

# Elaboration of Ion-Exchange Membranes with Semi-Interpenetrating Polymer Networks Containing Poly(vinyl alcohol) as Polymer Matrix

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**ABSTRACT:** Ion-exchange membranes were prepared with semi-interpenetrating networks (s-IPNs) by mixing a film-forming polymer, poly(vinyl alcohol) (PVA), for the crosslinked matrix and a polyelectrolyte for the specific ion-exchange property. Poly(sodium styrenesulfonate) (PSSNa), poly(styrenesulfonic acid) (PSSH), and poly(acrylic acid) (PAA) were used as anionic polyelectrolytes. Polyethyleneimine (PEI), poly(1,1-dimethyl-3,5-dimethylenepiperidinium chloride) (PDDPCI), and poly(diallyldimethylammonium chloride) (PDDMACl) were used as cationic polyelectrolytes. Membranes with PVA 60% and polyelectrolyte 40% showed the best compromise among mechanical, homogeneous, and ion-exchange properties. Gaseous dibromoethane was used as a crosslinking agent to form the PVA network and for efficient entrapment of the polyelectrolyte in the membrane. The crosslinking time ( $t_c$ ) was optimized for each type of membrane and its influence was studied by thermogravimetric analysis of the sample and scanning electron microscopy observations. The best results (large ion-exchange capacity and small swelling ratio) were obtained for PVA/PAA and PVA/PSSNa/PSSH membranes. Among anion-exchange membranes, PVA/PEI gave the best permselectivity (low co-ion leakage) and the highest ion-exchange capacity. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1572–1580, 2002; DOI 10.1002/app.10420

**Key words:** membranes; IPNs; polyelectrolytes

## INTRODUCTION

Ion-exchange membranes (IEMs) are increasingly used in industrial applications for the production of potable water, for industrial waste-water treatment, and in other processes. Although the commercially available membranes possess excellent performances and are widely marketed worldwide, there should be a demand for novel IEMs that would be less expensive and easier to prepare. The interest of this work was to develop

various and new cation- and anion-exchange membranes possessing tailor-made properties using the same method of preparation.

Various methods are described in the literature for the preparation of IEMs. One of the most interesting ways is to prepare semi-interpenetrating polymer networks (s-IPNs) by mixing two polymers. The ion-exchange characteristics are due to a polyelectrolyte (Pe), which is immobilized in a polymer matrix crosslinked network. IEMs prepared by this method present well-balanced properties<sup>1</sup> such as high ion permselectivity and low electrical resistance (due to the Pe), good mechanical strength, chemical stability, and durability (due to the stable polymer matrix), and reasonable cost.<sup>2</sup>

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Poly(vinyl alcohol) (PVA) was selected as a polymer matrix in view of its film-forming capacities, hydrophilic properties, and high density of reactive chemical functions favorable for crosslinking by irradiation, chemical, or thermal treatments. Thus, several articles have described PVA/Pe s-IPNs (or IPNs) with the purpose of developing pervaporation membranes to purify alcohols,<sup>3–5</sup> esters,<sup>6</sup> and acid<sup>7</sup> containing water or to separate components which have the same boiling point. These membranes with catalytic and separative properties show good stability at high temperature in various mixtures.<sup>5,6</sup> The s-IPN technique is also applied to produce membranes for the facilitated transport of gas (CO<sub>2</sub>)<sup>8</sup> or for reverse osmosis.<sup>9</sup>

In the present work, various Pe's mixed with PVA were tested to prepare tailor-made IEMs, cation-exchanged with poly(sodium styrenesulfonate) (PSSNa), poly(styrenesulfonic acid) (PSSH) and poly(acrylic acid) (PAA) and anion-exchanged as poly(ethylenimine) (PEI), poly(diallyldimethylammonium chloride) (PDDMACl), and poly(1,1-dimethyl-3,5-dimethylenepiperidinium chloride) (PDDPCL). Gaseous 1,2-dibromoethane (DBE) was used to crosslink the films to obtain the membranes. The miscibility of the components was examined on the casting solutions and on the films. Under conditions similar to those for crosslinking, the thermal stability of the films was tested by thermogravimetric analysis (TGA). The morphology of the membranes was examined by scanning electron microscopy (SEM). The efficiency of the crosslinking reaction was monitored by the swelling ratio (*Sw*) and the ion-exchange capacities (IECs) of the membranes. Our objectives were to prepare membranes with the *Sw* close to 0.5 (or less) and the IEC larger than 1 meq g<sup>-1</sup>. Afterward, ion-diffusion experiments were performed on the IEMs that presented the most interesting properties.

## EXPERIMENTAL

### Symbols

See Nomenclature list for the symbols used.

### Polymers and Reagents

PVA (99% hydrolyzed,  $\bar{M}_w = 124,000\text{--}186,000$  g mol<sup>-1</sup>), PEI ( $\bar{M}_w = 70,000$  g mol<sup>-1</sup>) in a 50 wt/vol % aqueous solution, PDDMACl and PDDPCL

(high molecular weight) in a 20 wt/vol % aqueous solution, and PAA ( $\bar{M}_w = 450,000$  g mol<sup>-1</sup>) were provided by Aldrich (Saint Quentin Fallavier, France). PSSNa and PSSH ( $\bar{M}_w = 70,000$  g mol<sup>-1</sup>) were purchased from Scientific Polymer Products (Ontario, NY). DBE was supplied by Aldrich.

### Preparation of Polymer Films

The polymers were dissolved separately in water (PVA 10 g L<sup>-1</sup> and Pe 13.3 g L<sup>-1</sup>) and stirred for about 4 h. The solutions were mixed in fixed proportions and cast into an appropriate plastic box. Films of average thickness of  $\approx 70$   $\mu\text{m}$  were obtained after complete evaporation of the solvent (4–5 days at room temperature).

### Crosslinking

Crosslinking experiments were performed in a reactor described previously.<sup>10,11</sup> First, the film under crosslinking was placed inside the reactor in an oven at 140°C. Then, DBE was boiled (DBE 99% boiling point is 131–132°C) in a flask joined to the reactor so that its vapor could react with the polymer film. The excess of the DBE vapor was condensed in a second flask placed outside the oven. The flow of gaseous DBE must be constant to obtain reproducible results.

### TGA

The thermal stability of the films was tested by TGA. The measurements were performed with a TGA 7 thermometric analyzer coupled with a PC computer, on small pieces of polymer films (about 10 mg) under a nitrogen atmosphere. The detection of the gaseous degradation products of the films was carried out by FTIR (Perkin–Elmer Spectrum 2000) measurements in the transmission mode.

### SEM

The influence of the crosslinking conditions on the morphology of the membranes was examined by SEM with 50-Å resolution. The samples were cut with a scalpel under liquid nitrogen at –190°C and covered with a gold layer. The observations were carried out with various enlargements on the surface and the section of the materials. Films (not crosslinked) and crosslinked membranes were compared. These observations were related to the compatibility between PVA and the associated Pe.

## Membrane Characterization

### Swelling Ratio

The process was similar for all membranes. A piece of membrane was dried, until constant weight  $W_D$  under reduced pressure at room temperature, and then weighed. This membrane sample was immersed in water at 25°C, then rapidly taken out of the bath, quickly wiped with filter paper, and weighed. The operation was repeated for different times of immersion until a constant weight  $W_S$  was obtained. The swelling ratio  $Sw$  was calculated from

$$Sw = (W_s - W_D)/W_D$$

### Ion-exchange Capacity

A preliminary conditioning of the membrane is required to obtain reproducible characterization measurements. First, the membrane was dried under a vacuum until a constant weight  $W_D$ . Then, the membrane was immersed in distilled water to swell it. After that, the membrane underwent two alternate treatments of three baths (for 4 h each) with NaOH ( $\approx 0.1 \text{ mol L}^{-1}$ ), water, and HCl ( $\approx 0.1 \text{ mol L}^{-1}$ ). The cation-exchange membranes (CEMs) were first treated with NaOH, and the anion-exchange membranes (AEMs), with HCl. At the end of the second cycle, the CEM (in acidic form) was washed with water, then introduced into a NaOH ( $n_1 = 0.01 \text{ mol L}^{-1}$ )/NaCl ( $0.5 \text{ mol L}^{-1}$ ) solution. After 4 h, the CEM was removed and the NaOH solution was titrated ( $n_2$ ). For an AEM, the same procedure was used, except that the membrane (in basic form) was introduced in a HCl ( $n_1 = 0.01 \text{ mol L}^{-1}$ )/NaCl ( $0.5 \text{ mol L}^{-1}$ ) solution. The HCl solution was titrated after 4 h to obtain  $n_2$ .

The IEC was calculated in meq/g from

$$\text{IEC} = (n_1 - n_2)/W_D$$

The IEC is compared with the theoretical IEC,  $\text{IEC}_{\text{th}}$ :

$$\text{IEC}_{\text{th}} = (1000 x)/m$$

where  $x$  is the Pe mass ratio, and  $m$ , the molecular weight of the Pe repetition unit ( $\text{g mol}^{-1}$ ).

### Diffusion Experiments

Electrolyte diffusion experiments were performed in the two-chambered Plexiglas vessel previously

used.<sup>12</sup> Each chamber, consisting of a 150-cm<sup>3</sup> cylindrical compartment, was jacketed for temperature control ( $25.0 \pm 0.5^\circ\text{C}$ ) and equipped with a magnetic stirrer ( $200 \text{ rev min}^{-1}$ ).

The IEM to test (CEM under  $\text{Na}^+$  form and AEM under  $\text{Cl}^-$  form) was inserted between the two halves of the diffusion vessel and carefully sealed with O-rings. The diffusion area  $A$  was  $4.15 \text{ cm}^2$ . The two chambers were filled with 25°C distilled water ( $100 \text{ cm}^3$  upstream,  $120 \text{ cm}^3$  downstream). The addition of  $20 \text{ cm}^3$  of a NaCl electrolyte at a high concentration in the upstream compartment started the experiment. The diffusion of solutes through the membrane was monitored by conductivity measurements in the downstream chamber. Before use, the conductivity cell, coupled with a thermometer, was calibrated by checking the linear relationship between the conductivity  $\chi$  ( $\mu\text{S cm}^{-1}$ ) and the electrolyte concentration  $C$  ( $\text{mol L}^{-1}$  expressed for the flux calculation in  $\text{mmol cm}^{-3}$ ;  $C = k \chi$ ). A conductimeter (Consort K220) and diffusion curve fitter were driven by a PC computer. Experimental runs lasted about 1000 s and were repeated several times for each electrolyte concentration.

The electrolyte flux  $J$  ( $\text{mmol cm}^{-2} \text{ s}^{-1}$ ) was determined from the concentration data at the steady state according to

$$J = S V/A$$

where  $S$  is the slope given by linear regression analysis of  $C$  versus  $t$ ;  $V$ , the chamber volume ( $120 \text{ cm}^3$ ); and  $A$ , the exposed membrane area,  $4.15 \text{ cm}^2$ . The permeability coefficient  $P$  ( $\text{cm}^2 \text{ s}^{-1}$ ) of NaCl in the membrane was deduced from

$$P = J l/C_0$$

where  $l$  (cm) is the swollen membrane thickness and  $C_0$  (expressed in  $\text{mmol cm}^{-3}$ ) is the initial solute concentration in the upstream chamber. In the case of PVA/PAA and PVA/PEI membranes, whose permeabilities depend on the pH because weak acidic and basic groups are involved, the membranes were conditioned in a pH 5 solution to ionize the active groups, then washed with water before insertion in the diffusion vessel.

## RESULTS AND DISCUSSION

### Homogeneity

The miscibility of the PVA/Pe mixtures was estimated by visual observation of the limpidity of

**Table I Preparation of Films**

PVA/Pe (60/40%)	Appearance and Remarks	Miscibility
PVA/PAA	Transparent, mechanical resistance, low flexibility	Yes
PVA/PSSNa	Transparent films, high mechanical resistance	Yes
PVA/PSSH	Transparent, mechanical resistance, high flexibility	Yes
PVA/PSSNa/PSSH (60/30/10)	Transparent films, high mechanical resistance	Yes
PVA/PDDMACl	Slightly translucent and very flexible film	Not significant
PVA/PDDPCL	Slightly translucent films, high mechanical resistance and flexibility	Not significant
PVA/PEI	Folds and grooves for pH 10.6 mixtures, flexible and slightly translucent films (for pH $\leq$ 7), films impossible to peel off for pH 3 mixtures	Yes if pH $\leq$ 7

the polymer blend solutions (in water) and the transparency of the films at different mass ratios (30/70, 40/60, 50/50, 60/40, and 70/30). PVA/PSSH and PVA/PAA blends appeared homogeneous for all mass ratios, in agreement with the literature. Park et al.<sup>13</sup> studied the homogeneity of PVA/PAA films by differential scanning calorimetry (DSC) and by measuring the glass transition temperatures ( $T_g$ ) of PVA, PAA, and their blends. At over 50% PVA content, the blends showed single  $T_g$  values, indicating that the films are homogeneous. David and Nguyen<sup>1</sup> studied PVA/PSSH blends in water by detection of the trouble point of solutions versus temperature and confirmed their results on the films by microscopy.<sup>6</sup> They concluded that PVA/PSSH blends are homogeneous for all ratios.

PVA/PSSNa and PVA/PDDMACl mixtures became translucent but wrinkled when the Pe ratio was above 40%. We detected the presence of little crystals in PVA/PSSNa films. David and Nguyen<sup>1</sup> also showed the presence of trouble for PVA/PSSNa blends when PSSNa was above 40% at 25°C. M'Bareck et al.<sup>14</sup> confirmed these results by viscosimetric measurements and showed an enhancement of the miscibility with increase of the

PVA molecular weight and its acetate group ratio (unhydrolyzed sites).

PVA/PDDPCL blends had lower clarity and transparency even at a low Pe ratio and waves appeared on the films, which prove the low miscibility of this system. PVA/PEI mixtures (pH 10.6) showed signs of high turbidity and translucence, which partially disappeared at neutral or acidic pH.

We chose the 60/40 mass ratio to prepare membranes for further study. They had an excess of a polymer matrix crosslinked network to improve the entrapment of the Pe. Furthermore, there is no great excess of one of the polymers at this ratio, which prevents a possible phase inversion during the solvent evaporation. Homogeneity and the appearance of the elaborated films are described in Table I. This process gave us the opportunity of preparing high-quality films.

### Influence of the Crosslinking Conditions

The crosslinking treatment with DBE at 140°C induced a change of the color of the films (from yellow to black with marble variation) but the surface was not altered except for the PVA/PSSH

**Table II Preparation of Membranes**

PVA/Pe (60/40%)	DBE $t_c$ (h)	Appearance
PVA/PAA	4	Dark brown, brittle
PVA/PSSNa	2	Light brown even for long $t_c$ , mechanical resistance
PVA/PSSH	0.5	Black, burnt, and crackled
PVA/PSSNa/PSSH (60/30/10)	2	Dark brown, brittle
PVA/PDDMACl	2	Light brown, flexible
PVA/PDDPCL	2	Dark brown, marbled, flexible
PVA/PEI	10	Irregular light brown (marbled), flexible (for pH $\leq$ 7)

films (Table II). Even at a low Pe mass ratio, the PVA/PSSH membranes always became quickly black and crackled because of the crosslinking of the PVA catalyzed by the present protons. For this reason, PSSH was used afterward, associated with PSSNa; the best appearance was obtained for PVA/PSSNa/PSSH films at a 60/30/10 mass ratio.

The evolution of the morphology of the membranes was examined by SEM (Fig. 1). We did not detect any alterations of the surface of the membranes due to the crosslinking conditions. Microscopy observations of the section of a PVA/PSSNa membrane showed a numerical increase of the aggregate number during crosslinking. An increase of the Pe ratio showed that the dispersed phase consists mainly of PSSNa. Crystallization of PVA occurs when the temperature exceeds the PVA  $T_g$  (measured  $T_g = 71^\circ\text{C}$ ) due to a plasticizing effect by the residual water.<sup>13</sup> The system  $T_g$  is shifted to higher temperature when PSSNa is added to PVA.<sup>1</sup> Thus, PVA induces PSSNa exclusion, which leads to the observed nodules and indicates the only partial miscibility of this blend.<sup>15</sup> The PVA/PSSNa/PSSH film and membrane appeared more homogeneous and without Pe clusters. The slightly crackled cut surface is probably due to the preparation of the sample. The PVA/PAA film and membrane were homogeneous and dense. The PVA/PDDMACl film and the crosslinked membranes also appeared homogeneous with small regular holes on the surface, which prove the departure of the solvent (linked water) during heating at  $140^\circ\text{C}$  for the crosslinking. The PVA/PDDPCL film section looked heterogeneous, with holes, and slightly crackled on one surface (probably because of the cut of the sample) but the membrane was denser. The polymer's tangled area and granular appearance indicate the partial homogeneity of the blend. Local heterogeneity appeared also in the PVA/PEI membrane structure. The partial aggregation detected for the PVA/PEI solution was found again on the dry material. Little holes on the cut view of the membrane could also be observed on the film before crosslinking, proving the departure of linked water during the solvent-evaporation phase. The crosslinked membrane was denser than was the film.

The thermal stability of the films was also examined by TGA measurements (starting at  $20^\circ\text{C}/\text{min}$ , then at  $140^\circ\text{C}$  during  $tc$ ). The thermograms (lost mass rate versus time) obtained for PVA/PDDMACl and PVA/PDDPCL showed the fast es-

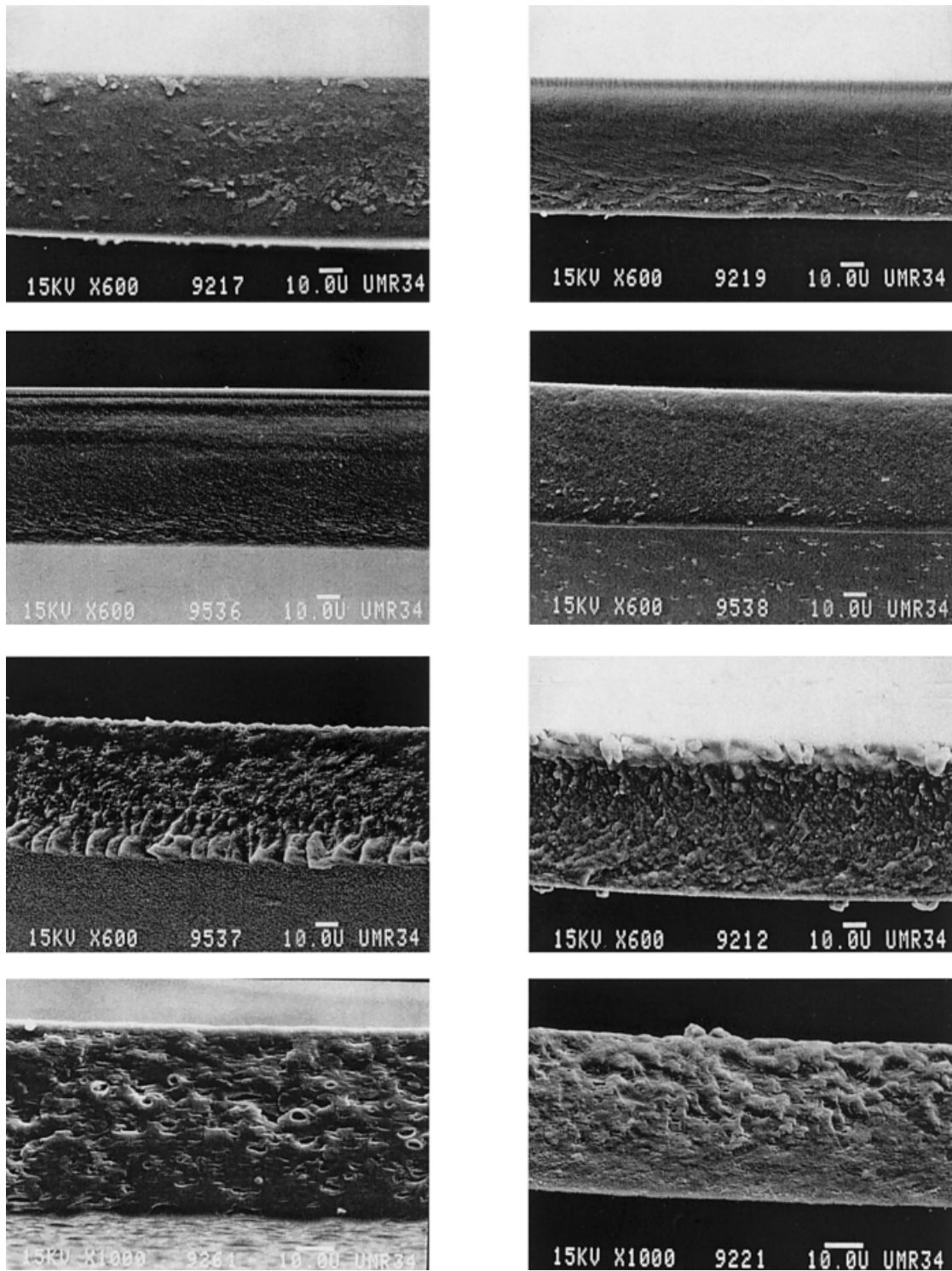
tablishment of a single step, stabilized after 20 and 25 min, respectively. The loss of weight was about 10.5 and 13 wt %, respectively, corresponding to the films' dehydration.<sup>16</sup> This loss of residual solvent is in agreement with the holes observed on the SEM pictures. Similar behavior was observed for the PVA/PSSNa film (loss of weight 8% after 125 min). The TGA curves of PVA/PAA and PVA/PEI films show a continuous loss of weight (6.5 and 10.5 wt %, respectively) during the  $tc$  experiments, which reflect a slight degradation of the polymers. These observations were confirmed by FTIR measurements of the gaseous products of degradation. FTIR spectra recorded for various heating times were similar for all films but more intense for PVA/PEI. Absorbance peaks correspond to water departure (stretching vibration at  $3600\text{ cm}^{-1}$  and bending between 1400 and  $1900\text{ cm}^{-1}$  for molecular vapor water). The TGA curve of PVA/PSSNa/PSSH (60/30/10) showed a fast loss of weight (5 wt % after 5 min), which continued during the thermal treatment ( $0.032\text{ wt \%}/\text{min}$  after 25 min). This behavior is a sign of degradation induced by the crosslinking catalyzed by the presence of the PSSH protons. FTIR analysis of the gas emission showed a most intense spectrum even for a short heating time. However, this spectrum was identical to those obtained previously.

### Membrane Characterization

The swelling ratio  $Sw$  and the IEC were evaluated to investigate the efficiency of the crosslinking reaction. The membrane characteristics are collected in Table III. The crosslinking times  $tc$  were optimized until no noticeable improvement of the membrane properties could be seen. For comparison, crosslinked PVA films ( $tc = 1\text{ h}$  and  $tc = 2\text{ h}$ ) showed, respectively,  $Sw$  values of 0.2 and 0.1.

PVA/PAA membranes showed the best characteristics with the highest IEC and a small  $Sw$  when crosslinked during 2 h. A decrease of IEC was observed for  $tc$  higher than 2 h and could be explained by the PVA degradation.<sup>10</sup> However, these IEC values must be considered with care because they depend on the ionic strength of the solutions, due to the presence of carboxylic groups from PAA.<sup>17</sup> The use of these IEMs is limited because their ionization ratio depends on the pH.

PVA/PSSH membranes with a  $\text{H}^+$  counterion showed lower swelling ratios than with  $\text{Na}^+$ , because of the proton-catalyzed PVA thermal



**Figure 1** SEM pictures of PVA/Pe films and membranes: cut views. (Top) PVA/PSSNa 60/40 membranes on the left; PVA/PSSNa/PSSH membranes (60/30/10) on the right. (Middle, first line) PVA/PAA on the left; PVA/PDDMACl on the right (membranes 60/40). (Middle, second line) PVA/PDDPCL film on the left; membrane (crosslinked) on the right (60/40). (Bottom) PVA/PEI film on the left; membrane on the right (60/40).

**Table III Characteristics of Crosslinked Membranes**

Membranes	DBE $t_c$ (h)	$Sw$	IEC (meq g <sup>-1</sup> )
PVA/Pe anionic membranes (60/40%)			
PVA/PAA	2	0.35	4.9
PVA/PSSNa	4	0.5	0.6
PVA/PSSH	0.5	0.4	1.4
PVA/PSSH	1	0.6	1.8
PVA/PSSH	2	0.6	0.6
PVA/Pe cationic membranes (60/40%)			
PVA/PDDPCI	2	3.0	0.2
PVA/PDDMACI	2	2.2	0.3
PVA/PEI	4	1.0	0.6
PVA/PEI	10	0.8	0.7

Reference capacities IEC were calculated from Pe content (40%) before crosslinking and treatments:  $IEC_{thPAA} = 5.5 \text{ meq g}^{-1}$ ,  $IEC_{thPSSNa} = 1.9 \text{ meq g}^{-1}$ ,  $IEC_{thPSSH} = 2.2 \text{ meq g}^{-1}$ ,  $IEC_{thPDDMACI} = 3.2 \text{ meq g}^{-1}$ ,  $IEC_{thPDDPCI} = 2.8 \text{ meq g}^{-1}$ ,  $IEC_{PEI} = 6.1 \text{ meq g}^{-1}$ .

crosslinking at 140°C, which assisted the DBE reaction. In this way, the PVA network appears tighter (small  $Sw$ ) and leads to an effective Pe entrapment. However, these membranes are not suitable for applications because they are burnt and brittle even at low  $t_c$ . For this reason, the sodium form of PSS was associated to PSSH and different PSSNa/PSSH ratios were tested (3/1, 1/1, 1/3; results given in Table IV). Only the first ratio (membrane PVA/PSSNa/PSSH 60/30/10) showed efficient characteristics and mechanical properties. A simple thermal treatment at 140°C during 2 h did not allow an efficient crosslinking of PVA/PSSNa/PSSH films (Table IV). They became black and burnt by a longer treatment, and PVA is known to be degraded by higher heating.<sup>18</sup>

PVA/PEI membranes appeared less sensitive to the temperature, contrary to the TGA observations and, thus,  $t_c$  could be increased. The IEC

and  $Sw$  were improved for  $t_c = 10$  h and gave the best characteristics for AEMs. However, these results are insufficient because the ionization ratio of these membranes depends on the pH due to the presence of ammonium groups from PEI.<sup>17</sup> The large  $Sw$  could be attributed to the swelling of the holes observed by microscopy. PVA/PDDPCI and PVA/PDDMACI membranes gave poorer results. We noticed a very large  $Sw$  and a poor IEC for  $t_c = 2$  h, which proved inefficient crosslinking. An increase of  $t_c$  slightly improved the  $Sw$ , but the membranes were altered.

Studies were carried out on the synthesized membranes to measure their ability to control electrolyte diffusion. Fluxes  $J$  of NaCl were measured through CEMs in the Na<sup>+</sup> form and through AEMs in the Cl<sup>-</sup> form. An IEM provides permeability to the counterion with exclusion of the co-ion. This phenomenon, called permselectiv-

**Table IV Characteristics of PVA/PSSNa/PSSH Crosslinked Membranes**

Membrane	$T_c$ (h)	$Sw$	IEC (meq g <sup>-1</sup> )
DBE Crosslink			
PVA/PSSNa/PSSH (60/30/10)	2	0.2	1.2
PVA/PSSNa/PSSH (60/20/20)	2	0.3	1.1
PVA/PSSNa/PSSH (60/10/30/)	2	0.6	0.2
Thermal Crosslink			
PVA/PSSNa/PSSH (60/30/10)	1	4.2	0.6
PVA/PSSNa/PSSH (60/30/10)	2	1.5	0.6

**Table V Diffusion of NaCl at 25°C Through the Prepared Membranes (CEMs: Na<sup>+</sup> Form, AEMs: Cl<sup>-</sup> Form)**

$C_0$ (mol L <sup>-1</sup> )	0.01		0.10		0.50		1.00		$q$ (%)
	$P \times 10^{-6}$	$P/D_w$	$P \times 10^{-6}$	$P/D_w$	$P \times 10^{-6}$	$P/D_w$	$P \times 10^{-6}$	$P/D_w$	
PVA/PAA (pH 5)	1.23	0.082	1.62	0.110	2.16	0.144	2.18	0.145	43.4
PVA/PSSNa	0.94	0.063	1.61	0.107	1.65	0.111	1.66	0.112	43.7
PVA/PSSNa/PSSH	1.05	0.070	2.44	0.164	5.46	0.369	8.91	0.602	88.4
PVA/PDDMACl	2.30	0.150	2.62	0.170	3.29	0.220	3.30	0.220	31.8
PVA/PDDPCl	1.65	0.110	2.38	0.160	2.50	0.170	2.50	0.170	35.3
PVA/PEI (pH 5)	0.58	0.039	0.59	0.040	1.11	0.074	1.22	0.081	51.8

Permeability coefficient  $P$  (in cm<sup>2</sup> s<sup>-1</sup>) of NaCl in the membrane. Diffusion coefficient of NaCl in aqueous solution  $D_w = 1.48 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>.<sup>20</sup> Relative decrease  $q$  (in %) of  $P/D_w$  ratio when  $C_0$  changes from 1.00 to 0.01 mol L<sup>-1</sup>. Thickness of swollen membrane in NaCl: PVA/PAA 70 μm, PVA/PSSNa 120 μm, PVA/PSSNa/PSSH 110 μm, PVA/PDDMACl 100 μm, PVA/PDDPCl 110 μm, and PVA/PEI 110 μm.

ity,<sup>17</sup> is more pronounced at a low electrolyte concentration (Donnan exclusion) and for homogeneous density of the charge inside the membrane. The  $P/D_w$  ratio between the permeability coefficient  $P$  of the electrolyte in the membrane and its diffusion coefficient  $D_w$  in water shows the effect of the membrane porosity and of the electrolyte exclusion.<sup>10</sup> The effect of the porosity does not depend on the concentration of electrolytes—it only depends on the structure of the membrane, resulting both in obstruction at the entrance of the pores and frictional resistance in the pores due to the tortuosity.<sup>19</sup> Thus, the variations of the  $P/D_w$  ratio with the concentration are only due to the electrolyte exclusion.

The  $P/D_w$  ratios for these membranes at various NaCl concentrations are listed in Table V, and their decrease for a 1/100 dilution is reported as a  $q$  value (in percent). The larger the  $q$  value, the better the membrane. CEMs (PVA/PSSNa, PVA/PSSNa/PSSH, and PVA/PAA) showed a larger  $q$  value than did the AEMs (except PVA/PEI), which can be explained by the efficiency of the electrolyte exclusion. The PVA/PSSNa/PSSH membrane showed a larger  $q$  value (88.4%) than that of PVA/PSSNa (43.7%) because the entrapment of the Pe is more effective in the PVA network and the density of charge is more homogeneous when PSSH is added, as previously shown. The largest  $P/D_w$  ratio obtained for PVA/PSSNa/PSSH membrane for high NaCl concentrations (0.50 and 1.00 mol L<sup>-1</sup>) showed that the exchange sites seem to be readily accessible and the pores of the membrane have the smallest tortuosity compared to the others. The electrolyte exclusion of the PVA/PEI membrane was efficient ( $q = 51.8\%$ )

and the small  $P/D_w$  ratio for NaCl 0.01 mol L<sup>-1</sup> showed a homogeneous density of charges inside the membrane. The PVA/PEI membrane kept the electrolyte exclusion for larger NaCl concentrations. The large values of  $P/D_w$  observed for PVA/PDDPCl and PVA/PDDMACl membranes at low NaCl concentrations are criteria of their poor permselectivity (high co-ion leakage).

## CONCLUSIONS

Two series of cationic and anionic IEMs were prepared from PVA/Pe blends. We selected the 60/40 PVA/Pe mass ratio to prepare homogeneous films with suitable mechanical properties. PVA crosslinking by gaseous DBE gave the desired s-IPN membranes. We did not observe, by microscopy and TGA measurements, any noticeable damage of the membranes due to the crosslinking conditions except when PSSH was used alone as Pe. The efficiency of the crosslinking of membranes was tested in solution by  $Sw$  and IEC measurements, and diffusion experiments were performed to evaluate the NaCl electrolyte behavior. PSSNa, mainly used in ion-exchange resins for its strong acidic character, appears to be a suitable Pe for the preparation of CEMs. The use of the associated acidic-salt forms of PSS appeared interesting to improve the membrane properties. DBE crosslinking seemed inadequate for cationic Pe. AEMs showed poor IEC except for PVA/PEI membranes, which showed good selectivity, depending on the ionic strength, for high  $tc$ . The use of other cationic Pe's will be considered in future studies.



## NOMENCLATURE

<i>A</i>	exposed membrane area (cm <sup>2</sup> )
<i>C</i>	NaCl concentration in downstream chamber (mol L <sup>-1</sup> ) at <i>t</i> time (s)
<i>C</i> <sub>0</sub>	NaCl concentration in the upstream chamber (mol L <sup>-1</sup> ) at <i>t</i> <sub>0</sub> time
<i>D</i> <sub>w</sub>	diffusion coefficient of NaCl in aqueous solution (cm <sup>2</sup> s <sup>-1</sup> )
IEC	ion-exchange capacity (meq g <sup>-1</sup> )
IEC <sub>th</sub>	theoretical ion-exchange capacity (meq g <sup>-1</sup> )
<i>J</i>	NaCl flux (mmol cm <sup>-2</sup> s <sup>-1</sup> )
<i>l</i>	thickness of the swollen membrane (cm)
<i>m</i>	molecular weight of the Pe repetition unit (g mol <sup>-1</sup> )
<i>P</i>	permeability coefficient (cm <sup>2</sup> s <sup>-1</sup> )
<i>q</i>	relative decrease (%) of <i>P/D</i> <sub>w</sub> ratio when <i>C</i> <sub>0</sub> changes from 1.00 to 0.01 mol L <sup>-1</sup>
<i>S</i>	slope of <i>C</i> versus <i>t</i> curve (mmol cm <sup>-3</sup> s <sup>-1</sup> )
<i>Sw</i>	swelling ratio
<i>tc</i>	crosslinking time (h)
<i>T</i> <sub>g</sub>	glass transition temperature (°C)
<i>V</i> <sub>g</sub>	chamber volume (cm <sup>3</sup> )
<i>W</i> <sub>D</sub>	mass of a dry membrane (g)
<i>W</i> <sub>S</sub>	mass of a swollen membrane (g)
<i>x</i>	weight of Pe in the membrane / weight of the membrane (%)
<i>χ</i>	conductivity (μS cm <sup>-1</sup> )

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