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Elaboration of a membrane with bipolar behaviour using the semi-interpenetrating polymer networks technique

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Abstract

The semi-interpenetrating polymer network technique was applied for the elaboration of three ion-exchange membranes. Poly(vinyl alcohol) (PVA) was chosen as polymer matrix. Commercial poly(styrene sulfonate) (PSSNa) was used as anionic polyelectrolyte (Pe). Poly(*N*-ethyl-4-vinylpyridinium bromide) (PEVPBr) and poly(vinylpyridinium chloride) (PVPCl) were synthesised and characterised in order to use them as cationic Pe. Membranes were obtained by mixing PVA and Pe solutions, followed by solvent evaporation and crosslinking with gaseous 1,2-dibromoethane. The influence of the crosslinking conditions on the sample properties was studied.

Various processes were used to elaborate the bipolar membranes (BMs). The most interesting result was obtained by sticking together a wet PVA/PEVPBr membrane on a wet PVA/PSSNa membrane using a PVA/PSSH (acidic form of PSSNa) solution as glue and by crosslinking the junction by heat treatment. Current–voltage experiments were performed on the BMs. Bipolar behaviour was observed when a water dissociation catalyst was introduced in the PVA/PEVPBr layer. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ion-exchange membranes; Bipolar membrane; Semi-interpenetrating polymer network

1. Introduction

Membrane processes, using the selectivity afforded by ion-exchange membranes, have been applied on a large scale in chemical and biotechnology industries and environmental technology. Thus, these membranes have proved of great interest in many industrial applications such as dialysis (the recovery of acids from salt–acids mixtures), fuel cell technology (conversion of chemicals into energy) [1], electrolysis (chlore–alkali process for the production of chlorine and caustic soda) [2] and electrodialysis (for desalination of foods and chemicals or for treatment of waste waters) [3].

Although already known since the 50s [4] a considerable interest has grown the last decade in a special type of ion-exchange membranes: the so-called bipolar membrane (BM). A BM is generally composed of one cation- and one anion-exchange layers joined together [3] or by a single layer in which one or the two faces are suitably modified [5]. Bipolar multilayers are also conceivable [6,7]. This particular arrangement allows many interesting properties such as high selectivity of univalent ions [6–11], rectification effect [5,12] and water splitting [13]. Water dissociation occurs at the junction of the membranes when a high electric current is forced [14,15]. In this way, the BM technology is an effective tool for the treatment of industrial effluents containing either toxic components which should not be released into the environment or valuable materials which can be recovered or re-used [16]. The electrodialytic water dissociation process is economically very attractive because water dissociation rate is accelerated up to 50 million times. For adequate water dissociation, the BM should have a low electrical resistance, a high permselectivity and a long-term chemical and mechanical stability under operating conditions [16]. However, nowadays, their development is affected by unsatisfactory properties met for BMs as well as ion-exchange membranes [17].

One interesting way for the elaboration of membranes is to use the semi-interpenetrating polymer network (s-IPN) technique by mixing two polymers. In this way, after a crosslinking treatment the polymer matrix forms a network in which the macromolecular chains of the polyelectrolyte (Pe) are immobilised. In ion-exchange membranes, the polymer matrix brings the film forming ability and the mechanical stability, and the Pe brings the specific ion-exchange property [18]. Thus, the s-IPN technique could be

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used to obtain homogenous tailor-made membranes, depending on the Pe ratio and the crosslinking time tc, with well-balanced properties [19] such as high ion permselectivity, good mechanical strength, chemical stability, and durability (due to the stable polymer matrix), at reasonable cost.

In this investigation, polyvinyl alcohol (PVA) was chosen as polymer matrix for its film-forming, hydrophilic properties and its capacities to be crosslinked by chemical way.

Poly(sodium styrenesulfonate) (PSSNa) was selected as Pe for the preparation of cation-exchange membranes according to a previous study [20] that showed its thermal stability and its compatibility with PVA. Moreover, the strong sulfonic acidic groups brought a high permselectivity to the membranes. For anion-exchange membranes no satisfying commercial cationic Pe was found [21]. Consequently, new Pe were synthesised by 4-vinylpyridine polymerisation and modification. Poly(*N*-ethyl-4-vinylpyridinium bromide) (PEVPBr) and poly(vinylpyridinium chloride) (PVPCl) were selected for the preparation of anion-exchange membranes because they possess basic quaternary ammonium groups or protonated tertiary amine groups, usually used for membranes elaboration [21]. In our work, gaseous 1,2-dibromoethane (DBE) was chosen in accordance with previous study [22] to crosslink PVA. In this paper membranes are defined as crosslinked film.

The homogeneity and the morphology of the obtained PVA/Pe films (defined in this paper as not crosslinked material) and membranes (defined as crosslinked films) have been examined by scanning electron microscopy (SEM), X-ray microanalysis and Fourier transform infrared (FTIR) spectroscopy. The thermal stability of the films has been tested by thermogravimetric analysis (TGA) under similar conditions to those for crosslinking. The efficiency of the crosslinking reaction was performed by measuring the swelling ratio and ion-exchange performances of the membranes. The anion-exchange membrane that presents the most interesting properties has been associated with the PVA/PSSNa cation-exchange membrane for the BM elaboration. Our objective was to assembly two membranes of opposite ion-charges but with similar swelling ratio (from 0.20 up to 0.60) [17] and similar ion-exchange capacity, as high as possible. Various processes of junction were tested, by gluing, cold-rolling and pressing. The bipolar behaviour of the elaborated membranes was checked by $I-V$ curves experiments. The effect of the addition of a water dissociation catalyst was also studied.

2. Experimental

2.1. Commercial polymers and reagents

Poly(vinyl alcohol) (PVA) 99% hydrolysed ($\bar{M}_w = 1\,240\,000 - 186\,000\ \mathrm{g\ mol^{-1}}$) was provided by Aldrich Chemicals.

Poly(sodium styrenesulfonate) (PSSNa) and poly (styrenesulfonic acid) (PSSH) ($\bar{M}_w = 70\,000\ \mathrm{g\ mol^{-1}}$) were purchased by Scientific Polymer Products Inc.

1,2-Dibromoethane (99%) (DBE) and ethylbromide (98%) were supplied by Aldrich Chemicals, *N*,*N*-diethyl methylamine (98%) by Jansen Chemicals.

2.2. Polymer synthesis, purification and characterisation

Distilled 4-vinylpyridine (4-VP) (40 g) (95% from Aldrich Chemicals) was polymerised during 6 h at 80 °C using radical initiator 2,2′-azo-bis-isobutyronitrile (AIBN) (1.64 g, 98%) (from Acros Organics) in anhydrous toluene solvent (200 cm^3). After filtration, poly(4-vinylpyridine) (4-PVP) was purified by washing with toluene and dried in oven (70 °C, 48 h). 4-PVP was dissolved in HCl (0.1 mol l^{-1}) to obtain poly(vinylpyridinium chloride) (PVPCl). 4-PVP (40 g) was modified by addition of ethylbromide (14.4 cm^3, 98%) in methanol solvent (100 cm^3) during 20 h at 50 °C in order to obtain poly(*N*-ethyl-4-vinylpyridinium bromide) (PEVPBr). PEVPBr was recovered by precipitation in toluene, washed by alternating treatment with toluene/methanol, filtrated on sintered glass and dried in oven (70 °C, 48 h).

Weight-average molecular weight ($\bar{M}_w$) of the 4-PVP and of the modified polymers were determined from the static light scattering technique using the Sematech SEM-Classical photogoniometer (laser He–Ne 3 mW; $\lambda_0 = 632.8$ nm) following the classical Zimm's plot graphic representation. The light scattering intensities were measured at various angles (from 20 to 150°) and various concentrations (20, 15, 10, 5 g l^{-1}) on PVPCl and PEVPBr dissolved in NaCl/HCl and NaBr 0.1 mol l^{-1} solvent, respectively. For 4-PVP, the procedure was similar but the solvent was methanol. Before experiments, samples were clarified by filtration under vacuum (Millex units from Millipore; 0.45 μm pore size). Refractive index increments ($\mathrm{d}n/\mathrm{d}C$) of the solutions, needed for $\bar{M}_w$ determination, were measured using a Shimadzu RID-6A refractive index detector associated to a peristaltic pump delivery system.

2.3. Elaboration of the membranes

2.3.1. Ion-exchange membranes

A PVA solution (20 g l^{-1}) was prepared by dissolving PVA powder in deionised water at 100 °C with reflux system during 4 h. Then, PVA and Pe (10 g l^{-1}) in aqueous solutions (in HCl 0.1 mol l^{-1} for PVPCl) were stirred separately during 4 h before being mixed together in the appropriate 60/40 mass ratio [22]. After stirring anew during 6 h, 55 cm^3 of the PVA/Pe solution were casted on a Petri box. A film of average thickness 50 μm was obtained after solvent evaporation at room temperature during 5 days.

The polymer films were crosslinked by gaseous DBE at

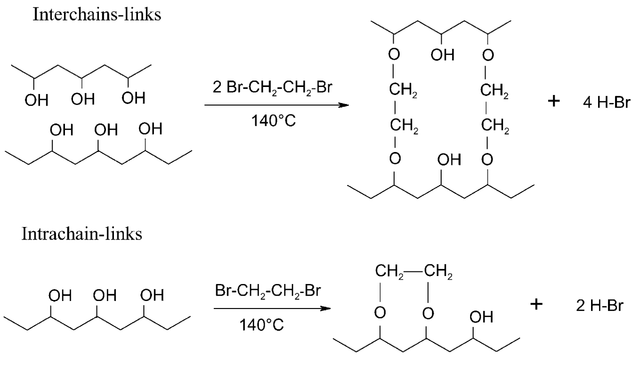

Fig. 1. Crosslinking PVA with gaseous DBE.

140 °C in an experimental set-up previously described [23]. The crosslinking reaction involves interchain and intrachain links on PVA (Fig. 1); this leads to a PVA network in which the Pe is entrapped. The crosslinking time was optimised for 4 h for PVA/PSSNa (60/40%) film [20].

After crosslinking, the membranes were soaked successively in different baths (HCl 1 mol l^{-1}, water, NaOH 1 mol l^{-1}, water) in order to wash and to condition them. This cycle was repeated two times and ended by dipping the membranes in NaCl 0.1 mol l^{-1} solution to put them under the salt form.

2.3.2. BMs

Different processes were tested to join together the two ionic layers of opposite charge. Two dry films were cold-rolled using a rolling mill (at slow speed of rotation) without or with water vapour spray or sprayed water for gluing. Finally, the obtained bi-layer was crosslinked by gaseous DBE to give a BM.

A wet anion-exchange film was superimposed on the top surface of a wet (gluing) pre-formed PVA/PSSNa film on the Petri box (PVA is well-known for its gluing properties). After drying at room temperature, the bipolar film was crosslinked by gaseous DBE.

A glue solution was used as intermediate layer between the two membranes and rolled-out with a brush, a pastry wheel or a blade. Various type of glues (PVA, PVA/PSSH) and crosslinking agents (gaseous DBE, H_2SO_4 or HCl at various concentrations) followed by a thermal treatment (80, 100, 140 °C) during various times (1, 12, 24, 48 h) were tested.

2.4. Characterisation of the membranes

2.4.1. Scanning electron microscopy

Ion-exchange membranes and BMs were observed by SEM using a Jeol JSM 35 CF microscope. Beforehand, samples were prepared by fracturing under liquid nitrogen at −190 °C with a scalpel, and covered with a gold layer. The observations of the section and the surface were carried out to discuss on the homogeneity of PVA/Pe systems, the influence of the crosslinking reaction on the morphology of the membrane, and the quality of the BM interface.

2.4.2. Fourier transform infrared spectroscopy

The thermal stabilities of the films were studied by FTIR measurements in transmission mode (ATR) using the Nicolet Avatar 360 FTIR. They were performed on films before and after a thermal treatment at 140 °C during 4 h in accordance with the crosslinking conditions to reveal the possible chemical modifications appeared.

The efficiency of the crosslinking reaction has been showed, using the same technique, by comparing the spectra of the PVA/Pe samples before and after DBE treatment.

2.4.3. X-ray microanalysis

X-ray microanalysis was used to obtain information on the miscibility of the films by measuring their elementary composition. First, the films were dried under vacuum before observing their surface by SEM (Hitachi S32000N Low vacuum). The zone to analyse was selected directly on the monitor. The analyses were performed using an Energy Dispersive X-ray Spectrometer by a X-ray probe (Kewex Sygma) coupled to a X-ray detector (Kewex Super-Drive).

2.4.4. Thermal gravimetric analysis

The thermal stability of the films was investigated by TGA (Perkin Elmer thermal gravimetric analyser TGA 7 coupled with a PC computer). Measurements were performed on small samples (about 10 mg) heated under a nitrogen atmosphere (heating rate of 10°C $\min^{-1}$—isotherm 4 h at 140 °C). The formation of gaseous degradation products during the heating process was examined by FTIR measurements in transmission mode (Perkin Elmer spectrum 2000).

2.4.5. Swelling behaviour

Strips of dry membrane (constant weight W_d) were immersed in water at 25 °C. After 24 h, they were taken out of the solution and carefully wiped with absorbent paper before being weighed. This procedure was repeated several times until constant weight W_s. The swelling ratio Sw was defined as:

$$\mathrm{Sw} = (W_s - W_d)/W_d$$

2.4.6. Ion exchange capacity

A preliminary conditioning is required for the characterisation of the ion-exchange membranes. The dry membranes (constant weight W_d) were immersed in deionised water to swell them before undergoing an alternate treatment with NaOH, water and HCl (≈0.1 mol l^{-1}). This cycle of three baths (for 4 h each) was performed for a second time. The cation-exchange membranes were first treated with NaOH and with HCl. At the end of the second cycle, the membrane was quickly washed with water, then immersed in NaOH ($0.01\ \text{mol l}^{-1}$)/NaCl ($0.5\ \text{mol l}^{-1}$) solution (or HCl/NaCl) for cation-exchange membranes (or anion-exchange membranes) to convert them in their salt form. The amount of ion-exchange sites n was determined by back titration. Ion-exchange capacity (IEC in mequiv. g^{-1}) was calculated as:

$$\text{IEC} = n/W_\text{d}$$

The theoretical ion-exchange capacity (IEC_th) was calculated for comparison with experimental measurement

$$\text{IEC}_\text{th} = (1000x)/M_0$$

where x is the polyelectrolyte mass ratio and m is the molecular weight of the polyelectrolyte repetition unit (g mol^{-1}).

For BMs, the method was different in order to perform the simultaneous measurement of the ion-exchange capacities of the two layers. After swelling, the BM to test underwent a HCl ($1\ \text{mol l}^{-1}$) treatment during 4 h in order to convert the ionic sites of the cation-exchange membrane (CEM), their acid form (H^+) and the ionic sites of the anion-exchange membrane (AEM) into their chloride form (Cl^-). After 4 h, the membranes were washed with water, and dipped in a $NaNO_3$ ($1\ \text{mol l}^{-1}$) solution to elute simultaneously the H^+ and Cl^- ions which were titrated by pH metric (n_{H^+}) and potentiometric (n_{Cl^-}) measurements, respectively. The ion-exchange capacity was calculated for each layer as

$$\text{IEC}_\text{(CEM)} = n_{H^+}/W_\text{d(CEM)} \qquad \text{IEC}_\text{(AEM)} = n_{Cl^-}/W_\text{d(AEM)}$$

both W_d are those measured before assembly of the BM.

2.4.7. Diffusion experiments

Electrolyte diffusion experiments were performed in a Plexiglas cell consisting of two separable cylindrical compartments ($110\ \text{cm}^3$ volume). Each compartment was jacketed for temperature regulation (25.0 ± 0.5 °C) and equipped with magnetic stirrers. An efficient magnetic stirring (200 ± 10 rpm) allowed the reduction of the thickness of the diffusion boundary layers on both sides of the membrane. The membrane to test was conditioned as previously described. After water washing, the sample was sandwiched between the two compartments of the cell and clipped with O-rings. Each compartment was filled with $100\ \text{cm}^3$ water to wash the membrane until constant and low conductivity value (range 1.0–2.0 μS). The addition of a NaCl solution ($V = 100\ \text{cm}^3$) at C_0 concentration (mol l^{-1} expressed in mmol cm^{-3} for the diffusion experiments) in the upstream chamber and a water solution ($V = 100\ \text{cm}^3$) downstream started the experiment. A conductivity cell, previously calibrated, coupled with a thermometer was placed in the downstream compartment to monitor the increase of the concentration C (mmol cm^{-3}) of NaCl due to the diffusion through the membrane. A conductimeter (Consort K220) and diffusion curve fitter were driven by a PC computer. Each experiment ran about 1000 s in order to reach the near-stationary state. The procedure was repeated several times to obtain an average value of slope S (given by linear regression of the curve C vs time) for each electrolyte concentration C_0.

The electrolyte flux J ($\text{mmol cm}^{-2}\ \text{s}^{-1}$) was determined by

$$J = (VS)/A$$

where A is the effective area of the membrane sample ($4.15\ \text{cm}^2$).

At the near-stationary state, the permeability coefficient P ($\text{cm}^2\ \text{s}^{-1}$) of the electrolyte in the membrane was obtained from

$$P = (Jd)/C_0$$

where d is the swollen membrane thickness (cm) and C_0 is expressed in mmol cm^{-3}.

2.4.8. Current–voltage curves

The current–voltage curves reflect the electrical properties of the membrane and give some information about the transport mechanism of ions. The I–V curves were performed by using a cell previously described [24]. The membrane under study ($A = 9\ \text{cm}^2$) was clamped between two symmetrical compartments equipped with magnetic stirrers and filled with $100\ \text{cm}^3$ NaCl ($0.1\ \text{mol l}^{-1}$). Two Ag/AgCl electrodes located near the membrane solution interfaces allowed the measurement of the potential difference across the membrane. The current was applied to the cell through two Pt plane electrodes by a generator. The measurements were carried out by recording the current density versus the potential difference applied to the membrane (50 mV impulse versus time).

3. Results and discussion

3.1. 4-PV polymerisation and modification

4-VP polymerisation during 6 h initiated by AIBN radical initiator gives 80% (w/w) of the maximum theoretical yield after filtration, washing and drying. The use of toluene favours the termination reactions by radical recombination and the transfer reactions to the monomer can be neglected [25].

For PEVPBr preparation, quaternisation of 4-PVP was achieved by mole to mole addition of ethyl bromide in methanol solvent. We noticed that the medium coloured in red when the reaction started and in light blue during the 20 h reaction.

In order to dissolve and ionise the 4-PVP, HCl ($0.1\ \text{mol l}^{-1}$) was added in slight excess. Higher concentration of HCl would cause the degradation of the membrane during crosslinking. A strong thermal crosslinking of the PVA accompanied by reactions of degradation is observed at 140 °C when it is catalysed by protons [20]. Also the

Table 1
Characteristics of the polymerised polyelectrolytes

Sample	dn/dC (cm^3 g^{-1})	$\bar{M}_w$ (g mol^{-1})	$\overline{\mathrm{Dp}_w}$
4-PVP	0.270	97 000	924
PVPCl	0.202	122 000	862
PEVPBr	0.182	190 000	888

$\overline{\mathrm{Dp}_w}$ was calculated from $\bar{M}_w = \overline{\mathrm{Dp}_w} M_0$ with $M_0 = 105$, 141.5 and 213.9 g mol^{-1} for 4-PVP, PVPCl and PEVPBr, respectively.

reaction is not completed the amine sites will become more ionised during the conditioning of the membrane.

dn/dC and $\bar{M}_w$ values of the synthesised polymers are summarised in Table 1. The high value of $\bar{M}_w$ showed an efficient reaction of polymerisation. The weight-average degrees of polymerisation $\overline{\mathrm{Dp}_w}$ of the two synthesised polyelectrolytes were calculated by considering an efficient ionisation of each pyridine site. Their $\overline{\mathrm{Dp}_w}$ values appeared similar to the $\overline{\mathrm{Dp}_w}$ of the 4-PVP which indicated a low degradation of the polymer during the modification reaction.

3.2. Elaboration and characterisation of the ion-exchange membranes

3.2.1. Homogeneity and morphology

The procedure for film elaboration involves the ability of the polymers blends to dissolve in water (or HCl 0.1 mol l^{-1} for PVPCl) without any phase separation. The miscibility of the PVA/Pe mixtures was checked by noticing the turbidity of the solutions before casting and the homogeneity of the films. No phase separation was observed for the prepared PVA/Pe mixtures whatever their ratio.

PVA/PSSNa films are less translucent for a PSSNa ratio above 40%. PVA/PVPCl and PVA/PEVPBr films exhibit higher clarity and transparency when the Pe ratio is lower than the PVA ratio. For these reasons we chose the 60/40 mass ratio to prepare membranes for our study. Thus, they contain an excess of the polymer matrix in order to improve the entrapment of the polyelectrolyte after crosslinking. Furthermore, there is no great excess of one of the polymers at this ratio, which prevents a possible phase inversion during the solvent evaporation. This process gave us the opportunity of preparing high-quality films.

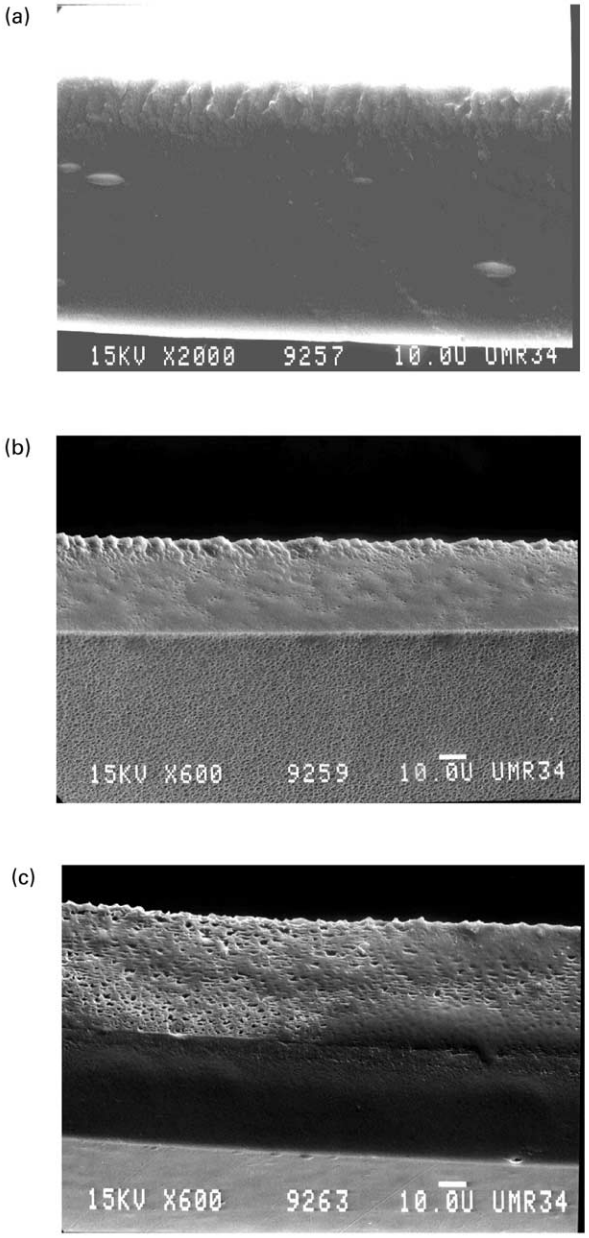

Fig. 2. SEM pictures of the cutview of the PVA/Pe films: (a) PVA/PSSNa (× 2000), (b) PVA/PVPCl (× 600), (c) PVA/PEVPBr (× 600).

The section of the films was observed by SEM (Fig. 2) and the surface was analysed by X-ray microanalysis. The presence of small aggregates was detected on PVA/PSSNa film and the X-ray microanalysis (Table 2) showed that these piles consist of sulphur, oxygen and sodium atoms in ratios corresponding to sodium sulfonate groups (–SO^{3-}, Na^{+}) of the PSSNa. There are no carbon atoms inside these aggregates, hence no polymer chains. This fact clearly shows the arrangement of the polymer to form ionic clusters. Thus, the tangle of the chains is not homogeneous. The continuous phase on the surface of the film appeared more homogeneous because its elementary analysis (Table 2) showed the simultaneous presence of PSSNa and PVA. Previous studies had also proved the partial miscibility of the PVA/PSSNa blends by trouble point [26] and viscosimetric measurements [22].

Table 2
Elementary composition of the surface of the films

Film	Elementary composition (%)	
PVA/PSSNa	Continuous phase	C (63.1), O (26.2), S (5.9), Na (5.8)
	Irregularities	O (62.3), S (18.8), Na (18.9)
PVA/PVPCl	Continuous phase	C (81.9), O (11.0), Cl (6.9)
PVA/PEVPBr	Continuous phase	C (81.3), O (11.2), Br (7.1)

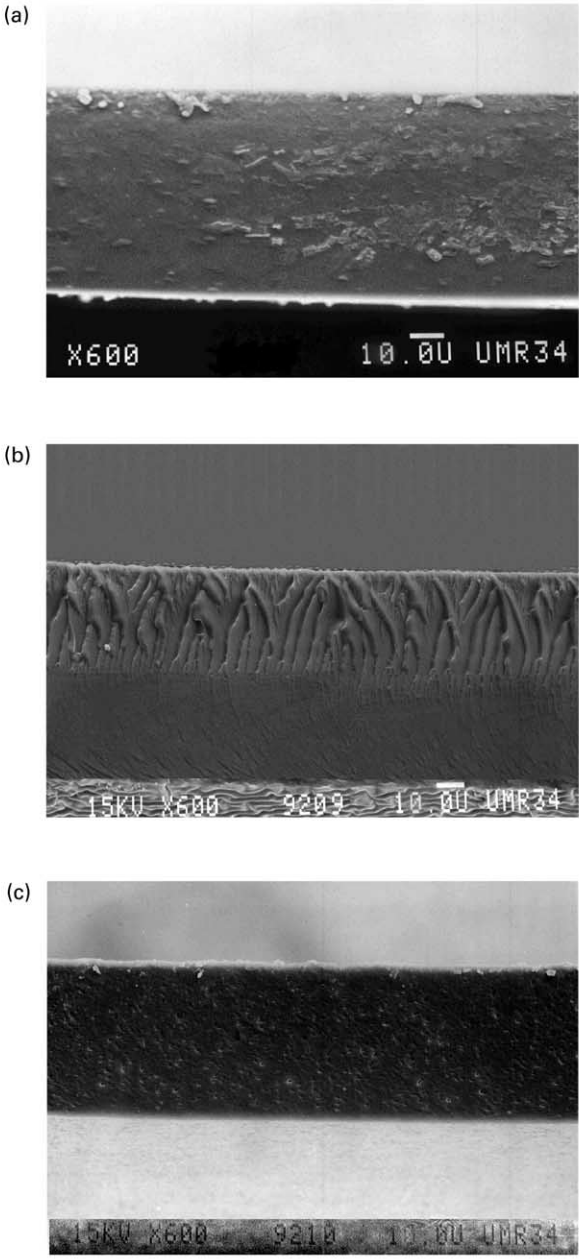

Fig. 3. SEM pictures of the cutview of the PVA/Pe membranes (× 600): (a) PVA/PSSNa, (b) PVA/PVPCl, (c) PVA/PEVPBr.

PVA/PVPCl films exhibited lower clarity and transparency than PVA/PEVPBr at similar composition. PVA/PVPCl and PVA/PEVPBR films appeared dense and homogeneous for the 60/40 mass ratio. The pictures of their section (Fig. 2) showed small regular holes, more numerous near the surface and larger for PVA/PEVPBr film, which prove the departure of the solvent (linked water) during the solvent evaporation phase [27]. Their slightly crackled cut surface is probably due to the preparation of the sample. Moreover, no discontinuity of the composition of the films was observed. For both films, the X-ray microanalysis gave for all points the same composition (Table 2). As remarks, all atoms contained in our polymers are detected by X-ray microanalysis, except nitrogen and hydrogen. Moreover, the sum of the percents of each atom contained in a film is not equal to 100% because of the presence of impurities in their surface coming from their handling.

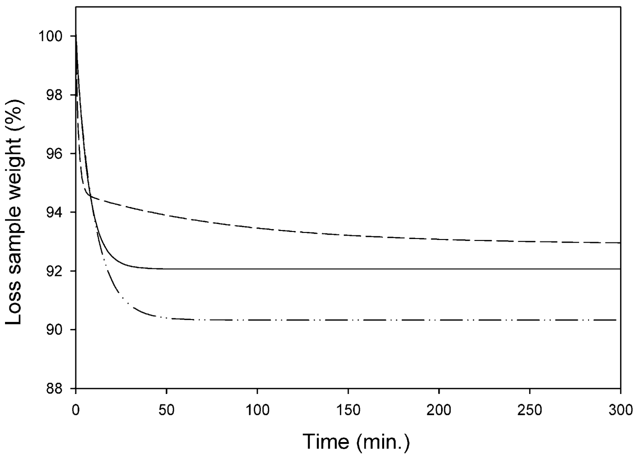

Fig. 4. Thermal gravimetric analysis at 140 °C of PVA/PSSNa (—), PVA/PEVPBr (– – –) and PVA/PVPCl (–··) (60/40 mixtures): loss of weight (%) vs. time (min).

3.3. Influence of the crosslinking reaction

DBE crosslinking treatment at 140 °C induced a brown colour modification of the films, but no surface modification could be noticed. The comparison between the SEM pictures, before and after the crosslinking, allowed the detection of the possible alterations of the morphology of the samples (Fig. 3).

SEM observations of the section of PVA/PSSNa membrane showed an increase of the aggregates number during crosslinking. The previous X-ray microanalysis has shown that the dispersed phase consists mainly of sulfonate groups of PSSNa. Crystallisation of PVA occurs when the temperature exceeds the PVA glass transition temperature T_g (measured $T_g = 71$ °C) due to a plasticising effect by the residual water [28]. The system T_g is shifted to higher temperature when PSSNa is added to PVA [26]. Thus, PVA induces PSSNa exclusion, which leads to the observed nodules and indicates the only partial miscibility of this blend [29].

The PVA/PVPCl membrane looked more heterogeneous than the film (Fig. 3). The mottled surface indicates an irregular crosslinking or a partial alteration of the polymers on the surface of film. However, the slightly crackled surface may also be due to the cut of the sample. The crosslinked PVA/PEVPBr membrane appeared denser than the film.

The thermal stability of the films was also examined by TGA measurements. In accordance with the crosslinking conditions, studies were run starting at a 20 °C min^{-1} rate, then at 140 °C during tc (Fig. 4). The thermograms (rate of

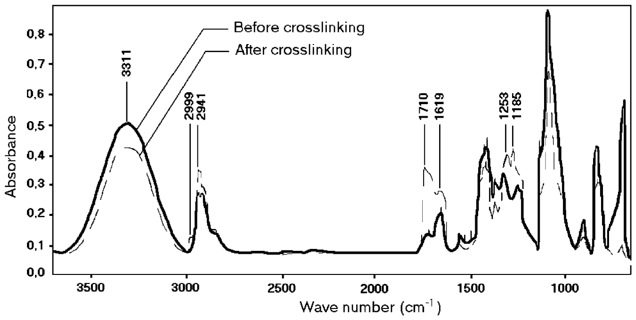

Fig. 5. FTIR spectra of PVA film before (—) and after (– – –) DBE crosslinking (4 h, 140 °C).

mass loss versus time) have shown for PVA/PSSNa a fast establishment of a stationary step, which practically ended after 1 h run. This step proves the absence of degradation of the polymers during the heating treatment at 140 °C. The loss of weight about 8% is caused by the departure of residual solvent (water). PVA/PVPCl and PVA/PEVPBr films have shown a similar behaviour with a slower loss of weight 10 and 7%, respectively. The slope corresponding to the PVA/PEVPBr film is the most pronounced (about 0.2% h^{-1} after 1 h run). This behaviour is also due to the dehydration of the samples during the heating treatment and was confirmed by FTIR analysis of the gaseous emissions. FTIR spectra recorded at various heating time were similar for the three films but more intense for PVA/PVPCl. Absorbance peaks corresponded to water departure (stretching vibration at 3600 cm^{-1} and bending between 1400 and 1900 cm^{-1} for molecular vapour water). No trace of residual toluene or methanol was detected for PVA/PVPCl and PVA/PEVPBr films. A difference of spectra intensity between the films was observed because of their respective hygroscopicity. These observations confirm that the little cavities observed on the SEM cut views (Fig. 2) are due to the departure of this bound water.

The comparison of FTIR spectra of films before and after thermal treatment was also carried out. PVA film was studied first. The two spectra looked superimposable, showing that there is no noticeable degradation of the PVA chains. A decrease in the intensity of the bands localised around 3310 cm^{-1} assigned to the hydroxyl groups, was logically observed after thermal treatment because they result in polymer dehydration during thermal treatment [29]. The comparison of FTIR spectra of the PVA/Pe films before and after thermal treatment showed no noticeable alterations.

Table 3
Characterisation of elaborated ion-exchange membranes (*tc* = 4 h)

Sample	Sw	IEC (mequiv. g^{-1})	IEC_{th} (mequiv. g^{-1})
PVA/PSSNa	0.49	1.1	1.94
PVA/PVPCl	0.38	0.6	2.36
PVA/PEVPBr	0.51	1.0	1.47

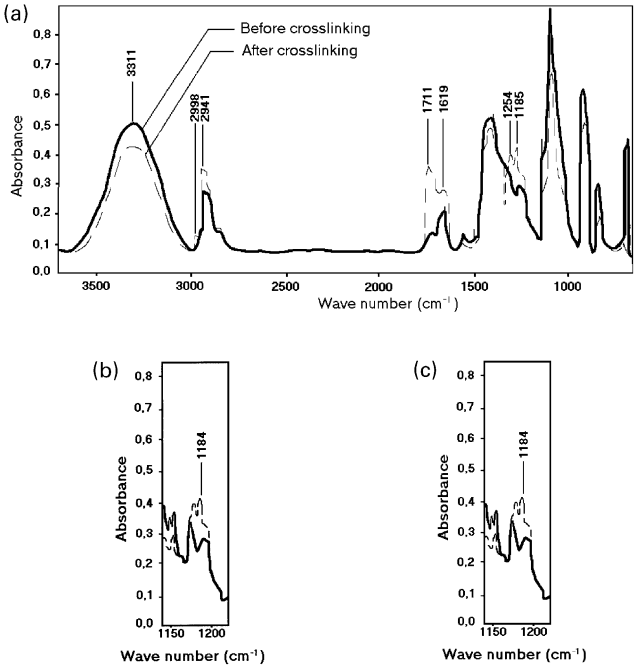

Fig. 6. FTIR spectra of PVA/PSSNa (a), PVA/PEVPBr (b) and PVA/PVPCl (c) film (60/40 mixtures) before (—) and after (– – –) DBE crosslinking (4 h, 140 °C).

DBE allows the crosslinking of the PVA chains that forms the network where the Pe is entrapped. Thus, it is interesting to characterise the efficiency of the reaction between DBE and PVA and investigate its influence on each PVA/Pe blend. FTIR spectra of PVA before and after DBE treatment (Fig. 5) showed a decrease of the intensity of the band located at 3311 cm^{-1} attributed to the vibration of the hydroxyl groups and the increase of the intensity of the band at 2941 cm^{-1} attributed to the $-CH_2-$ groups. The appearance of two new bands (1253 and 1185 cm^{-1}) indicated the formation of ether links (intra- and inter-chains, respectively) between the hydroxyl groups of PVA. This modification showed the crosslinking reactions of PVA chains. However, other reactions such as degradation can occur with cuts of the PVA chains, inducing mainly the formation of double bonds (1619 and 2999 cm^{-1}) and carbonyl groups (1709 cm^{-1}) [30].

The main modification appearing on the FTIR spectra of the PVA/Pe membranes was the 1185 and the 1253 cm^{-1} peaks due to the formation of ether links between the hydroxyl groups of PVA (Fig. 6). Consequently, the crosslinking reaction was efficient for each membrane. The appearance of the peak at 1711 cm^{-1} still characterised the cut of the PVA chains with formation of methyl and carbonyl groups (Fig. 6). No bands or peaks due to bromide groups or residual dibromine were detected which proves the efficiency of the preliminary washing and conditioning of the membrane.

3.4. Characterisation

In addition to the FTIR study, ion-exchange capacity and

Table 4
Diffusion of NaCl at 25 °C through the elaborated membranes (cation-exchange membrane: Na^+ form, anion-exchange membranes: Cl^- form)

	C_0 (mol l^{-1})						
	0.1		0.5		1.0		q
	P	P/D_w	P	P/D_w	P	P/D_w	
PVA/PSSNa	0.69	0.48	1.5	1.01	2.17	1.47	67.3
PVA/PVPCl	0.23	0.15	0.44	0.30	0.51	0.34	55.9
PVA/PEVPBr	0.24	0.16	0.50	0.34	0.67	0.45	64.4

Permeability coefficient P ($\times 10^7$ cm^2 s^{-1}) of NaCl in the membrane. Diffusion coefficient of NaCl in aqueous solution $D_w = 1.48 \times 10^{-5}$ cm^2 s^{-1} [33]. Relative decrease q (in %) of P/D_w ($\times 10^2$) ratio when C_0 changes from 1.0 to 0.1 mol l^{-1}. Thickness of swollen membrane in NaCl: PVA/PSSNa 117 μm, PVA/PVPCl 115 μm, PVA/PEVPBr 121 μm.

swelling measurements on each elaborated ion-exchange membrane have been carried out to investigate the efficiency of the crosslinking reaction. The results are given in Table 3. The crosslinking time tc = 4 h has been optimised for all membranes until no noticeable evolution of their properties. For comparison, crosslinked PVA films (tc = 1 and 2 h) showed swelling values of 0.20 and 0.10, respectively. PVA/PSSNa cation-exchange membrane was selected in a previous study [20] for its large ion-exchange capacity and its swelling in the range 0.20–0.60 [17]. PVA/PEVPBr membrane showed a higher exchange capacity and a swelling than PVA/PVPCl for similar reticulation time. Thus, PVA/PEVPBr membrane appeared the most promising anion-exchange membrane for the elaboration of the BM. This membrane showed efficient ionic sites in larger numbers because its ion-exchange capacity is the higher. Moreover, its swelling ratio is similar than the swelling ratio of PVA/PSSNa membrane for a same tc. Thus, these two membranes will swell in the same way when they are associated to form the BM, which will prevent the ballooning effect [4].

Studies were carried out on the elaborated membranes in order to measure their ability to electrolyte diffusion. The phenomenon of permselectivity [31] to electrolytes is specific of ion-exchange membranes and in this way interesting to highlight. As a general rule, a membrane presents a permeability to the counterion with exclusion of the co-ion. This property is more pronounced at low electrolyte concentration (Donnan exclusion) and for homogeneous density of charge inside the membrane. NaCl was chosen as electrolyte because it is often used to highlight this phenomenon [2,23]. Fluxes J of NaCl have been measured through the cation-exchange membrane in Na^+ form and through anion-exchange membranes in Cl^- form. 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. The effect of the porosity does not depend on the concentration of electrolyte, it only depends on the structure of the membrane, resulting both in their porosity and tortuosity [32]. 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 the elaborated membranes at various NaCl concentrations are listed in Table 4 and their decrease for a 1/100 dilution is reported as q value (in %). The larger the q value, the better the membrane. Elaborated PVA/PSSNa cation-exchange membrane showed a larger q value than anion-exchange membranes which can be explained by the efficiency of the electrolyte exclusion. PVA/PEVPBr membrane showed a larger q value (64.4%) than PVA/PVPCl (55.9%) because its density of charges is more important as previously showed. The sites of PEVPBr seemed to be more accessible with a homogeneous repartition. Moreover, the quaternary ammonium groups of PEVBr are stronger than the protonated tertiary amine groups of PVPCl which logically favoured a largest electrolyte exclusion. In this way PVA/PVPCl showed the poorest permselectivity (high co-ion leakage).

From these results, PVA/PEVPBr anion-exchange membrane was selected to be joined with the PVA/PSSNa cation-exchange membrane in order to elaborate the BM.

3.5. Elaboration and characterisation of the BMs

3.5.1. Junction

The different processes tested to join together the two ionic layers were not at all successful.

Dry films were torn during cold-rolling even at large air-gap. Previous moistening of the films by sprayed water did not allow a regular junction. No time stable gluing was obtained using a vapour spray.

The superimposition of a wet PVA/PEVPBr film on a wet PVA/PSSNa gave a regular bilayer but only on small area. Moreover, the BM obtained after gaseous DBE crosslinking had a poor stability in strong acid and basic solutions (4 mol l^{-1}).

Using a PVA solution (150 g l^{-1}) as glue allowed joining two layers but inducing a new crosslinking reaction. Gaseous DBE during 2 or 4 h allowed to crosslink only the edges of the BM. The membrane seems to become DBE-tight after the first treatment. An inefficient junction of the two MEIs was also obtained by the addition of a strong acid (HCl, H_2SO_4) to PVA glue to perform the proton catalysis. The acids were evaporated during the thermal treatment when they were used mole to mole with the hydroxyl groups of the PVA, or burnt the membrane they were used at higher concentration.

The best assembly of the two layers was obtained by using a PVA/PSSH glue solution. Various concentrations, ratios and technique were tested and the best result was obtained for PVA/PSSH 150 g l^{-1} in water, in the ratio 85/15 (w/w), rolled-out with a blade. After joining, the bilayer was pressed between two Plexiglas plates and dried

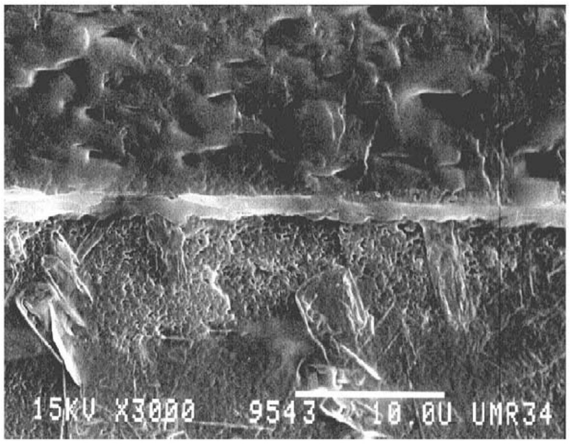

Fig. 7. SEM picture of the PVA/PSSNa//PVA/PEVPBr BM (× 3000).

during 1 h at room temperature. A stable BM was obtained after thermal treatment (80 °C during 1 h) for crosslinking catalysed by the protons present in PSSH (SEM picture given in Fig. 7). Longer crosslinking, time and higher temperature have cracked the junction. This technique was used to elaborate the BM studied afterwards.

3.5.2. Characterisation

The swelling ratio measurement of the elaborated BM has been performed to investigate the efficiency of the crosslinking reaction on the junction. The use of PVA/PSSH as glue followed by a thermal treatment allowed to obtain a BM with low swelling ($Sw = 0.43$ for a thickness $d = 241\ \mu m$). The ion-exchange capacity measurement in $NaNO_3$ electrolyte was carried out to verify simultaneously the influence of the association on the exchange properties of the two layers. A slight decrease of the ion-exchange capacities of the associated membranes in BM was observed ($IEC_{CEM} = 0.87$ mequiv. g^{-1}, $IEC_{AEM} = 0.85$ mequiv. g^{-1}). The chemical stability of the BM in strong acidic (HCl) and basic (NaOH) solutions was also checked in order to predict the behaviour of the junction during the water dissociation process. The junction of BM resisted until HCl and NaOH 4 mol l^{-1}.

To study the bipolar behaviour of the BMs, $I-V$ curves were recorded and compared to that obtained with commercial BM BP1 from Tokuyama-Soda (Fig. 8). The current density of BP1 was nil from 0 to about 0.5 V and increased linearly with a large slope above 0.8 V because water dissociation took place in the membrane (curve 1). The $I-V$ experiment was stopped before reaching the plateau corresponding to the diffusion limit. In the case of our BM, an ohmic behaviour was observed, indicating the absence of water splitting (curve 2). In order to increase the water dissociation rate in the BM, many authors agree that catalysts are required. Some of them advice to introduce tertiary amine groups in the junction or at the surface of the anion-exchange membrane in order to improve the water splitting [17,34]. In this way, we have dipped the PVA/PVPBr membrane in N,N-diethylmethylamine (98%) during 6 h before performing its assembly. This BM exhibited a bipolar behaviour (curve 3). Indeed, after the sharp increase of resistance due to salt ions departure from the junction, the current density increased linearly with a smaller slope than for BP1. Our BM showed lower efficiency than BP1 because of its higher electrical resistance. These results confirm that the presence of catalyst inside the BM is essential to allow the water dissociation and are encouraging because they show that a membrane with bipolar behaviour can be prepared by using the s-IPN technique.

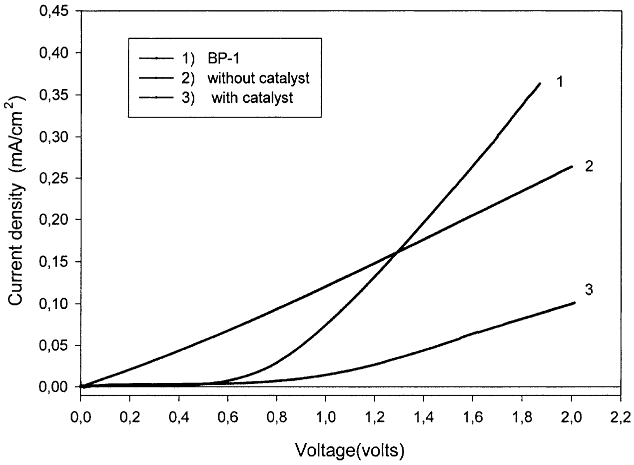

Fig. 8. $I-V$ curves of commercial BP1 (1), PVA/PSSNa/PVA/PEPBr BM without (2) and with (3) N,N-diethylmethylamine as catalyst.

4. Conclusion

Two cationic Pe were synthesised by polymerisation of 4-VP and chemical modification, and characterised in order to elaborate anion-exchange membranes. PSSNa commonly used in ion-exchange resins for its strong acidic character was selected for the elaboration of the cation-exchange membrane. The membranes were made by using the s-RPI technique. Each Pe was blended with PVA in the 40/60 mass ratio to prepare homogeneous films that were crosslinked afterwards by gaseous DBE. We did not observe, by microscopy, TGA and FTIR measurements, any noticeable damage in the membranes due to the crosslinking conditions. The efficiency of the crosslinking process was tested by comparison between the FTIR spectra of films and membranes, and swelling ratio and ion-exchange capacity measurements. Diffusion experiments were performed to evaluate the permeability of the elaborated membranes.

The PVA/PEVPBr membrane that presents the most interesting properties (swelling, ion-exchange capacity, electrolyte exclusion) was selected to be joined with PVA/PSSNa for the BM elaboration.

Various processes of junction were tested. The use of a glue solution PVA/PSSH (150 g l^{-1}) followed by a thermal treatment (1 h, 80 °C) gave suitable results. The bipolar behaviour of the elaborated BMs was checked by $I-V$ curves experiments. The introduction of tertiary amine groups in the anion-exchange membrane appeared interesting and improved water dissociation. Nevertheless, this membrane showed lower efficiency compared with the commercially available BP1 BM.

We are now investigating another way to assemble the layers by gluing and thermal pressing. The use of other catalysts such as chromium(III) cations will also be considered in future studies. The performances of the BMs in relevant industrial applications will be investigated as well.

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