Synthesis of Reverse Osmosis Membranes by Plasma Polymerization of Allylamine

Abstract. *The polymerization of allylamine in a radio-frequency electrodeless plasma to form thin polymer films on microporous filter media provides very effective dry composite membranes for reverse osmosis. Salt and urea rejections as high as 98 percent and 46 percent, respectively, have been achieved from a solution containing 10 grams of sodium chloride per liter and 10 grams of urea per liter. The plasma conditions and polymerization technique are discussed.*

For reverse osmosis the search for new membrane materials that are dry and environmentally stable can now proceed through the synthesis of organic polymer membranes by low-temperature, nonequilibrium plasma polymerization. Films produced by this technique have been used for such materials as biomedical coatings and insulator barriers. The chemistry and experimental technique of plasma polymerization have been described (*1*). Yasuda (*2*) has demonstrated that a variety of films prepared from several types of organic monomers do indeed have salt rejection capabilities in reverse osmosis.

We now report that allylamine, $H_2C{=}CHCH_2NH_2$, after plasma polymerization in a high-frequency (13.56 Mhz) discharge at ~ 0.1 torr, during which a thin polymer film forms on a Millipore filter substrate, exhibits as much as 98 percent NaCl rejection and a promising 46 percent urea rejection from a feed solution containing 10 g of NaCl and 10 g of urea per liter.

In the synthesis procedure (Fig. 1) degassed allylamine (Eastman, b.p. 52.5° to 53.5°C) was admitted from the liquid source via a needle valve after the system had been pumped down to $< 10^{-3}$ torr. At room temperature the vapor pressure of allylamine is high enough to produce a pressure of several torr in our system. When the pressure and flow of the monomer were stabilized at 0.1 torr, either argon or nitrogen (Matheson Gas Products, 99.998 and 99.97 percent stated purity, respectively) was admitted through a flow delivery system into the top of the bell jar. When this flow and the total pressure had stabilized at about 0.2 torr, energy from the radio-frequency (RF) generator was increased until a discharge was initiated (*3*). With the chosen set of conditions for plasma polymerization—power, pressure, gas composition, and flow rates—the reaction was allowed to proceed for the time desired for film deposit. The polymerization occurred on the support (Fig. 1); all films for evaluation of reverse osmosis were deposited on the "shiny side" of either 0.1- or 0.025-μm MF Millipore filter. For every deposition the distance from the substrate surface to the lower (ground) electrode was maintained at 4.0 cm. The membranes were tested for flux and rejection properties with the use of the recirculating hyperfiltration system described in (*4*). The reverse osmosis test cell (Universal Water Corporation, Del Mar, California) could accommodate a circular membrane 5.08 cm in diameter. Analyses for NaCl and urea have been described in an earlier paper (*4*).

Table 1. Flux and rejection for plasma polymerized membranes as a function of reverse osmosis time, film deposition time, and additive gas.

	Membrane constant (*A*)* (cm sec^{-1} atm^{-1} × 10^{6})	Flux (GFD)†	Percent rejection‡	
			NaCl	Urea
Reverse osmosis time (hours) §				
1.5	3.21	2.30	78.0	33.0
12.7	4.64	3.28	87.0	28.9
38.0	6.32	4.46	88.7	25.3
61.7	6.52	4.60	89.3	23.7
86.6	6.96	4.91	89.3	22.7
Deposition time (sec)‖				
600	6.32	4.46	88.5	25.3
2300	0.864	0.581	97.9	41.8
Additive gas‖				
Argon	8.76	6.23	90.8	15.2
Nitrogen	6.72	4.80	88.5	15.7
None	4.78	3.31	97.2	23.6

* Calculated from $J_1 = A\,(\Delta P - \Delta\pi)$ where J_1 is the solution flux (cm^{3} cm^{-2} sec^{-1}), A is the membrane constant (cm sec^{-1} atm^{-1}), and $(\Delta P - \Delta\pi)$ is the pressure difference and the osmotic pressure difference across the membrane (atm). † Gallons per square foot per day. ‡ Feed solution composition: 10 g of NaCl plus 10 g of urea per liter, $pH = 7.79$; temperature 19.5°C; pressure 600 pounds per square inch gauge pressure; linear flow rate across membrane 17 cm/sec. § Depositions were made on 0.1-μm MF Millipore. ‖ Depositions were made on 0.025-μm MF Millipore.

The polymerization of allylamine proceeds smoothly with a light tan film readily forming under the plasma conditions. Films produced at 600, 700, and 2300 seconds and 40 watts of net RF power demonstrated the rejection and flux values reported here. Films deposited at 5400 seconds appeared to be impermeable under our test conditions for reverse osmosis. Film thicknesses of polymerized allylamine, which were prepared with argon as an additive gas and which were estimated by weight gains on microscope cover slips (4.84 cm^{2}) and by an assumed density of the polymer of 0.98 g/cm^{3} (approximately the density of cross-linked polyethylene), ranged from 0.8 to 1.6 μm over deposition times of 500 to 2400 seconds.

The transmission infrared spectrum of the polymer film deposited for 4500 seconds on a KRS-5 crystal over the range 400 to 4000 cm^{-1} showed at least two notable differences from the infrared spectrum of the allylamine monomer. In the polymer film there was a new absorption at 2200 cm^{-1}, which indicated that a —CN moiety had formed (*5*). Hydrogen abstraction from the allylamine polymer or monomer precursor to form a polymer containing nitrile groups apparently occurred. The reverse of the above process for the monomer—that is, conversion of nitriles to amines—is well known by catalytic hydrogenation (*6*). In the infrared spectrum of the polymer film there remained strong contributions from amine and aliphatic absorptions. The polymer was also undoubtedly highly cross-linked and contained unsaturation sites, also evident in the infrared spectrum by a broad band centering at 1650 cm^{-1}, which is usually observed in films produced by plasma polymerization (*7*). The general appearance of the infrared spectrum of the polymer was structureless in the region 400 to 1400 cm^{-1}. During the time of formation of the polymer the film is subjected to constant bombardment by atoms, ions, and radicals which chemically alter surfaces of polymers (*8*), and to photochemical irradiation from the plasma itself (*9*). Thus, films deposited at longer times, 2300 seconds, may have structural entities different from films deposited at shorter times, 600 seconds.

Flux and rejection data as functions of time for a membrane formed during a 600-second polymerization on 0.1-μm filter substrate gave the results shown in Table 1: the flux and rejection of NaCl *both* increase up to 87 hours, unlike the behavior of asymmetric cellulose acetate membranes (*10*); urea rejection, however, decreases with time. This flux trend and rejection behavior were likewise observed with films of allylamine produced at various deposition times, with nitrogen instead of argon as the additive gas. While the rejection data were very encouraging for a film produced at 600 seconds, the rejection data improved and the flux decreased at longer polymerization times (Table 1) at the same plasma conditions: 40 watts net RF power, 0.2 torr total pressure, argon additive gas, and constant deposition geometry. The data reported in Table 1 were taken after the flux and rejection were changing very slowly, generally about 20 hours after the experiment was begun. When a Millipore filter with an average pore diameter of 0.025 μm is used, longer polymerization times probably cause the larger micropores to be filled with polymer more completely (see Table 1), thereby producing fewer membrane imperfections with a concomitant improved rejection and reduction in the value of the flux. The rejection and flux properties of these membranes, and perhaps plasma formed membranes in general, can be quite effectively controlled by variations in the electrical and gas dynamic plasma conditions, a departure from the conventional variations in synthesis one would employ by traditional techniques to form or cast thin polymer films—such as polymer concentration, casting formulation, drying time, humidity, atmosphere, and curing temperature.

Table 1 shows the effect on flux and rejection properties of nitrogen instead of argon as an additive gas compared to a film formed from the pure monomer at a total plasma gas pressure of 0.20 torr, 40 watts, and 700 seconds deposition time. In the case of the pure monomer, 0.2 torr was employed, while with additive gases the monomer was at 0.1 torr partial pressure. The highest rejection was obtained from polymerization of the pure monomer. Whether this effect is generally true under all conditions of plasma deposition has yet to be confirmed. The flux for the film deposited for 600 seconds (Table 1) is actually measured to be higher than that for films deposited for 700 seconds, with argon as the additive gas (Table 1). The reason for this unexpected behavior between flux and deposition time has yet to be determined.

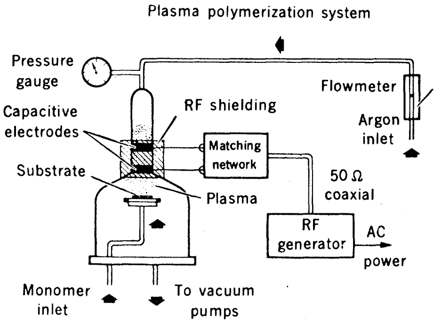

Fig. 1. Plasma polymerization system.

There are several obvious advantages and potential advantages to this synthetic approach for preparing membranes for reverse osmosis and their resultant performance properties: (i) a dry membrane is produced which does not require special handling or storage conditions; (ii) control can be maintained over the membrane thickness on selected substrates by control of plasma parameters; (iii) there is high adhesion of the polymer film on the substrate; (iv) only very thin films, 1.0 μm or less, are required to achieve high salt rejection; (v) a variety of substrates and substrate configurations are amenable to low-pressure plasma polymer deposition; (vi) membrane compaction is likely to be minimal during reverse osmosis since the polymer probably achieves a maximum density during deposition; (vii) uniform membranes with minimal imperfections—that is, pinhole free films—are capable of being formed; (viii) the plasma deposition times are short, 10 to 15 minutes in our laboratory; and (ix) it is conceivable that a large number of organic monomers can now be investigated and polymerized via plasma for preparation of reverse osmosis membranes, since most organic molecules can be readily polymerized in a low-temperature plasma (*1*).

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Motor Cortex Reflexes Associated with Learned Movement

Abstract. *In primates, sensory input can generate reflex motor cortex output in association with learned movement when the sensory input has a strong and direct connection to the motor cortex—for example, when a stimulus calling for repositioning of the hand consists of a perturbation of hand position. This finding supports the proposal that neurons of primate motor cortex may function in a transcortical servo-loop.*

Though commonly referred to as a motor area, the precentral cortex of the primate brain is a target for sensory input as well as a source of motor output (*1*). The strongest sensory input to a particular subdivision of the motor cortex arises from the body part whose movements it controls. For example, the motor cortex hand area receives its strongest input from receptors of the hand. It has been proposed that afferents to the