

A Study of the Performance and Chemical Characteristics of Composite Reverse Osmosis Membranes Prepared by Plasma Polymerization of Allylamine

ALEXIS T. BELL, *Department of Chemical Engineering, University of California, Berkeley, California 94720*, and
THEODORE WYDEVEN and CATHERINE C. JOHNSON,
Biotechnology Division, NASA-Ames Research Center, Moffett Field, California 94035

Synopsis

A study has been carried out of the performance and chemical characteristics of composite reverse osmosis membranes prepared by plasma polymerization of allylamine in a radio-frequency electric discharge. It has been shown that membranes can be prepared which simultaneously exhibit a high rejection for sodium chloride and a high water flux. The primary factors influencing the quality of the membranes are the choice of substrate material, the deposition time, and the power supplied to the discharge. Variations in rejection and flux as a function of applied pressure indicate that water flows through the membrane by both diffusive and bulk flow. A reduction in rejection and an increase in flux are observed when membranes are operated for prolonged periods or at higher temperatures (up to 60°C). Elemental analysis of plasma-polymerized allylamine shows that it can be represented by the stoichiometry $C_3H_{2.8}N_{0.9}O_{0.1}$. Infrared spectra show evidence for N—H, C=N, C≡N, and C—H bond vibrations. ESCA spectra of the polymer surface show that the surface contains substantial amounts of both nitrogen and oxygen and that the nitrogen is present as either a nitrile or an imine group but not as an amine group. ESCA spectra of membranes used for reverse osmosis show that the surface loses nitrogen and gains oxygen with time and that this phenomenon is accelerated at higher operating temperatures. A decrease in rejection and an increase in flux accompanies these changes. It is postulated that most of the nitrogen in the polymer is present in the form of $RR'C=NH$ or $RR'C=NR''$ type structures. The loss of nitrogen and gain in oxygen observed in the ESCA spectra of membranes run at elevated temperatures is explained by the hydrolysis of the proposed structures.

INTRODUCTION

Recently, a novel and potentially promising method for preparing reverse osmosis membranes has been demonstrated¹⁻³ which involves the use of the plasma produced in an electric discharge to deposit a thin polymer layer on the surface of a porous substrate (e.g., glass, cellulose acetate-cellulose nitrate, polysulfone). Solute rejection is accomplished by the plasma-polymerized film. The advantages of this technique over conventional casting techniques are that the finished membrane can be prepared and stored in a dry state, the substrate

and film compositions can be selected independently, and the rejecting layer can be made very thin thereby producing membranes possessing high water fluxes. An additional advantage is that a large number of both conventional and unconventional monomers can be polymerized in a plasma.

In an extensive survey of candidate monomers, Yasuda and Lamaze² noted that in order to prepare membranes possessing a reasonable water throughput, the polymer in the rejecting layer should be moderately hydrophilic. It was observed, however, that many hydrophilic organic compounds react in a plasma in such a way that the hydrophilic groups in the monomer are not incorporated into the polymer. Thus, a hydrophobic polymer was often produced from a hydrophilic monomer. As a class, only nitrogen-containing compounds, particularly olefinic amines, heteroaromatic amines, and aromatic amines, were found to form polymer films having good reverse osmosis characteristics.

Using a polymerization apparatus different from Yasuda's, Hollahan and Wydeven³ demonstrated the feasibility of preparing composite membranes using MF Millipore filters as the substrate and allylamine as the monomer.

The purpose of the present work was to extend further the initial results reported by Hollahan and Wydeven.³ Specific objectives included an identification of the influence of preparation conditions on the reverse osmosis characteristics of the final membrane and an evaluation of membrane performance as a function of applied pressure, salt concentration in the feed, and feed temperature. A separate series of studies was undertaken to help define the physical and chemical structure of the plasma-polymerized film.

EXPERIMENTAL

The experimental apparatus used for this study is shown in Figure 1 and was essentially identical to that described previously by Hollahan and Wydeven.³ To permit a more accurate control of operating conditions, a Baratron MKS pressure gauge was used to measure gas pressure, and a Hastings-Raydist mass flowmeter was used to measure monomer flow rate.

Two types of membrane substrate were used. The first was MF Millipore filter material which had an average pore size of 0.025 μm and a water permeability of 400×10^{-5} g/(sec cm^2 atm). The second was a cellulose acetate-cellulose nitrate film manufactured by Gulf Environmental Systems.⁴ This material was similar to that manufactured by Millipore in that it was asymmetric and possessed a shiny side which contained pores whose average diameter was 0.025 μm . The three samples of film obtained from Gulf had water permeabilities of 430×10^{-5} , 270×10^{-5} , and 270×10^{-5} g/(sec cm^2 atm), respectively, and are referred to subsequently as Gulf-1, -2, and -3.

The monomer used throughout this work was allylamine (Eastman, bp 52.5 to 53.5°C). Prior to use, this material was purified by distillation and then degassed by repeated freezing and thawing while pumping on it.

To prepare a membrane, a 4-in. disk of substrate was punched out and sandwiched, together with a piece of filter paper to protect the substrate backside from being coated, between two steel rings to maintain the substrate flat. The bell jar was then put in place and evacuated to a base pressure of about 10^{-2} torr. At this point, the desired flows of argon and allylamine were introduced. Once a stable pressure was established inside the system, the discharge was initi-

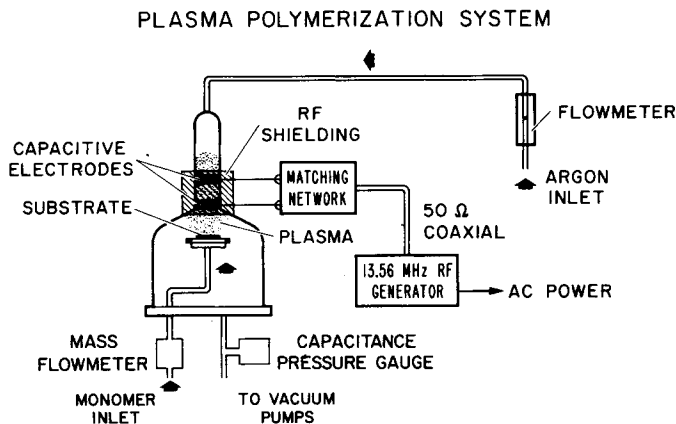


Fig. 1. Schematic of experimental apparatus.

ated by turning on the rf generator. All of the membranes were prepared at a total pressure of 0.25 torr using an argon flow rate of 6.5 S.T.P. cm^3/min and an allylamine flow rate of 16.1 S.T.P. cm^3/min . The discharge power was 40 watts, unless noted otherwise.

Testing of the composite membranes was carried out in a reverse osmosis test cell (Universal Water Corp.) connected to a high-pressure brine recirculation loop.⁵ For these tests, only the central 2 in. of the membrane were used in order to avoid the nonuniform regions present near the edge of the original 4-in. disk. Each membrane was allowed to operate for a minimum of 24 before the first samples of effluent were collected for a determination of rejection and flux. The techniques used for the measurement of rejection and flux were identical to those described in reference 5.

Chemical characterization of the plasma-polymerized films was obtained by elemental analysis, infrared spectroscopy, and ESCA (Electron Spectroscopy for Chemical Analysis). These three techniques were complimentary to each other—elemental analysis providing the overall polymer stoichiometry, infrared spectroscopy indicating the functional groups contained in the bulk of the polymer, and ESCA providing information on the structure and composition of the outermost layer ($<50 \text{ \AA}$) of the polymer. The samples used for infrared spectroscopy were prepared by polymer deposition on KBr windows using identical polymerization conditions to those used for the preparation of membranes. The infrared spectra were recorded on a Perkin-Elmer 521 spectrometer. Samples for ESCA were obtained by depositing polymer on aluminum foil or by using sections of actual membranes. ESCA spectra were recorded on a Varian IEE spectrometer.

RESULTS AND DISCUSSION

Reverse Osmosis Performance

Table I illustrates the effects of substrate type on the rejection, flux, and membrane constant. For a common deposition time, membranes prepared on the Gulf-1 substrate exhibited significantly higher fluxes and membrane constants than membranes prepared on the Millipore substrate. Furthermore,

TABLE I
Effects of Substrate on Rejection and Flux

Membrane	Substrate	Deposition time, sec	Rejection, ^a %	Flux, ^a gfd	Membrane constant,
					$\frac{\text{g}}{\text{sec cm}^2 \text{ atm}} \times 10^6$
279	Millipore-VS	900	92.8	3.09	0.41
280	Millipore	900	98.7	1.03	0.14
281	Millipore	900	97.4	1.69	0.24
282	Millipore	900	97.6	1.75	0.24
314	Gulf-1	900	98.7	4.19	0.59
315	Gulf-1	900	98.8	3.80	0.53
316	Gulf-1	900	97.1	5.19	0.72
403	Millipore	480	93.4	1.56	0.23
346	Gulf-1	480	98.4	7.10	1.01
404	Gulf-2	480	93.5	10.90	1.63
408	Gulf-2	480	98.1	16.30	2.34
409	Gulf-2	480	86.7	17.80	2.67
431	Gulf-3	480	88.1	12.10	1.76
432	Gulf-3	480	91.2	12.47	1.82
321	Gulf-1	240	98.8	4.94	0.67
344	Gulf-1	240	99.2	5.90	0.83
345	Gulf-1	240	99.1	8.40	1.19
351	Gulf-1	240	94.2	6.30	0.95
352	Gulf-1	240	97.9	8.90	1.23
375	Gulf-1	240	95.5	12.20	1.72
399	Gulf-2	240	73.8	23.10	3.32
400	Gulf-2	240	70.7	31.60	4.54
429	Gulf-3	240	72.1	30.97	4.64
430	Gulf-3	240	70.9	19.30	2.86

^a Feed concentration, 1% NaCl; feed temperature, 20°C; applied pressure, 600 psi.

membranes prepared on the Gulf-2 and Gulf-3 substrates exhibited similar performances, but the rejections were lower and the fluxes were higher than those for membranes prepared on the Gulf-1 substrate. While no explanation is available at this time for the differences in performance of membranes prepared on Millipore and Gulf substrates, the variations in the performance of membranes prepared on different batches of the Gulf substrate can be explained on the basis of uniformity of pore size distribution. The presence of a substantial number of pores of diameter larger than the mean would contribute to producing a membrane exhibiting low rejection and high flux. This point is discussed further below.

The membrane constants appearing in Table I are all considerably smaller than those for the substrates. As a result, we can conclude that the major resistance to water flow resides in the plasma-polymerized film, which is also responsible for salt rejection. A comparison of the membrane constants observed here with those reported by Riley et al.⁴ for composite membranes prepared on Gulf substrates by conventional techniques shows that the membranes prepared by plasma polymerization have comparable membrane constants.

The length of deposition of the plasma-polymerized layer was found to have a significant effect on both the rejection and flux exhibited by the membrane. This is clearly demonstrated in Figure 2, which shows the performance of mem-

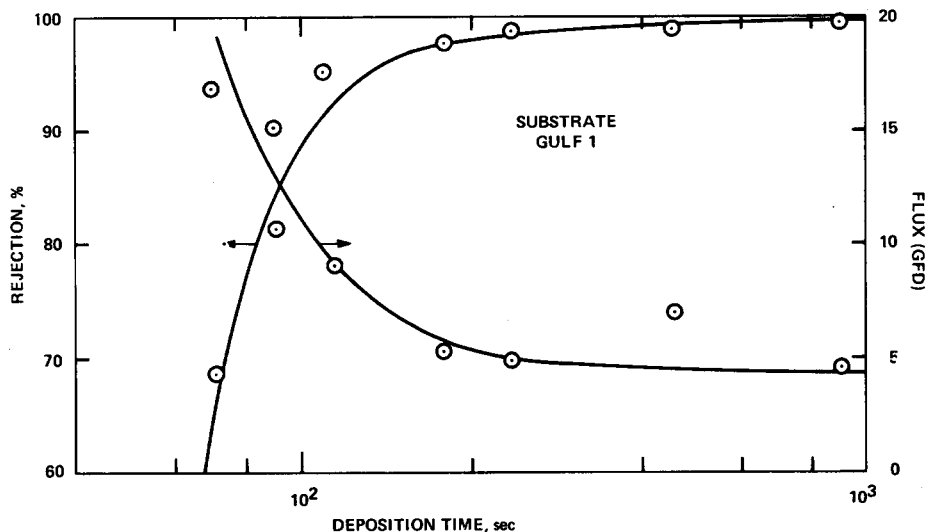


Fig. 2. Effect of deposition time on flux and rejection for a Gulf-1 substrate.

branes prepared on the Gulf-1 substrate. For deposition times of less than 120 sec, the rejection and flux show a rapid decrease and increase, respectively. At high deposition times, the rejection asymptotically approaches 100% while the flux approaches 4 gfd (gal/ft² day). The observed pattern can be explained by proposing that with increased deposition time, the pores in the surface of the substrate are gradually covered over by the deposited film. This interpretation is supported by the observation that the rate of polymer deposition is about 150 Å/min as measured by deposition on an aluminum foil substrate. Thus, in 2 min (120 sec), enough polymer is deposited to just bridge the 250 Å pores in the substrate. Somewhat longer times are necessary to assure that the larger pores are also covered over.

To further examine the significance of pore closure on reverse osmosis performance, a series of membranes were prepared on a Millipore substrate containing 0.1- μ m pores. The flux and rejection characteristics of these membranes are shown in Figure 3 as a function of deposition time. Here again, the rejection of sodium chloride increases rapidly, becoming substantial only for deposition times of greater than 900 sec. Scanning electron micrographs of the surfaces of membranes not subjected to reverse osmosis are shown in Figure 4. From Figure 4, it can readily be seen that with increased deposition time, the pores in the substrate are gradually filled in until at 900 sec only the largest pores are barely visible. From these observations, it can be concluded that in order to obtain membranes exhibiting high rejection, the microporous structure of the substrate must be completely covered over by the plasma deposited polymer. The latter should be as thin as possible in order to assure high water flux.

By depositing polymer on aluminum foil discs, it was established that the deposition rates were 1.75, 3.47, and 5.47 μ g/(sec cm²) for powers of 20, 40, and 80 watts, respectively. To determine how the rate of polymer deposition might affect membrane performance, membranes were prepared using 80 and 20 watts for comparison with those prepared using 40 watts. Based on these data, the deposition time for each power was determined to produce a fixed mass of

TABLE II
Effects of Power and Deposition Time on Rejection and Flux

Membrane	Substrate	Power, W	Deposition time, sec	Rejection, ^a %	Flux, ^a gfd
350	Gulf-1	80	154	87.3	7.3
369	Gulf-1	80	155	89.5	8.4
385	Gulf-2	80	159	81.9	9.31
387	Gulf-2	80	155	77.9	7.4
344	Gulf-1	40	240	99.2	5.90
351	Gulf-1	40	240	94.2	6.30
399	Gulf-2	40	240	73.8	23.10
400	Gulf-2	40	240	70.7	31.60
367	Gulf-1	20	490	73.0	51.2
368	Gulf-1	20	490	66.3	47.8
382	Gulf-2	20	490	58.9	39.6
384	Gulf-2	20	490	69.3	34.6

^a Feed concentration, 1% NaCl; feed temperature, 20°C; applied pressure, 600 psi.

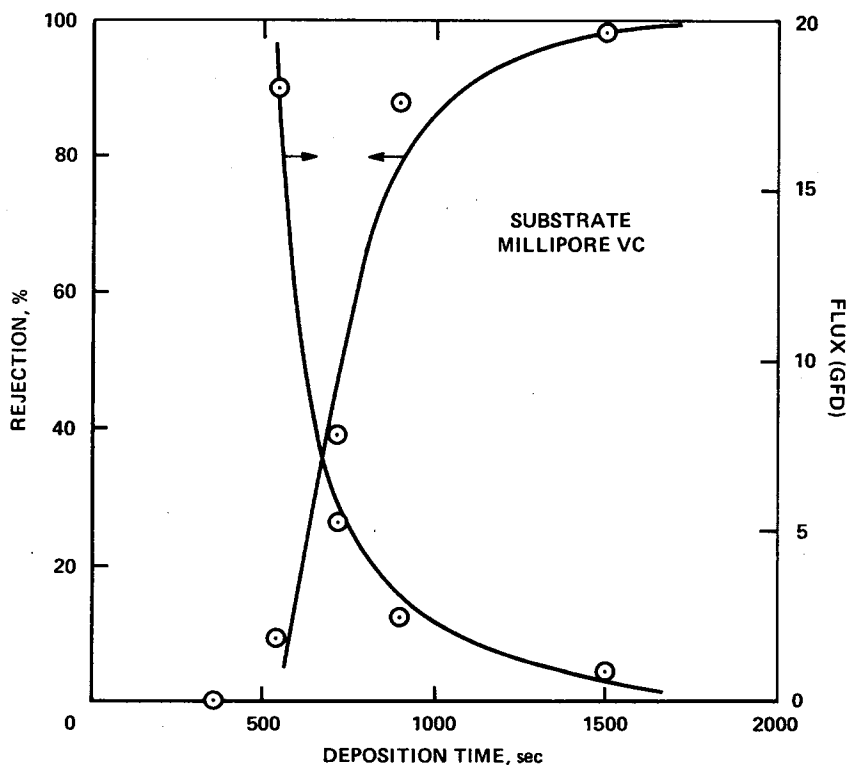


Fig. 3. Effects of deposition time on flux and rejection for a Millipore VC substrate.

polymer independent of the power level selected. All other polymerization conditions were set identical to those noted earlier. The results, presented in Table II, show that for membranes prepared on the Gulf-1 substrate, a sharp increase in rejection occurs when the power is raised from 20 to 40 watts. A slight decline in rejection is observed, though, when the power is raised to 80

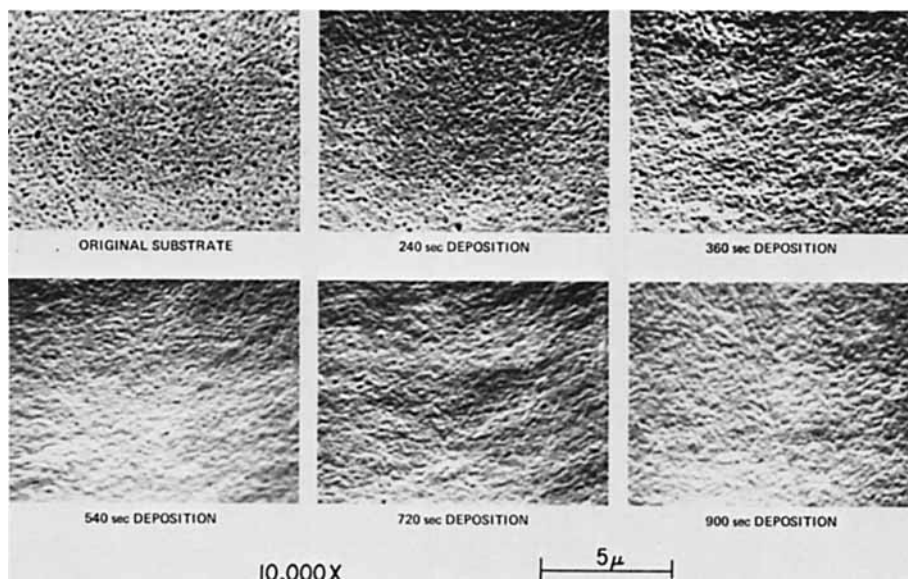


Fig. 4. SEM photographs of membranes deposited on a Millipore VC substrate as a function of deposition time.

watts. For membranes deposited on the Gulf-2 substrate, there is a monotonic increase in rejection with increasing power.

The results presented in Table II can be interpreted as follows. At low powers, the rate of polymer deposition is slow and the substrate must be exposed to the plasma for a relatively long duration in order to build up a desired mass of polymer. During this period, the substrate is exposed to bombardment by energetic particles present in the plasma and to ultraviolet irradiation produced by the plasma. Both of these sources of energy will cause a gradual degradation of the cellulose acetate-cellulose nitrate substrate, as has been noted by Yasuda and Lamaze.² In particular, it is anticipated that the very fine pores present in the topmost $1\ \mu$ of the substrate will be enlarged with prolonged exposure to the plasma. By increasing the power which accelerates the rate of polymer deposition, the substrate is exposed to the effects of the plasma for a shorter time, and hence one would anticipate a smaller degree of pore enlargement. A drawback of very high polymerization rates, however, is the observation⁶ that the polymer tends to be oily and more soluble, indicating that it is less highly crosslinked. This tendency to form a weaker polymer structure at high polymer deposition rates might account for the observed decrease in rejection for the membranes prepared at 80 watts on the Gulf-1 substrate.

With an aim toward identifying the mechanism of salt rejection, the performance of several membranes was studied as a function of the applied pressure Δp . The results for membranes 409 and 432 are shown in Figure 5. The abscissa in this figure is $(\Delta p - \Delta\pi)$, the difference between the applied pressure and the net osmotic pressure between feed and effluent. As the applied pressure is increased, the flux of water increases linearly. The rejection, however, increases and approaches an asymptotic limit as the pressure is increased.

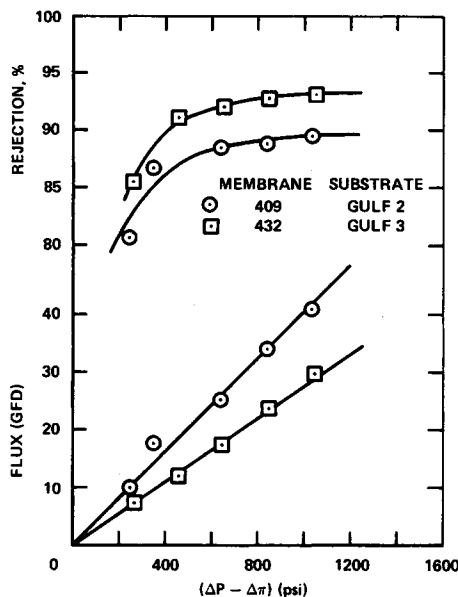


Fig. 5. Effects of applied pressure on flux and rejection.

The approach to an asymptotic rejection, less than 100%, seen in Figure 5 is characteristic of water-swollen membranes. For such membranes, water flow occurs as a result of both molecular diffusion and bulk flow, depending on the water content or degree of swelling of the membrane. Yasuda and Lamaze⁷ have shown that the salt rejection of a water-swollen membrane can be expressed as

$$R_s = \{ \omega + [P_2RT/P_1v_1(\Delta p - \Delta\pi)] \}^{-1} \quad (1)$$

where R_s is the salt rejection, P_1 is the diffusive permeability of water, P_2 is the diffusive permeability of salt, and v_1 is the molar volume of water. The parameter ω in eq. (1) is defined by

$$\omega = K_1 RT/P_1v_1 \quad (2)$$

where K_1 is the hydraulic permeability. For this model, the total water flux is given by

$$J_1 = K_1(\Delta p - \Delta\pi)/\Delta X \quad (3)$$

in which ΔX is the thickness of either the membrane (for a homogeneous membrane) or the rejecting layer (for a composite membrane). Therefore, eq. (3) defines the meaning of K_1 in this context. From eq. (1) it is seen that as $(\Delta p - \Delta\pi)$ approaches infinity, R_s approaches ω^{-1} . If water flow through the membrane occurs only by diffusion, $\omega = 1$ and R_s has a limiting value of 1. When water flow occurs by both diffusive and bulk transport, $\omega > 1$ and R_s has a limiting value of less than 1.

If a membrane obeys eq. (1), a plot of $1/R_s$ versus $(\Delta p - \Delta\pi)^{-1}$ should produce a straight line, with an intercept of ω and a slope of (P_2RT/P_1v_1) . Figure 6 illustrates such a plot for membranes 409 and 432. As may be seen, the points fall on a straight line, with the exception of the last point which corresponds to

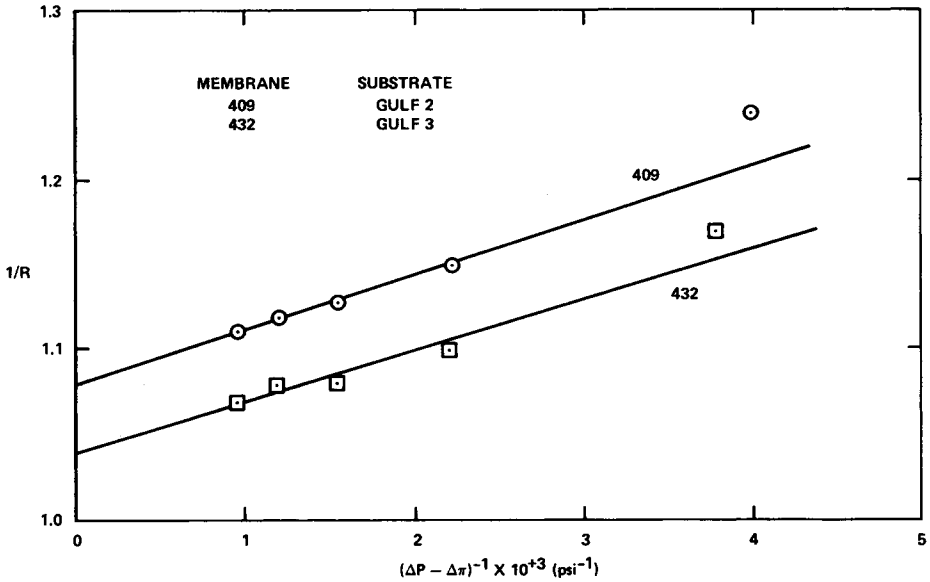


Fig. 6. Plot of $1/R_s$ vs. $1/(\Delta p - \Delta \pi)$.

an applied pressure of 400 psi. The deviation of the 400 psi points can be explained in terms of the sequence by which the data were obtained. Each membrane was operated first at 600 psi for 24 hr to obtain a steady state check of performance. The pressure was then raised to 800, 1000, and 1200 psi, the membrane being held at each pressure for 2 hr. Finally, the pressure was reduced to 400 psi and held there for another 2 hr. It is believed that cycling through the higher pressures first caused the membrane to undergo some degradation in performance (i.e., a decrease in rejection accompanied by an increase in flux). Evidence supporting this idea was obtained from other membranes which had been cycled through a period of high-pressure operation. Such an interpretation would explain the lower than anticipated rejection when membranes 409 and 432 were run at 400 psi.

The results shown in Figure 6 indicate that for pressures above 600 psi, the membranes produced in this study do obey eq. (1). By extrapolating the lines shown in Figure 6 to $(\Delta p - \Delta \pi)$ approaching infinity, it is determined that ω equals 1.08 and 1.04 for membranes 409 and 432, respectively. Since these values of ω are close to unity, it suggests that most of the water flow through the membrane is by diffusion and that a lesser part is due to bulk flow. We note further that the slopes of the lines appearing in Figure 6 are essentially identical, suggesting that the ratios P_2/P_1 are nearly the same for the two membranes.

A comparison of membrane performance for 1% and 3.5% salt solutions is shown in Table III. For the latter case, an applied pressure of 1500 psi was used. As may be seen, the rejection for a 3.5% solution is comparable to that for a 1% solution, but the water flux is higher for the more concentrated solution due to the higher applied pressure. The observed behavior of salt rejection is surprising since it was expected that use of a 3.5% solution and an applied pressure of 1500 psi which contribute to a larger value of $(\Delta p - \Delta \pi)$ would have

TABLE III
Comparison of Rejection and Flux for 1% and 3.5% Salt Solutions

Membrane	Substrate	Feed concentration, %	Applied pressure, psi	Rejection, ^a %	Flux, ^a gfd
351	Gulf-1	1.0	600	94.2	4.69
351	Gulf-1	3.5	1500	92.0	18.03
352	Gulf-1	1.0	600	93.3	6.77
352	Gulf-1	3.5	1500	92.2	16.78
356	Gulf-1	3.5	1500	80.3	26.17
357	Gulf-1	3.5	1500	91.8	15.04

^a Feed temperature, 20°C.

TABLE IV
Dependence of Rejection and Flux on Test Duration

Membrane	Rejection, ^a %	Flux, ^a gfd	Test duration, days
431	87.4	13.60	1
	86.6	13.49	1.25
	81.6	17.20	3
	80.7	17.92	4
432	89.0	13.95	1
	88.2	14.45	1.25
	83.0	17.99	3
	81.8	18.88	4

^a Feed concentration, 1% NaCl; feed temperature, 20°C; applied pressure, 600 psi.

brought about an increase in rejection over that observed for a 1% solution and an applied pressure of 600 psi. These results suggest that the rejection may be influenced independently by salt concentration.

Only a limited number of tests of membrane performance as a function of time were performed. The data shown in Table IV are representative of these tests. It should be noted that membranes 431 and 432 were prepared on the same day, one after the other, using substrate disks which were punched from adjacent portions of the substrate sheet. Both membranes were then tested simultaneously. The principle observations were a gradual decrease in rejection and a gradual increase in flux as a function of time with both membranes exhibiting essentially identical behavior. These results suggest that the rejecting layer is slowly degraded to yield a more porous structure capable of passing more of the feed solution by bulk flow.

The effect of feed temperature on membrane performance is illustrated in Figure 7. The data points shown were taken after 24 hr of operation at each temperature. As shown, salt rejection decreases very rapidly and water flux increases rapidly as the temperature is increased. Once heated, the membrane performance is degraded irreversibly. Thus when membrane 431 was cooled to 18°C after being cycled through higher temperatures, it exhibited a rejection and flux of 39.4% and 17.3 gfd, respectively. These values are to be compared with a rejection of 80.7% and a flux of 17.9 gfd when the membrane was first run at 18°C. The data shown in Figure 7 suggest that the plasma-

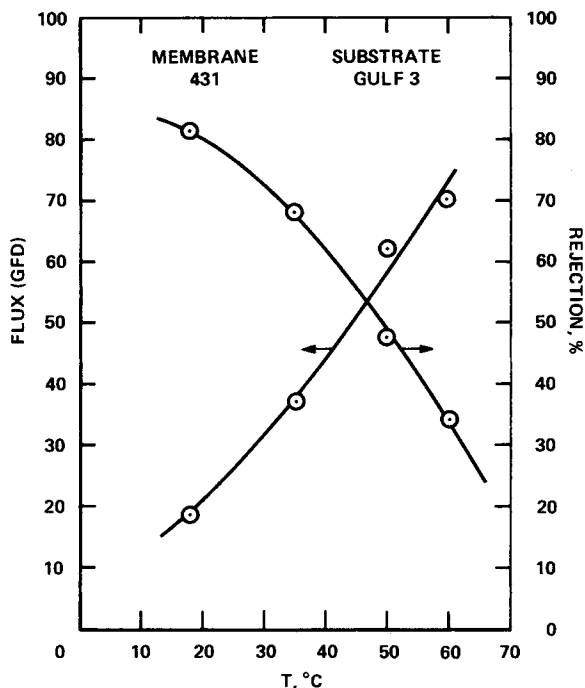


Fig. 7. Effects of temperature on flux and rejection.

polymerized film is degraded at higher temperatures so that imperfections develop in it which allow the passage of feed solution by bulk flow. This pattern is similar to that observed with time at a constant temperature.

Chemical Characterization of Plasma-Polymerized Allylamine

Elemental analyses of plasma-polymerized films deposited on aluminum foil showed that the polymer can be represented by the stoichiometry $C_3H_{3.8}N_{0.9}O_{0.1}$. Comparison of the polymer stoichiometry to that of allylamine, C_3H_7N , reveals that the polymer contains less hydrogen than the monomer, about the same amount of nitrogen, and a small amount of oxygen. The loss of hydrogen during the plasma polymerization of allylamine is similar to that observed when hydrocarbon monomers are used^{6,8} and is due to the collision of energetic electrons with the monomer as well as hydrogen abstraction by atomic hydrogen present in the plasma. The almost complete retention of nitrogen suggests that the amine group of the monomer is rapidly converted into a structure which strengthens the bonding between nitrogen and the hydrocarbon portion of the monomer. The presence of oxygen in the polymer is most likely due to a reaction between atmospheric oxygen and polymer-free radicals immediately after withdrawal of the film from the reactor. This process has also been observed to occur with films prepared from hydrocarbons and other monomers.⁹

An infrared spectrum for plasma-polymerized allylamine deposited on a KBr window is shown in Figure 8. For comparison, spectra are also shown for polymers prepared from propylamine and acrylonitrile. The conditions used to prepare these films and the deposition rates are tabulated in Table V. The

TABLE V
Operating Conditions Used in the Preparation of Samples for IR Spectroscopy and ESCA

Monomer	Partial pressure, torr		Power, W	Polymerization rate, ^a
	Monomer	Argon		$\frac{\mu\text{g}}{\text{cm}^2 \text{ min}}$
Propylamine	0.03	0.26	40	0.92
Allylamine	0.03	0.26	40	3.47
Acrylonitrile	0.03	0.26	40	26.96

^a Determined by deposition on aluminum foil.

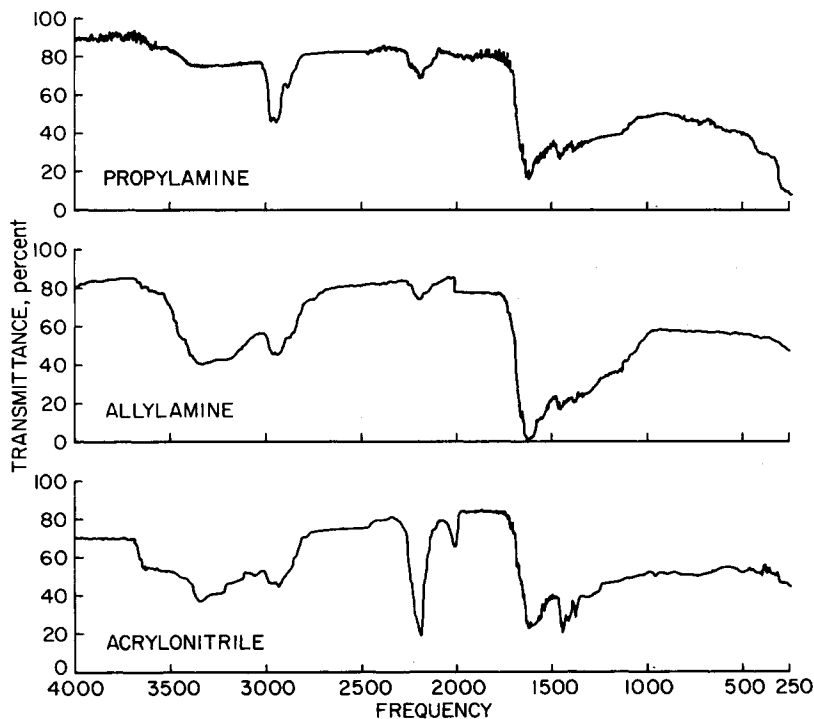


Fig. 8. Infrared spectra for plasma-polymerized propylamine, allylamine, and acrylonitrile deposited on KBr.

position of the major spectral features and their assignment to specific groups is shown in Table VI.

The spectra shown in Figure 8 are very similar, which suggests that the polymers obtained from propylamine, allylamine, and acrylonitrile contain similar types of structures. Of principal interest for determining the means by which plasma-polymerized materials act to effect reverse osmosis is the identification of the form in which nitrogen is contained in the polymer. The assignments given in Table VI show that three bands are related to nitrogen containing species. These occur at 3340, 2200, and 1620 cm^{-1} . The first of these bands corresponds to the vibration of N—H bonds. Due to the width of the band near 3340 cm^{-1} , it is not possible to determine conclusively whether the N—H bond is part of an amine or an imine group. It is also noted that the intensity of this band is greatest for the polymers derived from allylamine and acrylonitrile.

TABLE VI
Infrared Frequencies and Band Assignments

Frequency, cm^{-1}	Band assignments ^a
3340	$\nu(\text{N-H})3500\text{--}3300 \text{ cm}^{-1}$
2960	$\nu(\text{CH}_3)2962 \pm 10 \text{ cm}^{-1}$
2930	$\nu(\text{CH}_2)2926 \pm 10 \text{ cm}^{-1}$
2870	$\nu(\text{CH}_3)2872 \pm 10 \text{ cm}^{-1}$
2840	$\nu(\text{CH}_2)2853 \pm 10 \text{ cm}^{-1}$
2200	$\nu(\text{C}\equiv\text{N})2260 - 2240 \text{ cm}^{-1}$
2020	$\nu(\text{C}\equiv\text{C})2260 - 2100 \text{ cm}^{-1}$
1620	$\nu(\text{C}=\text{N})1690\text{--}1640 \text{ cm}^{-1}$
	$\delta(\text{N-H})1650 - 1590 \text{ cm}^{-1}$
1440	$\delta(\text{CH}_3)1450 \pm 20 \text{ cm}^{-1}$
	$\delta(\text{CH}_2)1465 \pm 20 \text{ cm}^{-1}$
1380	$\delta(\text{CH}_3)1380\text{--}1370 \text{ cm}^{-1}$

^a See reference 10.

The band at 2200 cm^{-1} is clearly identified as a nitrile group and is most intense in the spectrum of plasma-polymerized acrylonitrile. Finally, the band at 1620 cm^{-1} is very broad and intense in the spectra of all three polymers. One possible assignment for this band is to the bending vibrations produced by $-\text{NH}_2$ groups. A second possibility is that the band is due to the vibrations of a $\text{C}=\text{N}$ bond occurring in structures similar to those found in aldimines, $\text{RCH}=\text{NR}'$, and ketimines, $\text{RR}'\text{C}=\text{NH}$ or $\text{RR}'\text{C}=\text{NR}''$. Each of these structures exhibits a band in the vicinity of 1690 cm^{-1} ,¹¹ which in the presence of conjugation is shifted downscale to frequencies as low as 1600 cm^{-1} .

The remaining bands seen in the spectra of Figure 8 are due principally to the stretching and bending vibrations of CH_3 and CH_2 groups. A band at 2020 cm^{-1} seen only in the spectrum of plasma-polymerized acrylonitrile is assigned to the vibrations of $\text{C}\equiv\text{C}$ bonds. Interestingly, there are no bands observed near 1720 cm^{-1} which would indicate the presence of $\text{C}=\text{O}$ groups. The absence of such bands is probably due to the low oxygen content of the bulk polymers.

Binding energies of $1s$ electrons in C, N, and O obtained from ESCA spectra are shown in Table VII. Ratios of nitrogen to carbon and oxygen to carbon are also indicated. These were determined by ratioing the area of the band for each element multiplied by the relative atomic sensitivity of the element.¹²

To compare the measured binding energy for each element with those observed for the same element contained in compounds of known structure, it is necessary to correct the measured values for charging of the samples and shifts in the energy scale due to instrumental factors. These adjustments are frequently done by using an internal standard such as gold. Since such a procedure was not used in the present instance, the adjustment was made by shifting the position of all of the peaks of a given sample so that the C ($1s$) peak of lowest energy was fixed at 284.6 eV , the absolute binding energy for C ($1s$) electrons observed in polyethylene.¹³ This approach was adopted because the smallest binding energies of C ($1s$) electrons for the plasma-polymerized polymers as well as conventional polyethylene did not differ significantly from 284.6 eV . A second reason for choosing 284.6 eV as a reference point was that it corresponded to the binding energy of $1s$ electrons in carbon bonded only to carbon and

TABLE VII
Binding Energies and Elemental Ratios Obtained from ESCA Spectra

Polymer ^a	Sample	Substrate	Binding energy, eV			Elemental ratio		Comments
			C(1s)	N(1s)	O(1s)	Binding energy shift, eV	N/C	
PE	—	—	284.6	—	532.3	0	0.11	
PPPA	Aluminum	Aluminum	284.6	399.1	531.9	0.40	0.48	
PPAA	Aluminum	Aluminum	284.6	398.9	531.7	0.59	1.14	
PPAN	Aluminum	Aluminum	284.6	398.8	531.9	0.67	0.37	
—	Gulf-3	Gulf-3	284.6	403.7	533.5	0.49	1.98	
—	Gulf-3	Gulf-3	287.4	—	—	—	—	
PPAA	Gulf-3	Gulf-3	284.6	399.1	531.9	0.48	1.36	membrane 449—not used for R.O.
PPAA	Gulf-3	Gulf-3	284.6	399.1	532.1	0.36	1.00	membrane 450—not used for R.O.
PPAA	Gulf-3	Gulf-3	284.6	399.1	531.9	0.35	0.93	membrane 461—used for R.O. at 20°C; $R_s = 82.6\%$; $F = 5.41$ gfd
PPAA	Gulf-3	Gulf-3	284.6	399.2	531.7	0.28	2.20	membrane 460—used for R.O. at 60°C; $R_s = 64.9\%$; $F = 40.58$ gfd
PPAA	Gulf-3 ^b	Gulf-3 ^b	285.8	—	532.7	0	3.73	membrane 431—used for R.O. at temperatures between 20°C and 60°C; See Fig. 7 for rejection and flux
PPAA	Gulf-3	Gulf-3	284.6	—	532.7	0	6.64	membrane 432—used for R.O. at temperatures between 20°C and 60°C; Rejection and flux similar to membrane 431
—	—	—	286.0	—	—	—	—	
—	—	—	286.7	—	—	—	—	
—	—	—	289.1	—	—	—	—	

^a PE = polyethylene, PPPA = plasma-polymerized propylamine, PPAA = plasma-polymerized allylamine, PPAN = plasma-polymerized acrylonitrile.

^b Since no C(1s) peak was observed near 284.6 eV, this spectrum was adjusted relative to the O(1s) peak at 532.7 eV.

hydrogen atoms, a structure which was known to be present in the plasma-polymerized materials. The magnitude of the adjustment for each sample is indicated in Table VII.

A comparison of the ESCA results for plasma-polymerized propylamine, allylamine, and acrylonitrile show that all three polymers contain substantial amounts of nitrogen and oxygen. The content of nitrogen in the polymer follows a definite trend indicating that plasma-polymerized acrylonitrile contains the greatest amount of nitrogen and propylamine the least. The content of oxygen does not follow a similar systematic trend.

Comparison of the N/C and O/C ratios for plasma-polymerized allylamine obtained by ESCA with those obtained by elemental analysis suggests that the surface contains roughly twice as much nitrogen and thirty times as much oxygen as the bulk. While these ratios may not be exactly correct due to the inaccuracies of the elemental sensitivities used for reducing the ESCA results, there is positive indication that the surface layers of the polymer contain considerably more oxygen than the bulk.

The binding energy for N (1s) electrons in all three samples is very close to 399 eV. Comparison of this value with that for nitrogen containing compounds of known structure¹⁴ suggests that the nitrogen present near the polymer surface is in the form of a nitrile group. The presence of surface amine groups is ruled out since the binding energy for amines is closer to 398 eV. The possibility that the surface contains imine-type nitrogens can not be ruled out, however, since there are no known ESCA spectra of imines. The position of an imine N (1s) peak is expected to lie intermediate between that for amines and nitriles based upon the expected charge on the nitrogen atom.

The form in which oxygen is contained in the polymer surface cannot be determined from the position of the O (1s) peak, since an insufficient amount of data is available on compounds of known structure. The use of chemical shifts in the C (1s) peak is also precluded since resolved peaks for 1s electrons from oxidized carbon were not observed.

The ESCA spectra of plasma-polymerized allylamine deposited on a Gulf-3 substrate, membranes 459 and 460, show that the binding energies for 1s electrons in nitrogen and oxygen are essentially the same as those for plasma-polymerized allylamine deposited on aluminum. To ascertain that the observed peaks were derived from the deposited film and not the substrate, which is cellulose acetate-cellulose nitrate, a spectrum was taken of the substrate alone. As is seen from Table VII, this spectrum exhibits two peaks for carbon. The first peak at 284.6 eV is due to carbon atoms bonded only to other carbon atoms and hydrogen. The second peak at 286.7 eV is due to carbon atoms bonded to oxygen atoms in a C=O structure.¹⁵ The nitrogen peak in the spectrum of the substrate appears at 403.8 eV. This binding energy is considerably less than that for nitrogen present as an NO_3^- ion (407.2 eV)¹⁴ which may be due to the fact that the nitrate group in cellulose nitrate does not carry a full negative charge. The peak for oxygen atoms occurs at 533.5 eV, indicating that oxygen contained in the substrate is in a higher state of reduction than the oxygen contained in the plasma-polymerized film. From these observations, it is evident that the spectra for Gulf-3 and plasma-polymerized allylamine are different and that the spectrum of plasma-polymerized allylamine deposited on Gulf-3 shows no signs of peaks due to the substrate.

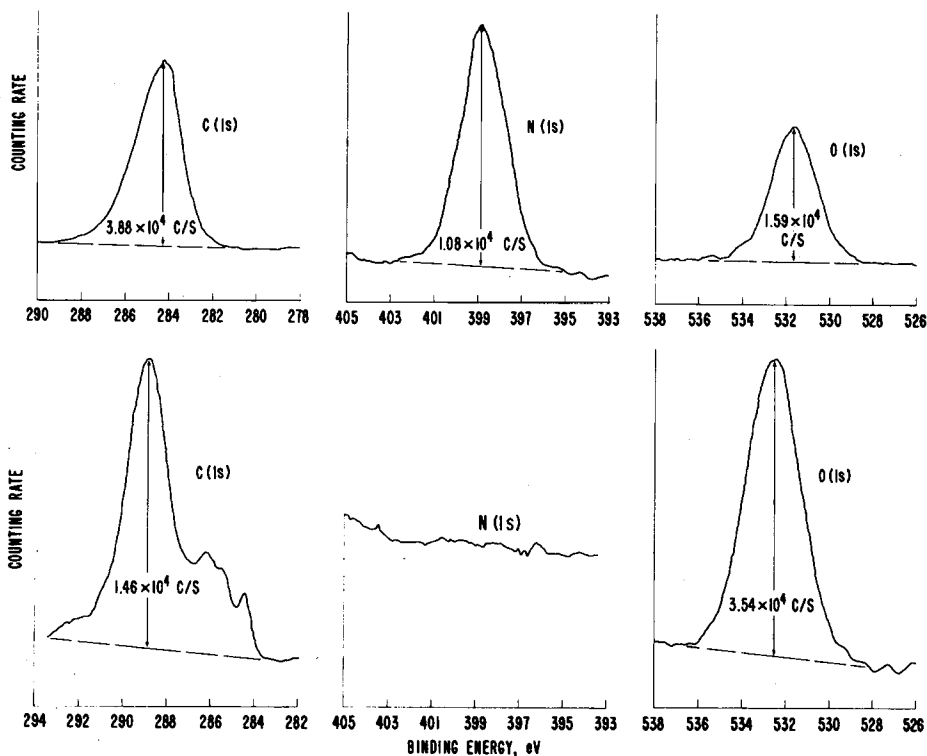


Fig. 9. ESCA spectra of membrane surfaces: top row, membrane 449, as prepared; bottom row, membrane 432, used for RO at temperatures between 18° and 60°C.

A comparison of the spectra of membranes used for reverse osmosis with those which were not used reveals several interesting points. The first is that the O/C ratio is increased after a membrane has been used for reverse osmosis, the change being particularly noticeable for those membranes run at higher temperatures and for longer periods of time. Concurrent with the increase in oxygen content there is a decrease in nitrogen content. This latter phenomenon is also accelerated by higher temperatures and longer test times. Finally, for membrane 432, which exhibits a particularly high oxygen content, it is observed that the intensity of the peak at 284.6 eV is greatly diminished and that three new peaks appear at 286.0, 286.7, and 289.1 eV which can be assigned to carbon

contained in $\begin{array}{c} | \\ -C-O- \\ | \end{array}$, $\begin{array}{c} \diagup \\ C=O \\ \diagdown \end{array}$, and $\begin{array}{c} O \\ || \\ -C \\ | \\ OH \end{array}$ groups, respectively.¹⁵ These

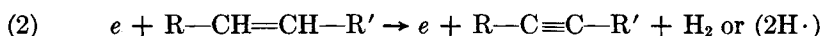
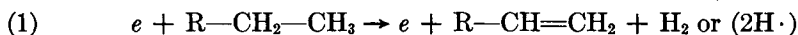
features, together with a comparison of the spectra of membranes 449 and 432, are shown in Figure 9.

The effects of increased temperature and duration under reverse osmosis conditions on the ESCA spectra of the membrane surface are particularly interesting since they can be correlated with changes in reverse osmosis performance as noted in Table VII (compare membranes 460 and 461). Thus, the decline

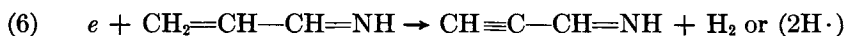
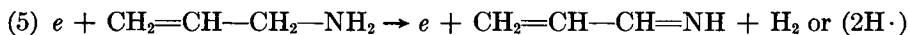
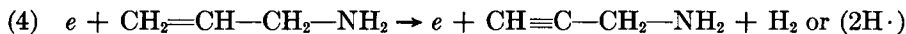
in rejection and the increase in water flux appear to be associated with the observed loss of nitrogen and gain of oxygen by the plasma-polymerized allylamine film. A possible interpretation for these observations is presented below.

Plasma-Polymerization Mechanism

The mechanism by which a monomer reacts in a plasma to form a polymer is quite complex and involves both homogeneous and heterogeneous processes. While a detailed mechanism for the plasma polymerization of a specific monomer has not been worked out, a number of general features of the mechanism have been resolved for hydrocarbon monomers.^{6,8} Among the most prominent of these features are the following: polymerization is initiated by the formation of free radicals via collisions between monomer molecules and free electrons or other energetic plasma species such as ions or metastables; increasing molecular weight is achieved by the reaction of radicals with unsaturation sites present in either the monomer or on the growing polymer mass and by the recombination of free radicals; free-radical sites on the polymer itself are constantly formed through collisions with energetic species present in the plasma or by absorption of UV radiation emitted by the plasma. In addition to these features, it is generally observed that monomers containing double or triple bonds between carbon atoms polymerize much more rapidly than do saturated monomers. The ratio of hydrogen to carbon in the polymer is always observed to be lower than in the monomer. This phenomenon is believed to be due to processes such as

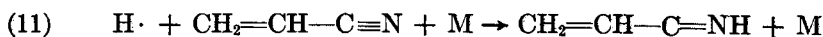
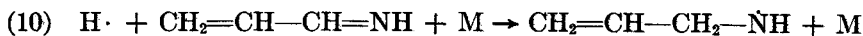
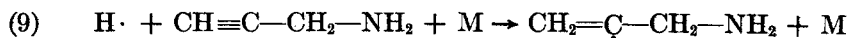
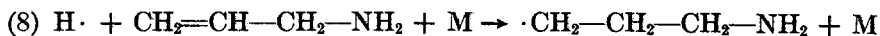


The plasma polymerization of allylamine is expected to be similar to that of hydrocarbon monomers. Thus, the initial interaction between the plasma and the monomer might involve reactions such as



The products of reactions (4) to (7) are more unsaturated than the original monomer and hence should polymerize more easily. This expectation is supported by the observations that acetylene polymerizes more rapidly than ethylene,⁶ that acrylonitrile polymerizes more rapidly than allylamine (see Table V), and that imines are generally susceptible to polymerization.¹⁶

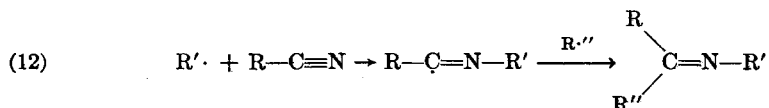
The hydrogen atoms released by reactions (4) through (7) are expected to form free radicals by reaction with allylamine and the derivative monomers produced by reactions (4) through (7). Examples of such reactions include the following:



Once formed, these radicals would react further with themselves, with monomer, and with the derivative monomer molecules, ultimately producing a polymer.

Reactions (4) through (11) suggest that the polymer should contain nitrogen atoms in the form of RNH_2 , $\text{RR}'\text{NH}$, $\text{RR}'\text{C}=\text{NH}$, $\text{RR}'\text{C}=\text{NR}''$, and $\text{RC}\equiv\text{N}$ type structures. With this in mind, it is appropriate to reexamine the infrared and ESCA spectra shown in Figures 8 and 9 to ascertain which of the five structures might predominate. The infrared spectrum of plasma-polymerized allylamine shows that the band for nitrile groups is relatively weak, indicating that the polymer does not contain a significant amount of nitrogen bound in this form. Correspondingly, the ESCA spectra show that the binding energy for nitrogen $1s$ electrons is too high for the nitrogen to be identified with amine groups. These two observations lead to the conclusion that most of the nitrogen in the polymer is contained in aldimine- and ketimine-type structures.

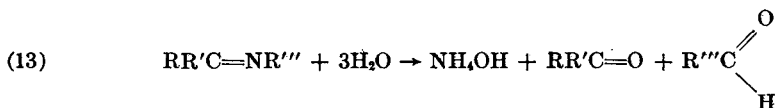
Based on the conclusions given above, it is suggested that the primary polymerization pathway involves a rapid conversion of the amine group in the monomer into a nitrile group. The nitrile group then reacts with a free radical in the following manner:



Two observations provide strong support for this sequence. The first is that acrylonitrile polymerizes much more rapidly than allylamine (see Table V). The second observation is that the infrared spectra of the polymers derived from allylamine and acrylonitrile are very similar. Both show strong evidence for the presence of $\text{C}=\text{N}$ bonds.

Mechanism of Polymer Degradation

The observed loss of nitrogen from membrane surfaces (see Table VII and Fig. 9), accompanied by a degradation in membrane performance, can now be interpreted in the light of the polymer structure proposed above. If the structures containing nitrogen are of the form $\text{RR}'\text{C}=\text{NR}''$ as suggested, then upon contact with water these structures will be hydrolyzed as follows:



Reactions such as (13) are well known in the chemistry of aldimines and ketimines.¹⁶

In addition to causing a loss of nitrogen, reaction (13) indicates that the remaining polymer would be broken into smaller segments. This polymer would be more open and more easily swollen. Both of these characteristics would

cause an increase in the value of ω in eq. (1) and therefore lead to a membrane exhibiting lower rejection but higher water flux. The results presented in Table VII indicate that this is exactly what happens.

Finally, reaction (13) indicates that the hydrolyzed polymer should contain a significant number of carbonyl groups. Here again, the ESCA spectra shown in Figure 9 confirm this expectation.

CONCLUSIONS

The present work has shown that composite reverse osmosis membranes can be prepared by plasma-polymerizing allylamine to form a thin layer on the surface of a porous substrate. The rejection of sodium chloride and the flux of water exhibited by such membranes is closely related to the choice of substrate material, the deposition time, and the power supplied to sustain the plasma. By a proper choice of these variables, it is possible to prepare membranes which possess both high salt rejection and high water flux. Operated over a period of days, the membranes show a gradual decrease in rejection accompanied by an increase in flux. These changes are rapidly accelerated when the membranes are operated at higher temperatures (up to 60°C).

Analyses of the chemical composition and structure of plasma-polymerized allylamine were used to determine the content and structure of nitrogen and oxygen in the polymer. It was found that the nitrogen content of the polymer was essentially the same as that of the monomer and that most of the polymer nitrogen was contained in aldimine- and ketimine-type structures. The oxygen content of the bulk polymer was observed to be small. However, a very substantial amount of oxygen was found at the external surface of the polymer. Analysis of membranes which had been used for reverse osmosis revealed a gradual build-up of oxygen in the outer surface of the plasma-polymerized layer. Operation at temperatures above ambient led to a very significant increase in the oxygen content and a total loss of nitrogen from the surface of the membrane. These observations together with the noted changes in rejection and flux for membranes, tested at higher temperatures, provide further support for the contention that most of the nitrogen present in the plasma-polymerized layer is present in aldimine- and ketimine-type structures.

The authors wish to acknowledge Dr. Merle Millard of the USDA Western Regional Laboratory for his assistance in obtaining the ESCA spectra presented here.

References

1. K. R. Buck and V. K. Davar, *Brit. Polym. J.*, **2**, 238 (1970).
2. H. Yasuda and C. E. Lamaze, *J. Appl. Polym. Sci.*, **17**, 201 (1973).
3. J. R. Hollahan and T. Wydeven, *Science*, **179**, 500 (1973).
4. R. L. Riley, G. Hightower, and C. R. Lyons, in *Reverse Osmosis Membrane Research*, H. K. Lonsdale and H. E. Podall, Eds., Plenum, New York, 1972.
5. S. Hossain, R. L. Goldsmith, M. Tan, T. Wydeven, and M. I. Leban, *J. Eng. Ind.*, 1023 (1973).
6. H. Kobayashi, M. Shen, and A. T. Bell, *J. Macromol. Sci.-Chem.*, **48**, 373 (1974).
7. H. Yasuda and C. E. Lamaze, *J. Polym. Sci. A-2*, **9**, 1537 (1971).
8. H. Kobayashi, A. T. Bell, and M. Shen, *Macromolecules*, **7**, 277 (1974).
9. M. Millard, in *Techniques and Applications of Plasma Chemistry*, J. R. Hollahan and A. T. Bell, Eds., Wiley, New York, 1974.

10. J. Bellamy, *Infrared Spectra of Complex Molecules*, 2nd ed., Methuen, London, 1958.
11. J. Fabian, M. Legrand, and P. Poirier, *Bull. Soc. Chim. Fr.*, 1499 (1956).
12. C. D. Wagner, *Anal. Chem.*, **44**, 1050 (1972).
13. J. Delhalle, J. M. Andre, S. Delhalle, J. J. Pireaux, R. Caudano, and J. J. Verbist, *J. Chem. Phys.*, **60**, 595 (1974).
14. D. M. Hercules, *Anal. Chem.*, **42**, 20A (1970).
15. W. E. Swartz, *Anal. Chem.*, **45**, 788A (1973).
16. N. V. Sidgwick, *The Organic Chemistry of Nitrogen*, 3rd ed., Clarendon Press, Oxford, 1966.

Received August 21, 1974

Revised December 11, 1974