

Reverse Osmosis Characteristics of Composite Membranes Prepared by Plasma Polymerization of Allylamine. Effects of Deposition Conditions

D. PERIC,* A. T. BELL, and M. SHEN, *Department of Chemical Engineering, University of California, Berkeley, California 94720*

Synopsis

A study has been conducted to determine the effects of flow configuration and reaction conditions on the performance of composite reverse osmosis membranes prepared by plasma polymerization of allylamine over a porous polymer substrate. It was established that superior membranes were obtained by using a gas-flow configuration avoiding direct monomer flow over the substrate. High rejections of NaCl could be attained when the plasma-deposited film was sufficiently thick to bridge all of the pores in the substrate. It was observed that in addition to influencing the rate of polymerization, the conditions used to sustain the plasma also affected the reverse osmosis characteristics of the deposited film. The effects of these conditions and other preparation procedures are discussed. Attempts to use infrared spectroscopy and ESCA to identify the relationship between polymer structure and reverse osmosis performance were not successful. ESCA did prove useful, though, in confirming an earlier postulated hypothesis that degradation of reverse osmosis performance is associated with the hydrolysis of nitrogen-containing structures in the plasma-deposited film.

INTRODUCTION

The preparation of composite reverse osmosis membranes by plasma deposition of a thin polymer film over a porous substrate has recently been demonstrated by several authors.¹⁻⁴ Work by Yasuda and Lamaze² established that membranes exhibiting high salt rejection and water flux can be obtained provided the monomer used to produce the rejecting layer contains nitrogen. An investigation of allylamine as a candidate monomer conducted by Bell et al.⁴ revealed that the quality of the membranes produced also depends strongly on the nature of the substrate and the conditions used to prepare the rejecting layer. The present studies were undertaken to further extend the work of Bell et al. Major objectives included a more extensive determination of the effects of deposition parameters on membrane performance. Investigations were also performed to determine the relationship between preparation conditions and the chemical structure of the plasma-deposited film.

EXPERIMENTAL

The reactor used in the present work is shown in Figure 1. It consisted of two 8-in.-diameter stainless steel electrodes enclosed in an 18-in.-diameter bell jar. The central portion of the lower electrode was hollow and could be cooled or

*Present address: Dow Chemical Co., Pittsburg, California.

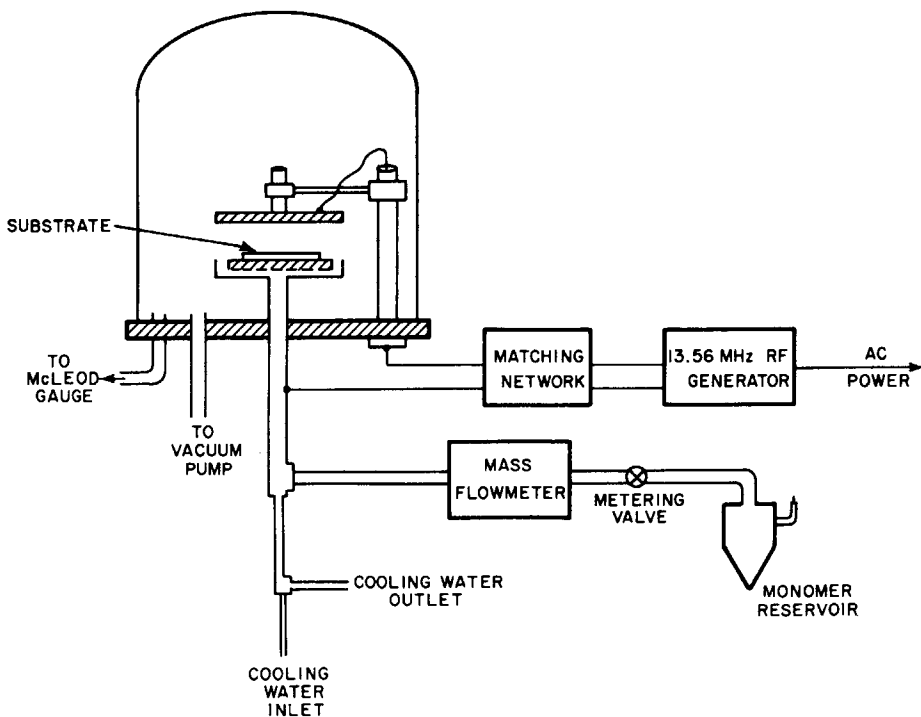


Fig. 1. Schematic of experimental apparatus.

heated by passing water through it. Surrounding the holder was a hollow cup which could be used to supply monomer or to evacuate the bell jar. The upper electrode was solid and could not be heated or cooled. The discharge was sustained between the two electrodes by a 13.56 MHz rf generator (Tracerlab Co.), capable of delivering up to 300 W. The gap between electrodes could be changed by moving either electrode upward or downward.

The monomer used was allylamine ($\text{CH}_2=\text{CH}-\text{CH}_2\text{NH}_2$, Aldrich Chemical Co., bp 53°C). Prior to use, it was degassed by repeated freezing and thawing while pumping on it. The substrate used was an asymmetric cellulose acetate-nitrate film manufactured by Gulf Environmental Systems.⁵ This material had a shiny side containing pores of $0.025\ \mu\text{m}$ average diameter and a water permeability of $170 \times 10^{-5}\ \text{g}/\text{cm}^2\text{-sec-atm}$.

The liquid monomer was stored in a small glass reservoir and fed to the system as a vapor. The vapor flow rate was monitored by a mass flowmeter (Matheson Model F50M). Unreacted vapor and volatile byproducts of polymerization were evacuated by a mechanical vacuum pump. The system pressure was monitored by a McLeod gauge connected to a port in the reactor base plate and also by means of a thermocouple gauge located in the line connecting the vacuum pump to the system.

The reactor was designed so that monomer could be fed and removed in a number of ways, as shown in Figure 2. The possible flow configurations were as follows: (1) monomer fed through the upper electrode and removed through the lower electrode, (2) monomer fed through the lower electrode and removed through the upper electrode, (3) monomer fed through the base plate and re-

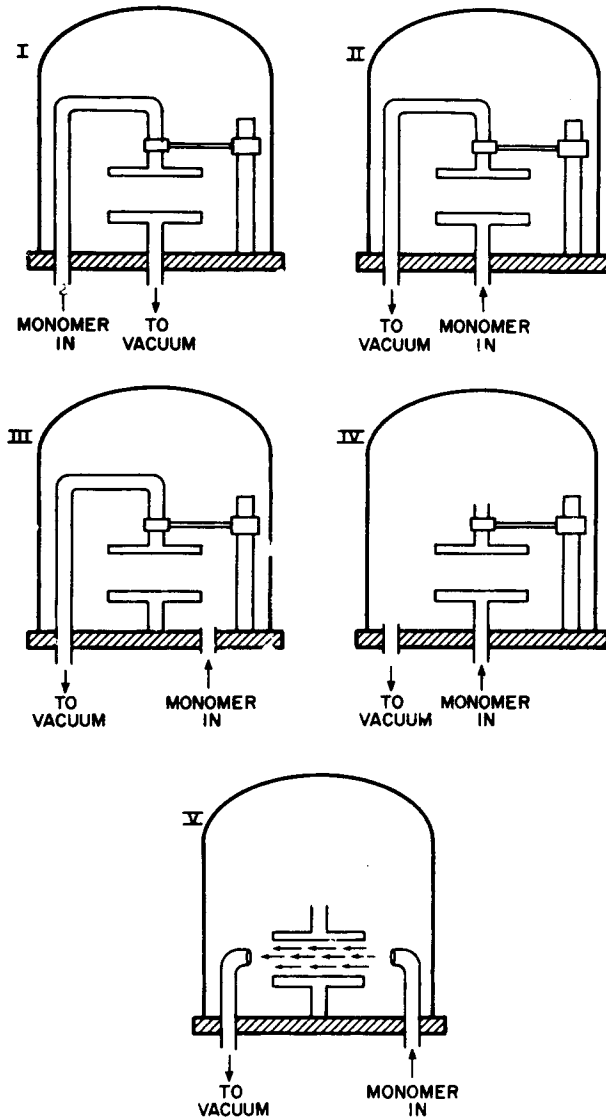


Fig. 2. Schematic of flow configurations.

moved through the upper electrode, (4) monomer fed through the lower electrode and removed through the base plate, and (5) monomer fed from one side of the electrodes and removed from the other side.

Membranes were prepared by placing a 4-in. disk of the substrate under a brass ring on the lower electrode. The bell jar was put in place and the system evacuated to about 0.010 torr pressure. The desired flow of monomer to the system was established, and the pressure was allowed to increase by closing a valve on the vacuum line until the desired pressure was reached. The discharge was initiated by turning on the rf generator and adjusting the matching network for minimum reflected power. During deposition, the lower electrode was water cooled to maintain the substrate surface temperature near 20°C. After depo-

sition, a 2-in. disk was cut from the center of the 4-in. disk for testing in the reverse osmosis loop.

The membranes were tested in a reverse osmosis test cell connected to a high-pressure brine recirculation loop. In all of the experiments, the brine concentration was maintained at 1% and the applied pressure across the membrane was kept at 1500 psi. Each membrane was allowed to operate for a minimum of 20 hr before the first sample of effluent was collected for determination of salt rejection and flux. The techniques used for measurement of rejection and flux were identical to those described by Hossain et al.⁶

Chemical characterization was accomplished by use of infrared spectroscopy and ESCA (Electron Spectroscopy for Chemical Analysis). Samples for infrared spectroscopy were prepared by deposition on a NaCl crystal. A Perkin-Elmer 137 spectrometer was used to record the spectra. Samples for ESCA were obtained by depositing polymer on aluminum foil or by using sections of actual membranes. Spectra were recorded on a du Pont Model 650 spectrometer.

RESULTS AND DISCUSSION

Effect of Deposition Parameters on Reverse Osmosis Performance

As mentioned earlier, the reactor was designed so that a number of flow patterns could be obtained. To determine which of the flow patterns produced membranes with the best reverse osmosis characteristics, membranes were prepared at various conditions using each of the possible flow configurations.

Configuration IV (see Fig. 2) was found to produce membranes with the best reverse osmosis performance of those tested. Configurations I, II, and III all produced membranes which exhibited poor rejection (less than 40%) and high flux. The films obtained with these configurations were observed to crack and break up when wetted, and, in some cases the films had an oily appearance. The crossflow configuration, V, produced membranes with better reverse osmosis characteristics than those obtained with configurations I, II, or III. The rejections for these membranes were generally lower, however, than those obtained using configuration IV. A comparison of the performance of membranes prepared using configurations IV and V is shown in Table I. While the results given in the table relate to one set of deposition conditions, similar results were obtained for other deposition conditions.

The results of the experiments just described suggest that superior reverse osmosis membranes are obtained when direct monomer flow over the substrate is avoided. A possible explanation for this conclusion is the observation that the rate of deposition is slower in the absence of flow over the surface on which deposition occurs. As a result, freshly deposited polymer has a longer period of exposure to the effects of the plasma and hence a greater opportunity to crosslink. These effects have been noted during the plasma polymerization of ethylene.⁷

On the basis of the flow configuration studies, it was decided to use configuration IV for the balance of the experiments which were devoted to the effects of deposition conditions on the reverse osmosis characteristics of the membranes. The first deposition parameter studied, deposition time, was found to have a significant effect on both flux and rejection, as shown in Figure 3. For deposition

TABLE I
Effect of Flow Configuration on Membrane Performance^a

Membrane no.	Configuration ^b	Rejection, % ^c	Flux, gfd ^c
392	V	79.3	10.3
393	V	70.0	11.6
394	V	96.5	8.1
414	V	69.5	17.0
413	V	82.5	20.0
415	V	74.6	22.0
361	IV	85.0	12.0
341	IV	97.0	5.0
355	IV	87.0	8.0

^a Membrane preparation conditions: flow config., IV; pressure, 200–250 μ Hg; power, 24 W; monomer flow, 4.4 cm³/min; elec. gap, 2⁷/₈ in.; dep. time, 13 min.

^b See Fig. 2.

^c Feed concentration, 1% NaCl; feed temperature, 20 °C; applied pressure, 1500 psi.

times greater than 800 s, the flux and rejection approach asymptotic limits of 10 gfd and 95%, respectively. The trends observed are similar to those noted by Bell et al.⁴ and are associated with the gradual closure of the pores present on the surface of the substrate. At short times, insufficient polymer is deposited to cover all of the surface pores, leaving holes in the surface through which salt solution can pass. At high deposition times, the deposited film completely covers all of the pores, leading to maximum rejection.

In the course of studying the effects of deposition time, it was found that higher salt rejections could be obtained by wetting freshly prepared membranes in

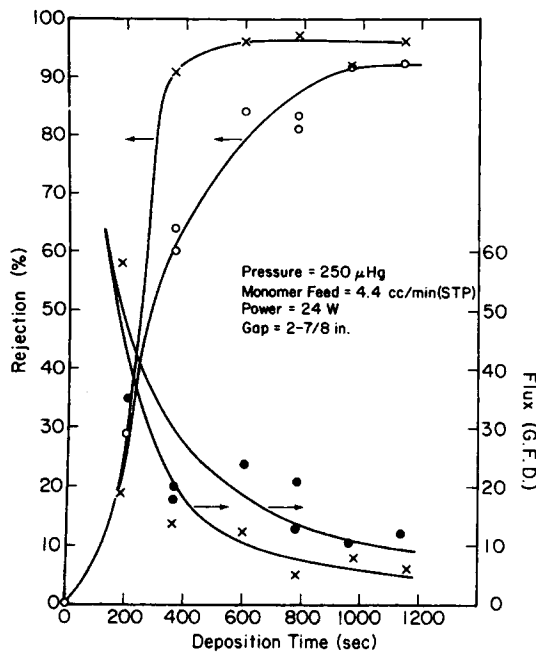


Fig. 3. Effect of deposition time on membrane rejection and flux (x) wetted before cutting. (●,○) not wetted.

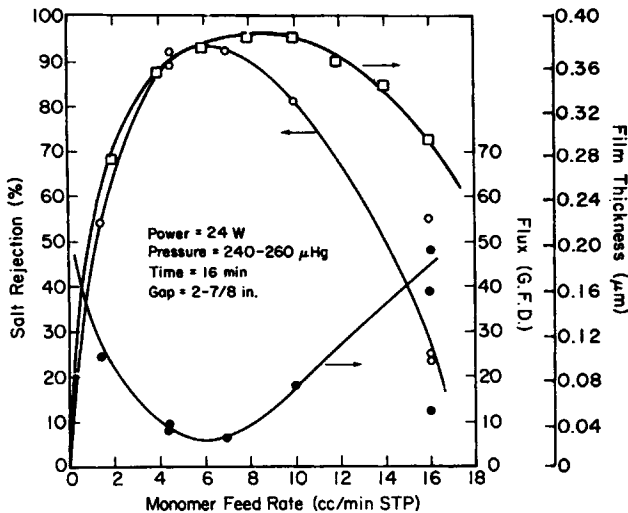


Fig. 4. Effect of monomer flow rate on membrane rejection (—○—), flux (—●—), and film thickness (—□—).

distilled water for 10 to 15 min prior to cutting out the 2-in. sample. The samples were then dried and stored until tested for their reverse osmosis performance. Figure 3 shows the results obtained with membranes treated in this fashion. Significant increases in salt rejection are observed for membranes prepared at intermediate deposition times. However, the improvement in rejection is accompanied by a decline in flux. Based upon these observations, all subsequent studies were performed using membranes which had been wetted before cutting.

Figure 4 shows the effect of monomer flow rate on membrane flux and rejection. The rejection passes through a maximum for flow rates between 4 and 7 cm^3/min . The flux, on the other hand, decreases with increasing flow rate, passing through a minimum when the rejection is at its maximum. Also shown in Figure 4 is a curve of the calculated thickness of the plasma-polymerized film. This curve is based on deposition rate studies performed on an aluminum foil substrate.

For flow rates below 6 cm^3/min , the observed dependence of rejection and flux on flow rate appears to be associated with the thickness of the deposited film. At low flow rates, the film thickness achieved in 16 min is inadequate to provide good rejection (see Fig. 3). At higher flow rates, the film thickness decreases gradually, but the rejection is seen to fall off much more rapidly than would be expected solely due to a decline in film thickness. It would, therefore, appear that the structural characteristics of films deposited at high flow rates are different from those of films of equivalent thickness deposited at lower flow rates.

The effect of the deposition pressure on membrane performance is shown in Figure 5. The rejection passes through a maximum at a pressure of about 250 μ and then levels off at higher pressures. The flux decreases rapidly as the pressure increases at low pressure and then levels off at higher pressures. A curve of the predicted film thickness is also shown in Figure 5.

For pressures below 250 μ , the effect of pressure on the reverse osmosis char-

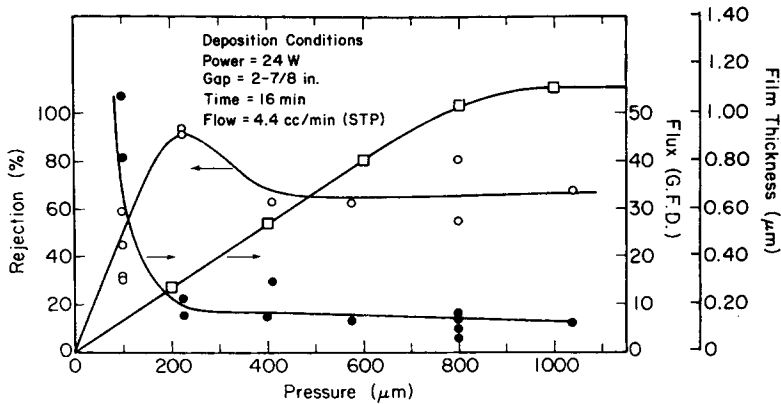


Fig. 5. Effect of pressure on membrane rejection (—○—), flux (—●—), and film thickness (—□—).

acteristics of the membranes can be attributed to the increasing thickness of the plasma-deposited film. At higher pressures, the film thickness continues to increase but the rejection declines. This behavior might possibly be explained by the presence of very fine faults or cracks in the film. Alternatively, the chemical and/or structural characteristics of the films prepared at higher pressures may be less favorable for good salt rejection.

The effect of the electrode gap on the rejection and flux of the membranes is shown in Table II. In preparing the membranes listed in this table, the deposition time was adjusted so that the same amount of polymer was deposited in each case. All other deposition conditions were held constant. The rejection of the membranes is found to increase as the gap size is decreased, although the overall variation is not large. The flux is found to be largest for a gap size between 1.5 and 2.0 in.

Finally, to test the effect of discharge power, membranes were prepared at 24 W, 42 W, and 62 W. The time of deposition was adjusted so that the same amount of film was deposited in each case. The results are shown in Table III. The rejection of the membranes is highest for films produced at a power of 42 W, although the overall variation with power is not large. The flux of the films

TABLE II
Effect of Electrode Gap on Membrane Performance^a

Membrane no.	Gap, in.	Deposition time, min	Rejection, % ^b	Flux, gfd ^b
408	1.0	21.6	94.2	10.2
409	1.0	21.6	94.4	12.9
406	1.5	19.1	94.2	10.4
407	1.5	19.1	91.1	15.4
410	2.25	19.1	91.3	15.4
411	2.25	19.1	94.4	15.2
390	2.85	16.0	89.0	7.2
401	2.85	16.0	87.5	11.7

^a Membrane preparation conditions: flow config., IV; pressure, 200–250 μ Hg; power, 24 W; monomer flow, 5.0 cm³/min; dep. time, see table.

^b Feed concentration, 1% NaCl; feed temperature, 20°C; applied pressure, 1500 psi.

TABLE III
Effect of Deposition Power on Membrane Performance^a

Membrane no.	Power, W.	Deposition time, min	Rejection, % ^b	Flux, gfd ^b
341	24	16.0	97.0	5.0
355	24	16.0	87.0	8.0
395	42	13.4	90.5	10.2
397	42	13.4	98.5	6.8
400	42	13.4	96.3	7.9
396	62	13.0	80.4	13.7
398	62	13.0	92.5	14.4
403	62	13.0	93.0	10.4

^a Membrane preparation conditions: flow config., IV; pressure, 200–250 μ Hg; monomer flow, 4.4 cm³/min; elec. gap, 2 $\frac{7}{8}$ in.; dep. time, see table.

^b Feed concentration, 1% NaCl; feed temperature 20 °C; applied pressure, 1500 psi.

increases with increasing power, and again the effect of power is not large. Bell et al.⁴ observed similar trends with deposition power in their studies and also found 40 W to be the optimum power. The occurrence of an optimum power was ascribed to a balance between increased deposition rate and increased substrate degradation which occurs as the power is increased.

Additional improvements in membrane performance could be obtained by feeding monomer to the reactor prior to the initiation of the discharge and by heating the base plate supporting the substrate. The first of these techniques was found to improve rejection without having any effect on flux. These results are summarized in Table IV which compares rejection and fluxes for membranes prepared with and without prefeeding of monomer. Similar results have been observed by Wydeven.⁸ A possible explanation for the improved rejection is that prefed monomer adsorbs on the substrate surface and, once the discharge is initiated, rapidly polymerizes forming an intimate bond with the substrate.

TABLE IV
Effect of Feeding Monomer Before Initiation of Discharge
on Membrane Performance^a

Membrane no.	Rejection, % ^b	Flux, gfd ^b
381 (monomer fed for 15 min before discharge)	94.1	10.9
383 (monomer fed for 15 min before discharge)	94.5	11.3
416 (monomer fed for 15 min before discharge)	95.3	7.4
417 (monomer fed for 15 min before discharge)	90.0	10.3
361 (monomer not prefed)	85.0	12.0
341 (monomer not prefed)	97.0	5.0
355 (monomer not prefed)	87.0	8.0

^a Membrane preparation conditions: flow config., IV; pressure, 200–250 μ Hg; power, 24 W; monomer flow, 4.4 cm³/min; elec. gap, 2 $\frac{7}{8}$ in.; dep. time, 13 min.

^b Feed concentration, 1% NaCl; feed temperature, 20 °C; applied pressure, 1500 psi.

TABLE V
Effect of Using a Heated or Cooled Base Plate
on Membrane Performance^a

Membrane no.	Rejection, % ^b	Flux, gfd ^b
386 (heated base plate, $T = 38^{\circ}\text{C}$)	90.4	16.9
387 (heated base plate, $T = 38^{\circ}\text{C}$)	87.0	18.0
388 (heated base plate, $T = 38^{\circ}\text{C}$)	87.7	18.0
361 (cooled base plate, $T = 20^{\circ}\text{C}$)	85.0	12.0
341 (cooled base plate, $T = 20^{\circ}\text{C}$)	97.0	5.0
355 (cooled base plate, $T = 20^{\circ}\text{C}$)	87.0	8.0

^a Membrane preparation conditions: flow config., IV; pressure, 200–250 μHg ; power, 24 W; monomer flow, 4.4 cm^3/min ; elec. gap, $2\frac{7}{8}$ in.; dep. time, 13 min.

^b Feed concentration, 1% NaCl; feed temperature, 20°C ; applied pressure, 1500 psi.

Heating the lower electrode to a temperature of 38°C had a significant effect on the flux through the membranes, but little effect on salt rejection. Table V compares the results for membranes prepared on a heated and cooled base plate.

On the basis of results obtained with prefed monomer and using a heated base plate, a series of membranes were prepared using both techniques together. The monomer was prefed to the reactor at the same flow rate and pressure used during deposition. The base plate was heated only during deposition. Rather than obtaining membranes with both improved salt rejection and higher flux, as was hoped for, the performance of the membranes prepared using both techniques was poorer than if neither of the techniques had been used. These results are summarized in Table VI.

The infrared spectra recorded of plasma-polymerized allylamine deposited on a NaCl crystal resembled those reported by Bell et al.⁴ The assignment of the bands observed in these spectra are given in Table VII. Spectra taken of films prepared at different pressures and flow rates were practically indistinguishable, suggesting that although films prepared at different conditions have different reverse osmosis characteristics, their chemical structures are essentially the same.

In an effort to detect differences in membrane surface composition as a function of deposition conditions, a series of samples were examined by ESCA.

TABLE VI
Effects of Heating Substrate Holder and Feeding Monomer Before Initiation of
Discharge on Membrane Performance^a

Membrane no.	Rejection, % ^b	Flux, gfd ^b
404	86.0	7.9
405	75.6	9.9
412	82.5	5.2
418	96.0	5.3
417	87.2	15.0

^a Membrane preparation conditions: flow config., IV; pressure, 200–250 μHg ; power, 24 W; monomer flow, 4.4 cm^3/min ; elec. gap, $2\frac{7}{8}$ in.; dep. time, 13 min.

^b Feed concentration, 1% NaCl; feed temperature, 20°C ; applied pressure, 1500 psi.

TABLE VII
Infrared Frequencies and Band Assignments

Frequency, cm^{-1}	Band assignments
3340	$\nu(\text{N—H})$
2960	$\nu(\text{CH}_3)$
2930	$\nu(\text{CH}_2)$
2870	$\nu(\text{CH}_3)$
2840	$\nu(\text{CH}_2)$
2200	$\nu(\text{C}\equiv\text{N})$
1620	$\nu(\text{C}=\text{N})$ and $\delta(\text{N—H})$
1440	$\delta(\text{CH}_3)$ and $\delta(\text{CH}_2)$
1380	$\delta(\text{CH}_3)$

The binding energies for 1s electrons in carbon, nitrogen, and oxygen and the ratios of peak areas are shown in Table VIII. The positions of the three bands were found to be independent of film deposition conditions, and the ratios of peak areas exhibited no significant trends. Thus, it would appear that ESCA, like infrared spectroscopy, is incapable of identifying the structural characteristics of the plasma-deposited films which control their reverse osmosis performance.

In the study performed by Bell et al.,⁴ it was noted that the reverse osmosis performance of the membranes tended to degrade with the duration of use. ESCA studies performed on the membranes before and after they were used for reverse osmosis revealed a decrease in the amount of nitrogen and increase in the amount of oxygen on the membrane surface after the membrane had been used for reverse osmosis. This same behavior was also observed by Yasuda.¹⁰ It was proposed by Bell et al. that the degradation observed was due to the hydrolysis of imine and ketimine groups in the film to form carboxylic acid groups. The hydrolysis reaction was believed to be responsible for the destruction of crosslinks in the film and weakening of the film structure. To further verify this interpretation, additional studies were conducted.

In performing the monomer flow rate studies noted earlier, it was observed that membranes produced at high monomer flow rates had a greater tendency to degrade than those produced at the optimum flow rate of 4–7 cm^3/min S.T.P. To determine whether exposure to water produced differences in film structure, membranes were prepared using monomer flow rates of 5 and 16 cm^3/min S.T.P. Samples of each film were placed overnight in a dish of salt water maintained at 20° or 40°C. A third sample of each membrane was stored dry in a desiccator. The wetted samples were allowed to dry, and then all of the samples were analyzed by ESCA. The results are shown in Table IX.

TABLE VIII
ESCA Binding Energies and Peak Area Ratios

Binding energy, eV ^a			Peak area ratio ^b		
C(1s)	O(1s)	N(1s)	O/C	N/C	O/N
284.6	532.6	399.6	0.34	0.20	1.7

^a Adjusted to $E_B = 284.6$ eV for C(1s) to account for charging of sample.⁴

^b Average values.

TABLE IX
ESCA Results for Dry and Wetted Membranes^a

Sample	Binding energy, eV			Peak area ratio		
	C(1s)	O(1s)	N(1s)	O/C	N/C	O/N
365 Dry	284.6	532.2	399.7	0.31	0.20	1.5
365 Wetted in 40°C water	284.6	532.6	399.8	0.28	0.15	1.9
365 Wetted in 20°C water	284.6	532.2	399.9	0.37	0.16	2.3
378 Dry	284.6	532.5	399.6	0.30	0.22	1.3
378 Wetted in 20°C water	284.6	532.9	400.1	0.37	0.18	2.1
378 Wetted in 20°C water	284.6	532.6	399.5	0.26	0.18	1.5
366 Dry	284.6	532.6	399.6	0.35	0.36	1.1
366 Wetted in 40°C water	284.6	532.5	399.9	0.34	0.18	1.9
366 Wetted in 20°C water	284.6	532.6	399.9	0.37	0.02	17.0
384 Dry	284.6	532.6	399.6	0.35	0.15	2.3
384 Wetted in 20°C water	284.6	532.6	399.8	0.40	0.01	32.0
384 Wetted in 20°C water	284.6	532.7	399.9	0.50	0.04	13.0
Gulf substrate dry	284.6	533.8	400.1	1.5	0.03	52.0
	286.1					
Gulf substrate wetted in 20°C water	284.6	533.5	399.8	2.1	0.02	92.0
	286.2					

^a Membrane preparation conditions:

	365 and 378	366 and 384
Flow configuration	IV	IV
Pressure	230 μ Hg	240 μ Hg
Power	24 W	24 W
Monomer flow	5 cm ³ /min	16 cm ³ /min
Electrode gap	2 $\frac{7}{8}$ in.	2 $\frac{7}{8}$ in.
Deposition time	16 min	16 min

A comparison of the positions of the C(1s), N(1s), and O(1s) peaks for dry membranes and membranes wetted in either 20° or 40° salt water shows only small differences. A change can be noted in the elemental ratios of the membranes as a result of wetting them. The membranes produced at the optimum flow rate (membranes 365 and 378) show a slight increase in oxygen and a decrease in nitrogen on the surface of the films after wetting in both 20° and 40°C water. The membranes produced at the higher monomer flow rate (366 and 384) show a large decrease in the amount of nitrogen on the surface of the films after being wetted in 20°C water. A decrease in nitrogen was also noted when the films were wetted in the 40°C salt water, but the effect was surprisingly much smaller. A sample of the substrate alone was also analyzed by ESCA before and after being wetted. The results obtained were quite different from those obtained with the membranes, indicating that the spectra obtained with the membranes are characteristic of the plasma-polymerized allylamine film alone (see Table IX).

Further tests of the correlation between membrane degradation and changes in the surface contents of oxygen and nitrogen were carried out with membranes prepared at different pressures. These membranes were analyzed by ESCA before and after they were used for reverse osmosis. In Table X, it is seen that all of the membranes which degraded (it should be noted that degradation in all cases corresponded to a decline in rejection of less than 1% in 24 hr) showed

TABLE X
ESCA Analyses of Membranes Before and After Testing of
Reverse Osmosis Performance^a

Sample	Binding energy, eV			Peak area			Deposition pressure, μ Hg	Degree of degradation
	C(1s)	O(1s)	N(1s)	O/C	N/C	O/N		
368 Before RO	284.6	532.4	399.4	0.41	0.25	1.64	95	beginning to degrade
368 After RO	284.6	532.4	399.6	0.68	0.12	5.66		
369 Before RO	284.6	532.6	399.3	0.30	0.17	1.76	410	no
369 After RO	284.6	532.0	399.5	0.33	0.12	2.75		
370 Before RO	284.6	532.2	399.5	0.26	0.19	1.37	575	yes
370 After RO	284.6	532.3	399.4	0.35	0.11	3.18		
371 Before RO	284.6	532.6	399.4	0.32	0.17	1.88	850	yes
371 After RO	284.6	532.4	399.8	0.75	0.16	4.70		
372 Before RO	284.6	532.6	400.3	0.29	0.15	1.93	850	yes, after
372 After RO	284.6	532.3	399.3	0.39	0.09	4.34		25 hr
373 Before RO	284.6	532.5	399.5	0.28	0.23	1.22	1050	yes,
373 After RO	284.6	532.6	399.9	0.62	0.16	3.89		slightly
374 Before RO	284.6	532.6	399.7	0.37	0.17	2.18	225	yes,
374 After RO	284.6	532.5	399.4	0.56	0.11	5.10		slightly
375 Before RO	284.6	532.6	399.3	0.33	0.20	1.65	440	no
375 After RO	284.6	532.2	399.5	0.43	0.20	2.32		

^a Membrane preparation conditions: flow config., IV; pressure, see table; power, 24 W; monomer flow, 4.4 cm³/min; elec. gap, 2 $\frac{1}{8}$ in.; dep. time, 16 min.

a fairly large increase in the O/C ratio and a concurrent decrease in the N/C ratio. Membranes 369 and 375, which did not degrade, also showed increases in the O/C ratio, and membranes 369, in addition, showed a decrease in N/C ratio after use for reverse osmosis. The changes in the elemental ratios for these membranes were smaller, though, than those noted for membranes which did degrade.

From the data given in Tables IX and X, it is evident that the rejecting layer of all of the membranes undergo hydrolysis to some degree upon contact with water and that membranes which degrade undergo a greater degree of hydrolysis. The extent to which hydrolysis occurs does depend on the conditions under which the membrane is prepared. However, it is still not apparent why some of the membranes degrade and others do not.

CONCLUSIONS

The present work has further confirmed that the reverse osmosis characteristics of membranes prepared by plasma polymerization of allylamine are a sensitive function of the preparation conditions. Superior membranes were obtained by using a gas flow configuration which avoided direct monomer flow over the substrate. To achieve high rejections, the plasma-deposited film must be sufficiently thick. It was determined that while monomer flow rate, pressure, interelectrode gap distance, and discharge power influence the rate of polymerization, these variables also influence reverse osmosis characteristics of the deposited film. Thus, films of equivalent thickness prepared under different conditions exhibited difference in their reverse osmosis performance.

The effects of several variations in the membrane preparation procedure were

also explored. Wetting membranes with distilled water and then allowing them to dry before testing their reverse osmosis performance resulted in an improved performance over membranes which had not been treated in this fashion. Higher water fluxes, without loss of salt rejection, could be obtained by heating the substrate holder during deposition. On the other hand, the salt rejection characteristic of the membranes could be improved by passing monomer over the substrate prior to initiating the discharge. Attempts to use both of the methods just mentioned on a single membrane, however, did not result in a simultaneous improvement in flux and rejection.

Characterization of the plasma-polymerized films by infrared spectroscopy and ESCA has established that neither of these techniques can identify significant differences in the chemical composition and structure of films prepared under different conditions. As a result, these techniques do not help to explain the variations in reverse osmosis performance observed. ESCA, however, has been useful in confirming the hypothesis that degradation in reverse osmosis performance is associated with the hydrolysis of nitrogen-containing structures in the plasma-deposited film.

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