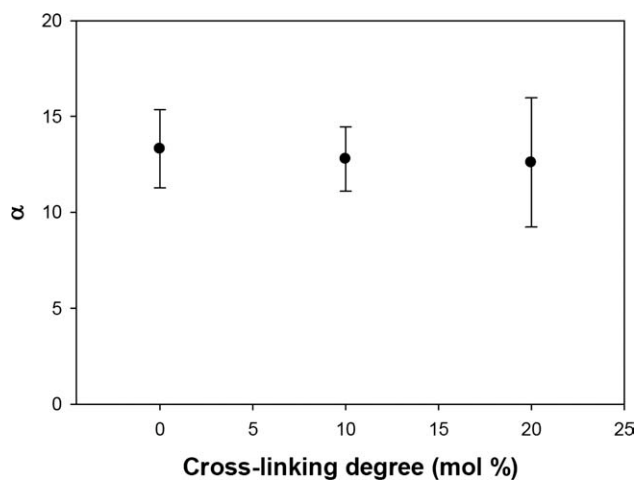

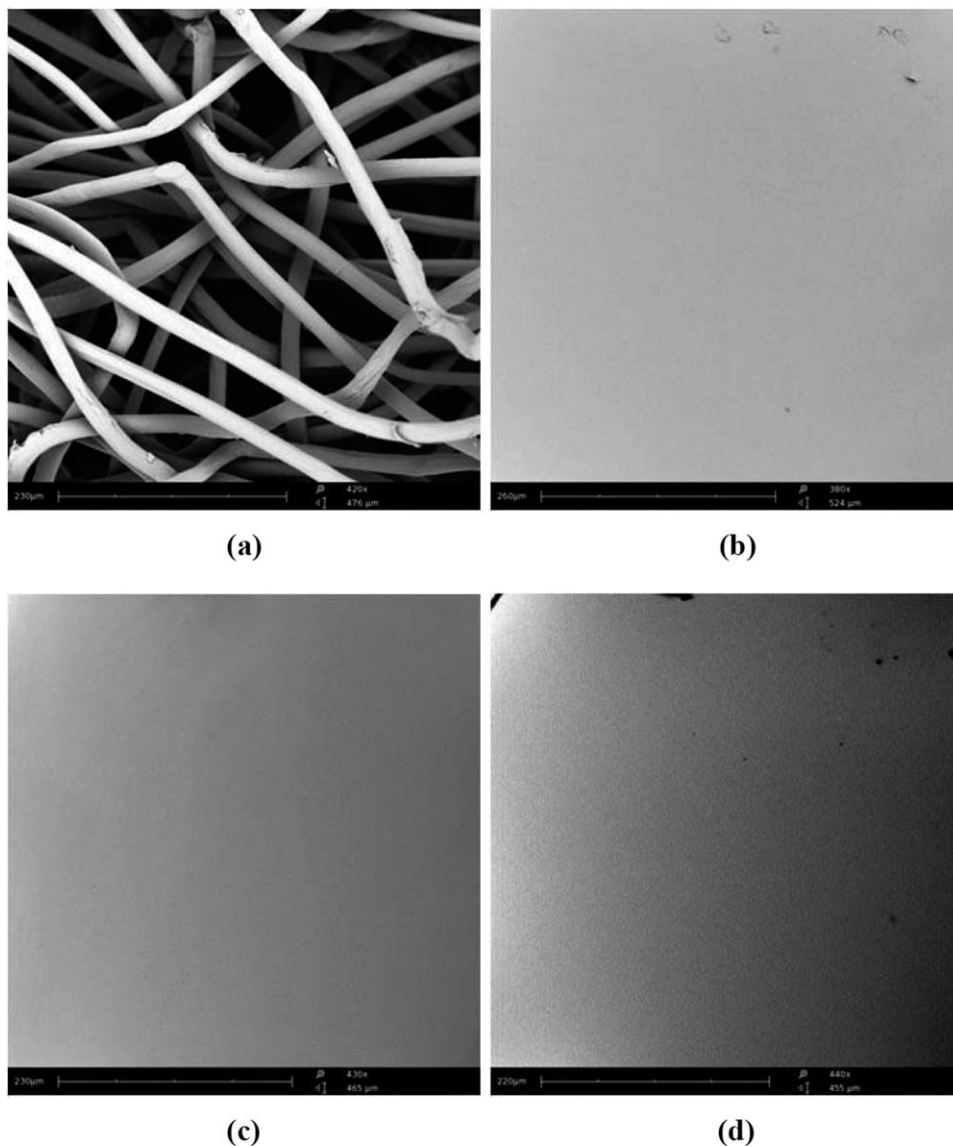**Figure 3** Selectivity of PSS membrane as a function of crosslinking degree.

Figure 4 SEM images of (a) PP nonwoven, (b) PAMPS-filled nonwoven, (c) PSS-filled nonwoven, and (d) PMA-filled nonwoven membranes.
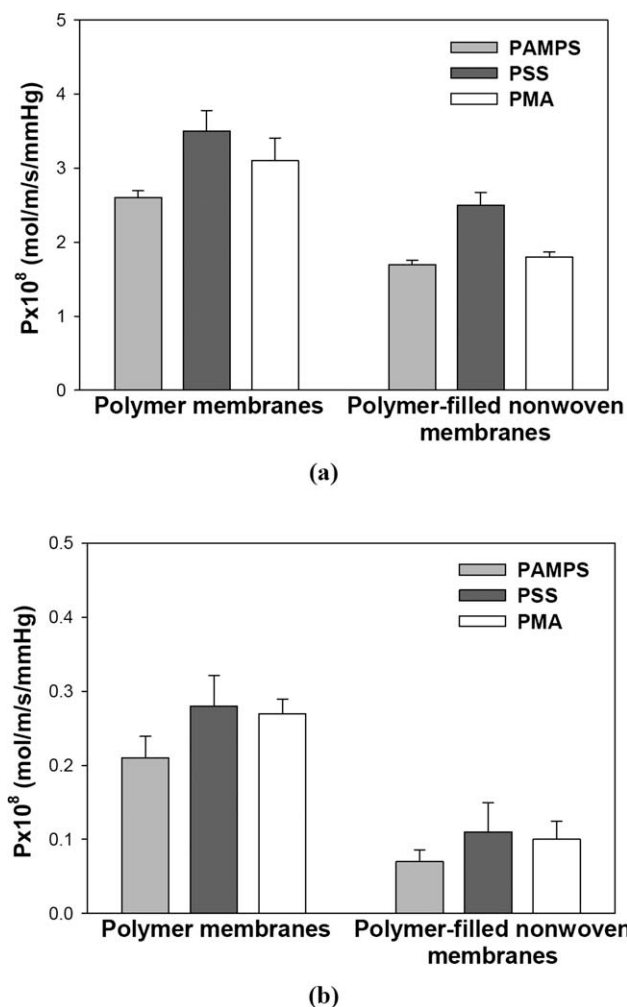
Figure 5 (a) Water and (b) DMMP permeabilities of polyelectrolyte-filled nonwoven membranes.

To investigate the effect of crosslinking degree on the permeation behavior of polyelectrolyte membranes, PSS membranes with three different crosslinking degrees, i.e., 0, 10, and 20%, were prepared and their permeabilities and selectivities were measured. Figure 2 shows the effect of crosslinking degree on the water and DMMP permeabilities of PSS membranes. It has been reported that the crosslinking process can decreases the permeabilities of some polymer membranes.[18,19] However, from Figure 2, it is seen that both water and DMMP permeabilities increase as the crosslinking degree of PSS increases. In un-crosslinked polyelectrolytes, significant physical networks are formed due to the ionic attraction between the ionic groups (such as sulfonic acids of PSS) on neighboring polymer chains.[20–22] The physical networks restrict the mobility of polyelectrolyte chains. When the chemical crosslinking is introduced to the polyelectrolyte system, physical networks are weakened, which causes increased diffusion rate. This might be the main reason for PSS membranes to have increasing permeabilities with

increasing crosslinking degree. Krumova et al. also showed that T_g can decrease as the crosslinking degree of poly(vinyl alcohol) (PVA) increases, especially at relatively low crosslinking degrees.[21] This is because the crosslinking weakened the intermolecular interactions between PVA chains, which complying with our result, i.e., the crosslinking of polyelectrolytes, weakened the physical interaction caused by ionic attraction.

Selectivities of PSS membranes as a function of the crosslinking degree are shown in Figure 3. It is seen that that the membrane selectivity does not have apparent change when the crosslinking degree increases. This means that both water permeation and DMMP permeation are comparably affected by the crosslinking of polyelectrolytes.

Permeabilities and selectivities of polyelectrolyte-filled nonwoven membranes

In addition to the type and crosslinking of polyelectrolytes, the introduction of a secondary component is also an effective means to control the permeation behavior of polyelectrolyte membranes.[23–26] In this study, nonwoven, a web of randomly oriented fibers through interlocking or bonding, was used to host polyelectrolytes. Polyelectrolyte-filled nonwoven membranes were prepared by synthesizing polyelectrolytes in the presence of nonwovens and the open pores of nonwovens were filled with polyelectrolytes. The weight fraction of nonwovens in polyelectrolyte-filled nonwovens is about 33 wt % and the total membrane thickness is about 0.4 mm. Figure 4 shows the surface of PP nonwoven and polyelectrolytes-filled nonwoven membranes. It is seen that the nonwoven surface is completely covered by PAMPS [Fig. 4(b)], PSS [Fig. 4(c)], and PMA [Fig. 4(d)], respectively.

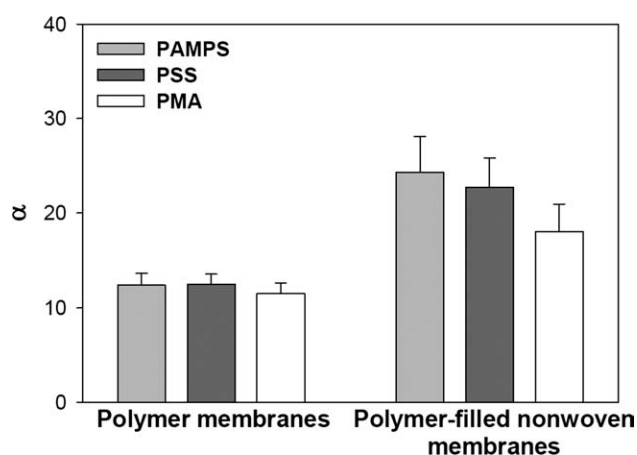Figures 5 and 6 show the permeabilities and selectivities of PAMPS-, PSS-, and PMA-filled nonwoven

Figure 6 Selectivities of polyelectrolyte-filled nonwoven membranes.

Permeant	Membrane	$P \times 10^8$ (mol/m/s/mmHg)	S (mol/m^3/ mmHg)	$D \times 10^{11}$ (m^2/s)
Water	PSS	3.5	320	10.9
	PSS-filled nonwoven	2.5	260	9.6
DMMP	PSS	0.28	220	1.3
	PSS-filled nonwoven	0.11	210	0.5

membranes, respectively. As shown in Figure 5, both water and DMMP permeabilities of polyelectrolyte-filled nonwoven membranes are lower than those of the corresponding polyelectrolyte membranes. At the same time, the selectivities of polyelectrolyte-filled nonwoven membranes are greater than those of corresponding polyelectrolyte membranes (Fig. 6). In addition, PAMPS-filled nonwoven has higher selectivity than all other membranes. More work is needed to understand the mechanism.

Table III compares the sorption and diffusion coefficients of PSS and PSS-filled nonwoven membranes. It is seen that the introduction of PP nonwoven reduces both the sorption and diffusion coefficients, and hence the membrane permeabilities decease for both water and DMMP. In addition, PP nonwoven is hydrophobic, and hence the presence of nonwoven in PSS membrane reduces the water sorption by 20%, but decreases the DMMP sorption by only 5%. However, the effect of nonwoven on the diffusion coefficient is different. As shown in Table III, with the introduction of nonwoven, the DMMP diffusion decreases by 60% while the water diffusion only decreases by 10%. The introduction of nonwoven leads to higher tortuosity, and hence the permeant experiences lengthened and tortuous pathways while penetrating through the membrane. DMMP has a large molecular size than water, and the penetration of the larger molecule is more interrupted by the tortuosity caused by the nonwoven. Therefore, DMMP permeation is more affected by the presence of nonwoven compared to water permeation and this causes the higher selectivities of polyelectrolyte-filled nonwoven membranes, as shown in Figure 6.

CONCLUSIONS

Polyelectrolyte membranes, PAMPS, PSS, and PMA, were prepared and their permeation behavior was investigated. Among all three polyelectrolytes, PSS membrane showed the highest permeabilities for both water and DMMP due to the high diffusion coefficients of PSS caused by its high polymer chain flexibility. All three polyelectrolyte membranes showed selective permeation of water over DMMP because of the high hydrophilicity of polyelectrolyte and the molecular size discrimination between water and DMMP. In addition, it was found that membrane permeability increased as the crosslinking degree of polyelectrolyte increased because of the weakened ionic attraction between polymer chains. While the permeation behavior of polyelectrolyte membranes was obviously affected by their chemical structure, the membrane selectivity did not change apparently. Polyelectrolyte-filled nonwoven membranes were also prepared and it was found that the presence of nonwoven enhanced the selective permeation behavior due to the generation of tortuous pathways for diffusion.

References

1. Kim, T. H.; Koros, W. J.; Husk, G. R.; O'Brien, K. C. J Membrane Sci 1988, 37, 45.
2. Stern, S. A.; Mi, Y.; Yamamoto, H.; Clair, A. K. S. J Polym Sci Part B: Polym Phys 1989, 27, 1887.
3. Teplyakov, V.; Meares, P., Gas Separat Purificat 1990, 4, 66.
4. Lu, X.; Nguyen, V.; Zeng, X.; Elliott, B. J.; Gin, D. L. J Membrane Sci 2008, 318, 397.
5. Rivin, D.; Meermeier, G.; Schneider, N. S.; Vishnyakov, A.; Neimark, A. V. J Phys Chem B 2004, 108, 8900.
6. Napadensky, E.; Elabd, Y. A. U.S. Army Res Lab Report No. ARL-RP-79. 2004.
7. Wijmans, J. G.; Baker, R. W. J Membr Sci 1995, 107, 1.
8. Almquist, C. B.; Hwang, S.-T. J Membrane Sci 1999, 153, 57.
9. Yampolskii, Y. P.; Pinnau, I.; Freeman, B. D. Materials Science of Membranes for Gas and Vapor Separation; Wiley: Chichester, England/Hoboken, NJ, 2006.
10. Freeman, B. D.; Pinnau, I. In: American Chemical Society Division of Polymeric Materials Science and Engineering Meeting, Washington, DC, 1999.
11. Chikh, L.; Girard, S.; Teyssie, D.; Fichet, O., J Appl Polym Sci 2008, 107, 3672.
12. Zhou, J.; Childs, R. F.; Mika, A. M. J Membrane Sci 2005, 254, 89.
13. Tanigami, T.; Iwata, H.; Mori, T. J Appl Polym Sci 2007, 103, 2788.
14. Qiao, J. L.; Hamaya, T.; Okada, T. J Mater Chem 2005, 15, 4414.
15. Rivin, D.; Lindsay, R. S.; Shuely, W. J.; Rodriguez, A. J Membrane Sci 2005, 246, 39.
16. Neto, C. G. T.; Dantas, T. N. C.; Fonseca, J. L. C.; Pereira, M. R. Carbohydr Res 2005, 340, 2630.

17. Carraher, C. E.; Moore, J. A. Modification of Polymers; Plenum Press: New York, 1983.
18. Guilherme, M. R.; da Silva, R.; Rubira, A. F.; Geuskens, G.; Muniz, E. C. React Funct Polym 2004, 61, 233.
19. Nakatsuka, S.; Andrady, A. L. J Appl Polym Sci 1992, 44, 17.
20. Weiss, R. A.; Agarwal, P. K.; Lundberg, R. D. J Appl Polym Sci 1984, 29, 2719.
21. Krumova, M.; Lez, D.; Benavente, R.; Mijangos, C.; Pere, J. M. Polymer 2000, 41, 9265.
22. Orler, E. B.; Yontz, D. J.; Moore, R. B. Macromolecules 1993, 26, 5157.
23. Paul, D. R.; Kemp, D. R. J Polym Sci: Polym Symp 1973, 41, 79.
24. Nielsen, L. E. J Macromol Sci 1967, A1, 929.
25. Alberti, G.; Casciola, M. Ann Rev Mater Res 2003, 33, 129.
26. Karthikeyan, C. S.; Nunes, S. P.; Prado, L. A. S. A.; Ponce, M. L.; Silva, H.; Ruffmann, B.; Schulte, K. J Membr Sci 2005, 254, 139.