Ionically Crosslinked Poly(acrylic Acid) Membranes.
II. Dry Technique

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Synopsis

The ionic crosslinking of poly(acrylic acid) for dialysis and reverse osmosis applications has been studied. A new dry technique has been developed that is faster than the wet technique reported in the previous paper to synthesize aluminum/poly(acrylic acid) membranes. It is based on casting a solution containing both the aluminum salt and the unneutralized poly(acrylic acid) (PAA) and subjecting the cast film to a heat treatment (curing step) to promote ionic crosslinking. Postcuring treatment in nonsolvents for PAA such as acetone induced structural modifications in the membrane. Membranes with optical clarity ranging from colorless and transparent to white and opaque were obtained and were characterized by their water and aluminum contents. Transport properties of these membranes were investigated and indicated a selective rejection of ionic solutes such as NaCl compared to organic solutes such as ethylene glycols. Typical results for reverse osmosis under static conditions at fluxes of 1250 g/hm^2 (0.75 U.S. gallons/ft^2-day) gave rejections of 85% for a feed of 0.1% (by wt.) NaCl at 600 psi. Much lower rejection (28%) for ethylene glycol suggests the possible use of these membranes in the fractionation of mixtures of ionic and nonionic solutes by reverse osmosis.

INTRODUCTION

In discussing work previously carried out in our laboratory with the wet technique for ionically crosslinking membranes, it was pointed out that the crosslinking process was a result of two other processes, namely, diffusion of the metal ion and chemical reaction.[1] In order to avoid any potential problems that diffusion of external reagents into the film may present, it was decided to eliminate the role of diffusion. This elimination may be accomplished by incorporating the metal ion into the casting solution. A thermal treatment of the cast membrane may then prove to be the instigator of the crosslinking reaction. It has been pointed out in our discussions of the wet technique that heat does increase the rate of the crosslinking, as expected.

The previously reported results indicate that acidic crosslinking solutions could suppress the ionization of the polyacid.[1] Thus, the use of undissociated poly(acrylic acid) (PAA) solution should serve as an effective retarder of the reaction in conjunction with an appropriate salt to prepare a relatively stable casting solution. Besides the possibility of curing a cast film, one would also have the potential to promote "phase inversion" without the limitations imposed by a slow diffusion and reaction of metal ions.

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EXPERIMENTAL

Materials

The sources of the materials, their quality, and the preparation of the polymers have been previously discussed, as have been the means of membrane characterization. In the present experiments only two of the metal ions, Al^{3+} and Cr^{3+}, were tested. These two metals were selected because of their relative inertness at room temperature, their trivalent charge, and because their soluble salts produce relatively acidic solutions in water.

Preliminary experiments with cast aqueous solutions of PAA and $Al(NO_3)_3 \cdot 9H_2O$ cured at 45 and 60°C showed a fast reaction characterized by extensive desolvation and bubble formation in the resulting film. Reduction of the volatility of the solvent should prolong the mobility of the reacting species allowing an appropriate conversion before extensive desolvation has occurred. This may be accomplished by the incorporation of a solvent with a low rate of evaporation into the aqueous PAA solution. Dimethylformamide (DMF) proved to be acceptable in this role. Preliminary experiments showed that solutions of the metal and polymer in water plus DMF had a shelflife of at least one week before any signs of gelation appeared.

A typical casting procedure was as follows: A solution of PAA in water and a solution of $Al(NO_3)_3 \cdot 9H_2O$ in DMF were prepared separately, the DMF solution being subsequently filtered. Predetermined weights of each solution were added to an Erlenmeyer flask, the PAA/water first and the Al/DMF slowly with agitation until a uniform, room-temperature solution was produced. Using a Gardner casting knife with a specified drawdown thickness (δ_w), a sample of the casting solution was cast on a glass plate. The plate and film were heated in the oven for various times and temperatures. The plate was then immersed overnight in an acetone bath at room temperature. Upon removal this film was removed from the plate and soaked in deionized water at room temperature for at least 24 hr, with frequent water changes.

Transport Properties

The dialysis system was similar to the one used by Jarvis, and a detailed description may be found elsewhere.[3] The effective membrane area was 31.1 cm^2, and P, the permeability coefficient, was calculated from the slope of the plot ln C_0/C versus time.

Water flux was determined with an Amicon ultrafiltration cell Model 52 at 70 psig and room temperature by collecting permeated liquid until steady state was achieved.

The reverse osmosis tests were conducted in a high-pressure Amicon cell Model 320. It is provided with a stainless steel suspended magnetic stirrer and has an internal volume of 400 ml, with an effective area of 39.2 cm^2. The membrane is supported by a porous stainless steel disc. A schematic representation of the experimental setup is shown in Figure 1. Samples of permeated solution or water were taken and weighed until steady state fluxes were observed. The concentrations were determined by differential refractometry.

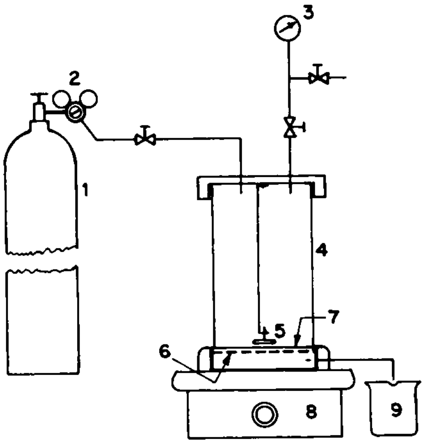

Fig. 1. Reverse osmosis apparatus: 1, nitrogen cylinder; 2, regulator; 3, manometer; 4, reverse osmosis cell; 5, stirrer bar; 6, porous support; 7, polymer film; 8, magnetic stirrer plate; 9, sample collector.

RESULTS AND DISCUSSION

Initial membrane synthesis was aimed at evaluating the effects of variables such as the molar ratio of metal to carboxyl, the crosslinking time and temperature, and postcuring treatments. Qualitative results for Al systems are summarized in Table I. The major conclusions were as follows: (i) A practical working formulation resulted from the casting solution with a molar ratio of 7:1 for AAc:Al, a polymer concentration of 13% by weight and approximately equal weights of H_2O and DMF. (ii) Postcuring treatment in acetone resulted in improved films. Acetone appeared to be a nonsolvent capable of modifying the membrane structure.

Chromium-based PAA membranes did not exhibit mechanical properties comparable to their Al counterparts, the films being brittle, with a tendency to curl. The remainder of the discussion deals only with Al-crosslinked membranes, their structure and properties, and the effect of a number of variables on these membranes.

TABLE I

Synthesis of Al/PAA Membranes by the "Dry" Technique

Casting Solution				
c_p,[a] wt. %	AAc:Al (molar)	DMF:H_2O (wt)	Curing conditions	Postcuring treatment and results
18.4	5.6:1	1.06:1	30 min at 80°C	wrinkled, clear films upon soaking in H_2O; films become more brittle with time when soaked in H_2O
16	5:1	1:1	30 hr at 40°C	
16	5:1	1:1	30 hr at 40°C	treated in acetone, peeled off, then soaked in H_2O; clear smooth film, but also more brittle after 48 hr
13.2	7:1	1:1.2	2 hr 30 at 60°C	acetone treated; clear, smooth film
16.4	11:1	1.2:1	1 hr 15 at 60°C	acetone treated; opaque, rubbery film
16.4	11:1	1.2:1	3 hr 20 at 80°C	acetone treated; weak rubbery, clear

[a] c_p is wt. % concentration of polymer.

Effect of pH

By equilibrating samples of films in solutions of varying pH, it was observed that the membrane retained its integrity best in weakly acidic solutions. A stable working range appeared to be pH 5 to 7. For weakly basic solutions (pH 8 to 9), strong swelling was observed; while at pH values below 3 and above 9, degradation occurred. The influence of pH is easily understood. For a fixed pH the swelling of the membrane is a result of two processes. First, the carboxylic group may be deprotonized, increasing the charge density along the chains and causing the carboxylic groups to repel each other. Secondly, Al is being hydrolyzed at the same time so that decrosslinking occurs. Because of these pH effects on the membrane, metal and water content were considered as practical and essential structural parameters to characterize the membranes.

Water Flux, Hydration, and Metal Content

In addition to water and metal content, pressure-induced water flux proved to be an important property to characterize the membranes since different morphologies would result in different fluxes.

The preparation and properties of a number of membranes are summarized in Table II. Generally, a membrane containing less Al is more hydrated, probably because of a smaller degree of crosslinking. When the water flux is examined as a function of these latter two parameters, it is seen that the flux increases with the hydration of the films. For homogeneous (clear) membranes it appears that this trend follows the correlation that hydration is inversely proportional to the Al content. Past a certain limit, however, an increase in metal content does not correspond to a less hydrated film. For example, as shown in Table

TABLE II
Preparation and Appearance of Al/PAA Membranes[a]

	Curing conditions			
Film code	Time, hr	*T*, °C	Treatment in acetone, hr	Appearance
901-2	2.66	60	0.58	C
901-3	3.5	60	2.0	C
901-4	3.5	60	none	C$^-$
828-4	6.0	60	3.0	C
828-5	5.5	60	12.0	C
918-7	none	—	12.0	T
916-3	0.38	55	12.0	W
918-4	0.42	60	8.0	C$^-$
914-5	0.50	60	20.0	C$^-$
914-7	0.17	60	5	C
902-8	2.0	60	1.5	C
902-7	3.5	60	12.0	C
902-6	0.75	60	1.5	T
916-1	0.25	55	12.0	T
918-6	0.66	60	8	C

[a] All casting solutions with an AAc:Al molar ratio of 7:1 and a 1:1 wt ratio for H_2O:DMF. 2) All membranes are clear after curing; C = clear colorless; W = white opaque; T = hazy translucent; C$^-$ = slightly cloudy.

III, films 828-4, 902-8, and 918-6 all appear to have a limiting water content of about 35% in spite of increased metal contents. On the other hand, water fluxes for the nonhomogeneous films were higher than for homogeneous films.

These observations suggest that the differences in water fluxes may, in fact, be related to the different morphologies, which dictate the type of transport mechanism. In the homogeneous swollen membranes, it is possible to consider, besides the diffusive component, a viscous (bulk) type of flow mechanism. The movement of water is retarded by the frictional resistance of the polymer chains. However, in the opaque (nonhomogeneous) films one could assume that pores or open cells have been formed and the water molecules would therefore move with less restriction. The intermediate film would obviously present a combined effect of these two mechanisms.

Characterization of the Al/PAA membranes produced by the dry technique seems to indicate therefore that the Al and water content will change in more than one way, depending on the morphology imposed by the preparation conditions. The dry technique is characterized by two distinct stages, the curing and the postcuring treatment. If the extent of the crosslinking reaction is advanced enough during the curing stage, then postcuring treatment will have little effect on the morphology, i.e., a clear homogeneous film results. Otherwise, a change of properties in the cured film may be achieved either by leaching the unreacted metal and/or inducing precipitation in acetone. This opacity can be obtained in cases of short curing times. For example, opacity is observed when the curing time is less than 1 hr at 60°C as well as in the case of film 914-6, which was not heat treated (Table III).

TABLE III
Analyses and Flux Rates of Al/PAA Membranes

Film code	δ_w, mils	Water,[b] wt. %	Al content,[c] wt. %	Water flux at 70 psi, g/hm^2
901-2	1.9	37	4.8	135
901-3	1.85	37.3	4.9	—
901-4	3.75	65	3.2	432
828-4	1.6	35.8	5.15	—
828-5	1.8	36.2	4.8	—
916-3	2.0	55	5.7	192
918-4	1.65	33	4.7	86.7
914-5	1.85	36.5	4.65	133
914-7	2.25	37.5	4.8	144.7
914-6	4.5	61	3.9	295
902-8	1.5	35.3	57.2	103.5
902-7	3	38	4.9	103.7
902-6	—	62	3.27	476
916-1	2.5	46	5.6	178
918-6	1.75	35.2	5.7	—

[a] Curing conditions and post treatment given in Table II; δ_w = drawdown thickness.
[b] g H_2O/g wet membrane.
[c] g Al/g dry membrane.

Permselectivity

A first evaluation of solute selectivity of the Al/PAA membrane was done by comparing the permeabilities measured under a concentration gradient such as in dialysis. The continuous flow system previously described was used with solutions containing 0.1% by weight of NaCl and a series of glycols to determine size effects. A permeability coefficient P was determined by means of eq. (1):

$$\ln \frac{C_0}{C} = \frac{PAt}{V} \tag{1}$$

where C_0 and C represent initial and final concentrations, t represents the time, and V represents the volume of the system. P is determined from the slope of the least-squares line of the plot ln C_0/C versus time. The data for a typical membrane are presented in Figure 2 and Table IV.

The results show a molecular weight cutoff of 200 for the organic molecules

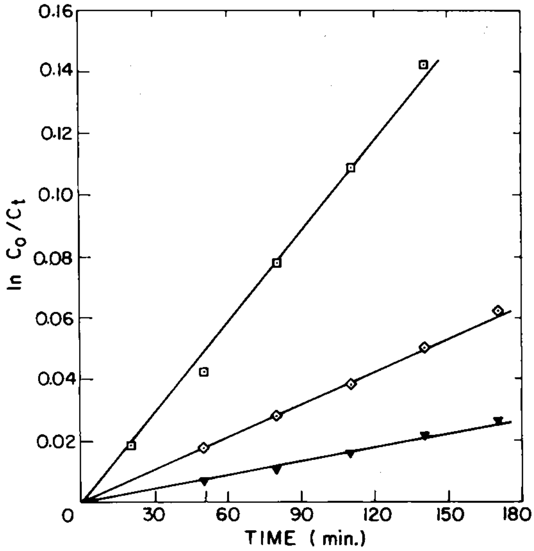

Fig. 2. Dialysis of Glycols through an Al/PAA membrane: (□) EG (ethylene glycol); (◇) di-EG (diethylene glycol); (▽) tri-EG (triethylene glycol); membrane, 901-3 (Tables II and III). Resulting permeability coefficients are given in Table IV.

TABLE IV
Dialysis Results at 37°C for Membrane 901-3[a]

Solute	MW	P, (cm/min) × 10^4 [b]
EG	62	58
Di-EG	106	21
Tri-EG	150.0	9.7
Tetra-EG	194.0	nil
NaCl	—	9.5

[a] Feed concentration: 1000 ppm; EG: ethylene glycol.
[b] From Fig. 2.

TABLE V
Reverse Osmosis Results

Membrane/class[a]	H_2O, wt. %	Al, wt. %	Feed	Applied pressure, psi	Solution flux, g/hm^2	R, %	Pure H_2O flux,[b] g/hm^2
918-6/C	35.2	5.7	0.1% NaCl	500	1250	87.6	—
901-2/C	37	4.8	0.1% NaCl	600	1161	84.7	—
916-3/W	55	5.7	0.1% NaCl	650	1270	85.1	1236†
916-3/W	55	5.7	0.1% NaCl	800	1578	88	1500†
916-3/W	55	5.7	0.5% NaCl	800	1255	67.5	—
916-3/W	55	5.7	0.5% NaCl	1000	—	—	1910†
902-8/C	35.3	5.7	0.1% NaCl	1000	1409	80	1050‡
902-8/C	35.3	5.7	0.1% EG	1000	1208	28.5	—
$\overline{W}$/C[c]	—	—	0.1% NaCl	1000	609	94	—

[a] Class legend at bottom of Table II.

[b] Water flux experiments done (‡) before (†) after the solutions runs.

[c] $\overline{W}$ = produced by the wet technique.[1]

TABLE VI
Comparison of Performance of Al/PAA Film with Commercial Ion Exchange Membranes[5]

Membrane[a]	Applied pressure, psi	Feed, % NaCl	Flux,[b] gfd	R, %
Nalfilm-1 (−)	1400	0.585	0.1	61
Permaplex C-10	1200	0.585	0.8	19
AMF (+)	1000	0.585	0.02	73
Nalfilm-2 (+)	1000	0.585	0.02	90
Al/PAA (916-3)	800	0.50	0.74	67.5

[a] Sign in parentheses is indicative of membrane's charge; Nalfilm-1 contains (SO_3^-) groups; Nalfilm-2, (NR_3^+) groups.[6]

[b] gfd = U.S. gallons/ft^2-day.

and a significant exclusion of an ionic solute such as NaCl, suggesting a definite influence of the carboxylic groups in the polymer matrix via Donnan exclusion.[4] Such an ionic exclusion should be particularly advantageous in a more efficient membrane separation process, such as reverse osmosis.

The reverse osmosis tests were conducted statically at room temperature with applied pressures varying from 300 to 1000 psi. The cell was provided with a suspended magnetic stirrer that helped to decrease (but probably not eliminate) any concentration buildup ("polarization") at the film surface. The solute rejection (R) was calculated by the definition

$$R = \frac{C_{\text{feed}} - C_{\text{product}}}{C_{\text{feed}}} \tag{2}$$

The use of large volumes of feed solutions compared to the permeated product ensured approximately constant concentration of feed (C_{feed}) during the experiments.

The results of the reverse osmosis tests are reported in Table V, along with some characteristic parameters for several membranes. It is worth noting some suggested trends. The observed selective exclusion of NaCl in dialysis is well confirmed in reverse osmosis, and relatively high rejections are obtained for dilute solutions. Also, increasing the applied pressure appears to increase both salt rejection and solution fluxes. The effect of increasing the concentration of the feed is to decrease both flux and rejection. Compared to the wet technique, membranes prepared by the dry technique appear to have at least 100% higher fluxes without substantially losing their rejection.

It should also be mentioned that the reverse osmosis results registered with the Al/PAA membranes indicate a better performance when compared with results for commercial ion exchange membranes, given in Table VI for comparison. However, cellulose acetate membranes are more efficient for rejecting NaCl with fluxes at least an order of magnitude higher than the Al/PAA films tested here. It is felt that evaluation of the Al/PAA membrane with a flowing system could probably show a higher rejection than those observed here because of reduced concentration polarization.

The relative exclusion of ionic species by the Al/PAA membrane suggests therefore an interesting application in cases where solutions containing a mixture of organic and electrolyte solutes must be treated to remove the latter. Reverse osmosis of these solutions with applied pressures as low as 500 psi can be used effectively.

CONCLUSIONS

It has been shown that the synthesis of ionically crosslinked poly(acrylic acid) membranes by a dry casting technique is a viable means of preparing dialysis and reverse osmosis membranes. Such films demonstrate high water flux while maintaining a high permeability. For dilute solutions of NaCl, separations up to 94% were observed. Typical flux for a 0.1% NaCl solution was 1250 g/hm^2 (0.75 gfd) at 600 psi with a separation of 85%.

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