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Preparation of ion-exchange membranes using pullulan as polymer matrix

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Abstract

The purpose of the present work is to apply the semi-Interpenetrating Polymer Network technique to the preparation of tailor-made membranes from pullulan/polyelectrolyte blends. Two types of polyelectrolyte (Pe) containing sulfonate (PSSNa) or carboxylic groups (PAA) were chosen. The 60/40 pullulan/Pe mass ratio was selected to prepare a homogenous film with suitable mechanical properties. Isocyanate and glutaraldehyde were tested as crosslinking agents to form the pullulan network in which the Pe is entrapped. The efficiency of the entrapment was monitored by swelling and ion-exchange measurements. The most efficient crosslinker was glutaraldehyde. Ion-diffusion experiments were performed on the pullulan/PAA membranes that had the most interesting properties.

Keywords: Pullulan; Polyelectrolyte; Ion-exchange membranes; Crosslinking

1. Introduction

There are many ways to obtain ion-exchange membranes. One interesting method is to prepare a semi-Interpenetrating Polymer Network (s-IPN) by mixing two polymers. After crosslinking by a reagent, one of the polymers forms a network in which the chains of the second are immobilised.

In our case, a polyelectrolyte (Pe) was immobilised in a polymer matrix crosslinked network. Poly(sodium styrenesulfonate) (PSSNa) and poly(acrylic acid) (PAA) were selected as the cation-exchange Pe. The exopolysaccharide pullulan, produced by a fungus-like yeast called *Aureobasidium pullulans*, was selected as the polymer matrix because it has good film-forming properties (Gontard, Thibault, Cuq, & Guilbert, 1996). In addition, pullulan is hydrophilic and has a high density of reactive chemical groups facilitating chemical crosslinking.

The purpose of the present work is to use the s-IPN process to prepare tailor-made ionic membranes. Isocyanatopropyltriethoxylane (SiNCO) and glutaraldehyde were tested as reagent to crosslink the pullulan matrix. The efficiency of the crosslinking reaction was monitored by the degree of swelling (*Sw*) and the ion-exchange capacities (IEC) of the membranes. Our objective was to prepare membranes with *Sw* close to 0.5 (or less) and IEC as high as possible. Electrolyte (NaCl) diffusion experiments were performed on the membranes that had the most useful properties.

2. Experimental

2.1. Polymers

Commercial pullulan (PI-20) from Hayashibara Biochemical Laboratories Inc. were used as the polymer matrix ($\bar{M}_w \approx 300,000$ g mol^{-1}).

PSSNa ($\bar{M}_w = 70,000$ g mol^{-1}) was provided by Scientific Polymer Products Inc. PAA ($\bar{M}_w = 450,000$ g mol^{-1}) was supplied by the Aldrich Co.

2.2. Reagents

SiNCO (Interchim) associated to dibutyltin laurate (DBTL)(Sigma Aldrich Co.), and aqueous solution of glutaraldehyde 25% (v/v)(Merck-Schuchardt) associated to magnesium chloride hexahydrate (Sigma Aldrich Co.), were tested as crosslinking reagents.

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2.3. Preparation of the membranes

For SiNCO crosslinking, 2 g of pullulan (12.3×10^{-3} mol of saccharide unit) were first dried (80 °C during 24 h) under vacuum. Then, 25 cm^3 of anhydrous dimethylsulfoxyde (<30 ppm H_2O) was added. After 6 h stirring at 60 °C under gaseous nitrogen, the mixture was cooled at 40 °C and 0.1 cm^3 of DBTL catalyst followed by 1 cm^3 of SiNCO were carefully introduced. The reaction was continued for 15 h. The crosslinking reaction started when 20 cm^3 of Pe (66.6 g L^{-1} in water) was added (Fig. 1a). The viscous solution obtained was casted on an appropriate plane support (glass, stainless steel, polypropylene (PP) or polyethylene (PE)) and placed in an oven at 80 °C in a high humidity atmosphere until complete hydrolysis (5 days).

For the glutaraldehyde crosslinking, pullulan and Pe solutions (10 g L^{-1} in water) were mixed in a fixed proportion with a trace of magnesium chloride (Okuno, & Uragami, 1992) and various amounts of glutaraldehyde were added (n_0, 5 n_0, 10 n_0, 10 n_0, 20 n_0, where $n_0=2.26\times10^{-3}$ mol is the number of maltotriose repeat units in pullulan). After casting in a polystyrene Petri box (diameter: 85 mm) and evaporation of the solvent, films were obtained with an average thickness about 70 μm. They were then annealed at 80 °C for 24 h in an oven in order to perform the crosslinking reaction (Fig. 1b).

2.4. Characterisation of the membranes

2.4.1. Swelling ratio

A strip of dry membrane (constant weight W_D) was immersed in water at 25 °C. After 24 h the sample was carefully wiped with filter paper and weighed. The operation was repeated until constant W_S was obtained. The swelling ratio S_w was calculated from:

$$S_w = (W_S - W_D)/W_D$$

2.4.2. Ion-exchange capacity

The membrane was first dried and weighed (W_D), then swollen in water. After that, the membrane was immersed sequentially for 4 h each in baths of NaOH (≈0.01 mol L^{-1}), water, and HCl (≈0.01 mol L^{-1}). This cycle was repeated. At the end of the second cycle, the membrane was washed with water, and placed in an NaOH ($n_1=0.01$ mol L^{-1})/NaCl (0.5 mol L^{-1}) titrated solution. After 4 h, the membrane was removed and the NaOH solution was titrated again (n_2). The IEC was calculated in meq g^{-1} from:

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

IEC is compared with the theoretical IEC, $\mathrm{IEC_{th}}$:

$$\mathrm{IEC_{th}} = (1000x)/M$$

where x is the Pe mass ratio, and M, the molecular weight of the Pe repeat unit.

2.4.3. Diffusion experiments

Electrolyte diffusion experiments were performed using the diffusion apparatus previously described (Da Silva, Lebrun, & Métayer, 2002). Various concentrations C_0 (mol L^{-1}) of NaCl were tested. The diffusion of the solute through the membrane in the Na^+ form was monitored by conductivity measurement. Experimental runs lasted about 10000 s.

During these experiments, the membrane reached a (pseudo) steady state of diffusion. In that case, a linear increase in the electrolyte concentration in the downstream chamber versus time t is observed and can be expressed by:

$$C(t) = (AD^*C^*/VL)[t - (L^2/6D^*)]$$

where A is the exposed membrane area (4.15 cm^2), D^* and C^* are the diffusion coefficient ($cm^2\,s^{-1}$) and the concentration of the solute inside the membrane

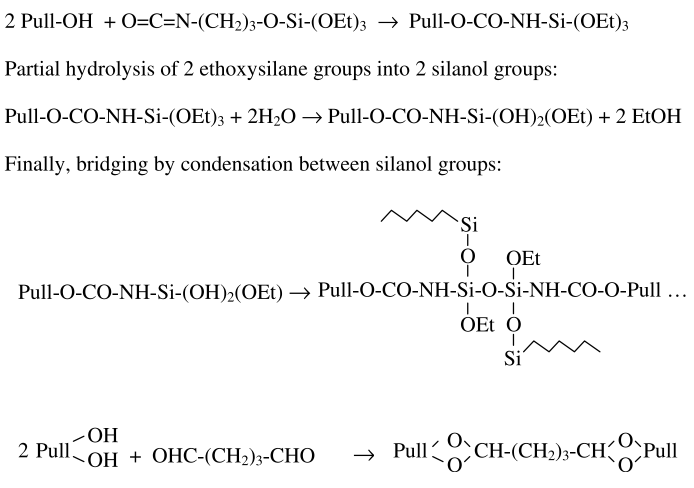

Fig. 1. Crosslinking pullulan with SiNCO (a) and glutaraldehyde (b).

(mol cm^{-3}), V is the chamber volume (120 cm^3), L (cm) is the membrane thickness.

The extrapolation of the linear portion of the curve $C(t)$ intercepts the time axis at the time-lag $t_l = L^{2/}6D^*$ when $C(t) = 0$. D^* was obtained from t_l. C^* was calculated from the slope $AD^*C^*/V\,L$.

The solute partition coefficient λ between the membrane and bulk solution was obtained from the concentration data using

$$\lambda = C^*/C_0$$

The permeability coefficient P (cm^2 s^{-1}) of NaCl in the membrane was obtained from:

$$P = \lambda D^*$$

3. Results and discussion

3.1. Preparation of membranes

3.1.1. Homogeneity and morphology

No phase separation was observed for the pullulan/Pe mixtures whatever their ratio. Pullulan/PSSNa films became slightly translucent at a PSSNa level above 40%. Pullu-lan/PAA films exhibited high clarity and transparency whatever the Pe ratio. We have chosen the 60/40 mass ratio to prepare our membranes because there is no great excess of one of the polymers at this ratio, which prevents a possible phase inversion during solvent evaporation. Moreover, the membranes contain an excess of the polymer matrix in order to improve the entrapment of the Pe after crosslinking. This process allowed high-quality films to be prepared.

3.1.2. Crosslinking

With SiNCO as a crosslinker, we observed that the plane support on which the polymer solution was cast had an effect on the final quality of the membrane. The membrane was impossible to peel off a glass or stainless steel support.

Pullulan/PSSNa membranes obtained on a PP support appeared homogeneous, but gave opaque films which swelled substantially in water ($S_w = 8.7$) and had a low IEC (IEC = 0.3 meq g^{-1}) (Table 1). They showed better properties, with a lower thickness and swelling and higher IEC when they were prepared on a PE support.

Pullulan/PAA membranes prepared on a PE support also showed characteristics meeting our objective ($S_w = 0.6$, IEC = 3.3 meq g^{-1}) (Table 1) but had an irregular thickness. The IEC value must be considered with care, because it depends on the ionic strength of the solutions, due to the presence of carboxylic groups in PAA. Moreover, these membranes show a poor resistance at high pH because the urethane functions resulting from the crosslinking are hydrolysed at pH > 12.

Table 1
Characterisation of elaborated membranes: SiNCO crosslinking

Membranes	Support	S_w	IEC (meq g^{-1})	Appearance
Pullulan/PSSNa	PP	8.7	0.3	Homogeneous hydrogel
	PE	0.4	1.5	Homogeneous, irregular thickness
Pullulan/PAA	PP	1.3	0.7	Homogeneous, not plane
	PE	0.6	3.3	Homogeneous, not plane

Reference capacities IEC$_{th}$ were calculated from Pe content (40%) before crosslinking and treatments: IEC$_{th\ PSSNa}$ = 1.9 meq g^{-1}, IEC$_{th\ PAA}$ = 5.5 meq g^{-1}.

Efficient crosslinking of the pullulan films was observed using an amount n_0 of glutaraldehyde ($S_w = 1.1$).

The Pullulan/PSSNa membranes were translucent whatever the glutaraldehyde concentrations. An increase in the Pe ratio showed that the aggregates consisted mainly in PSSNa. The crosslinking reaction between pullulan chains seems to induce more PSSNa exclusion and indicates partial miscibility of this blend. The characteristics of pullulan/PSSNa membranes were poor (Table 2) even for a high glutaraldehyde concentration (20 n_0). Moreover, the membranes showed a heterogeneous appearance with holes and folds. No noticeable further development of the membranes properties was observed for a thermal treatment at 80 °C longer than 24 h.

Pullulan/PAA membranes appeared glassy and light brown, homogeneous and transparent, which showed the compatibility between crosslinked pullulan and PAA. For low glutaraldehyde concentrations ($1n_0$, $5n_0$) the membranes showed low mechanical resistance. The membrane prepared

Table 2
Characterisation of the membranes crosslinked by glutaraldehyde (*crosslinking time:* 24 h-$T = 80$ °C) (IEC$_{th\ PSSNa}$ = 1.9 meq g^{-1}, IEC$_{thPAA}$ = 5.5 meq g^{-1})

Membranes	n_0	S_w	IEC (meq g^{-1})	Appearance
Pullulan/PSSNa	1	2.6	0.1	Translucent
	5	2.0	0.25	Folds on the surface, heterogeneous, brittle
	10	1.8	0.7	Folds, brittle, opaque and heterogeneous
	20	1.8	0.8	Folds, brittle, opaque and heterogeneous
Pullulan/PAA	1	2.4	0.6	Light brown, homogeneous
	5	0.82	2.2	Light brown, brittle and homogeneous
	10	0.61	3.0	Brown, glassy, flexible
	20	0.43	3.1	Irregular brown (marble), glassy, flexible

Table 3
Diffusion of NaCl at 25 °C through Pullulan/PAA membranes (pH = 5, Na^+ form) crosslinked by glutaraldehyde (10 and 20 n_0, respectively)

Membranes pullulan/PAA	C_0 (mol L^{-1})	t_l (*s*)	$D^* \times 10^{-7}$ ($cm^2\ s^{-1}$)	λ	$P \times 10^{-7}$ ($cm^2\ s^{-1}$)	$P/D_w \times 10^{-2}$
(10 n_0)	0.05	2450	0.18	1.04	0.19	0.128
	0.10	800	0.57	0.97	0.55	0.371
	0.50	105	4.32	0.63	2.72	1.838
	1.00	68	6.67	0.52	3.43	2.317
(20 n_0)	0.05	5050	0.05	0.95	0.04	0.027
	0.10	1500	0.16	0.93	0.15	0.060
	0.50	670	0.36	0.78	0.28	0.189
	1.00	65	3.69	0.68	2.51	1.696

Thickness of swollen membrane in NaCl: 10 n_0: 165 μm, 20 n_0: 120 μm. Diffusion coefficient of NaCl in aqueous solution $D_w = 1.48 \times 10^{-5}$ $cm^2\ s^{-1}$.

with 10 n_0 of glutaraldehyde was very swollen and impossible to handle and therefore should be prepared with higher Pull/Pe concentration (20 g L^{-1}) to be usable. The membrane prepared with 20 n_0 glutaraldehyde showed a higher rigidity and was easier to handle after swelling. The 10 n_0 and 20 n_0 membranes had a high IEC (IEC = 3.0 meq g^{-1} and IEC = 3.1 meq g^{-1}, respectively), and low S_w ($S_w = 0.61$, $S_w = 0.43$ respectively). For these reasons they appeared the most promising, however, these membranes showed poor low pH stability. The acetal function resulting from the crosslinking was hydrolysed after 5 days at pH < 3.8.

3.1.3. Diffusion of electrolyte

Studies were carried out on the glutaraldehyde-crosslinked pullulan/PAA membranes to measure their ability to control electrolyte diffusion. Permeability coefficients *P* were membranes conditional at pH 5.0 because weak acidic groups are involved.

A cation-exchange membrane selects the counterion (Na^+) and excludes the co-ion (Cl^-) (Helfferich, 1962). This phenomenon is more pronounced at a low electrolyte concentration and for a homogeneous density of the charges inside the membranes.

The 20 n_0 membrane as expected showed the longest t_l, and the lowest D^* and *P* coefficients, whatever the C_0 concentrations (Table 3), because its pullulan network is tighter (smallest swelling: $S_w = 0.43$) and its IEC is higher (IEC = 3.1 meq g^{-1}). For each membrane t_l, D^* and *P* coefficients depend on C_0. However, this concentration effect is too large: t_l is too small and the slope AD^*C^*/VL is too low particularly for the diluted C_0 concentrations, which have consequences on the *D* and the *P* values.

The calculation of the P/D_w ratio, between *P* and the diffusion coefficient D_w of NaCl in water ($D_w = 1.48 \times 10^{-5}$ $cm^2\ s^{-1}$) (Stokes, 1950), highlights the electrolyte exclusion. The 20 n_0 membrane showed electrolyte exclusion for larger NaCl concentration than the 10 n_0 membrane (Table 3). However, the partition coefficient λ is around 1 in the absence of attractive interaction (adsorption), or exclusion between the solute molecules and the pores of the membrane. In the case of our membranes, it is surprising to find a decreasing λ when C_0 increases, whereas electrolyte exclusion is more efficient at low electrolyte concentration.

The pullulan/PAA films became glassy and showed a hydrophobic surface when crosslinked with glutaraldehyde. Glutaraldehyde replaced the hydrophilic hydroxyl groups of the pullulan by $–O–CH–(CH_2)_3–CH–O–$ hydrophobic links. Thus, the thickness of the diffusion boundary layers on both sides of the membrane should be large in spite of a strong magnetic stirring. These Nernst layers strongly influence the diffusion phenomenon when their widths are larger than the thickness of the membrane, because they increase the overall resistance to the diffusion in the membrane.

4. Conclusion

These first results demonstrate that pullulan can be crosslinked to prepare cation-exchange membranes using the s-IPN technique. Glutaraldehyde was the most efficient crosslinker and appeared suitable for membranes containing PAA. The use of cationic polyelectrolytes will be considered in future studies.

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