

Preparation of Reverse Osmosis Membranes by Plasma Polymerization of Organic Compounds

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Synopsis

The plasma polymerization of organic compounds was used to prepare a composite reverse osmosis membrane which consists of an ultrathin semipermeable membrane formed by plasma polymerization of an organic compound or compounds and a porous substrate. Many nitrogen-containing compounds (aromatic amines, heteroaromatic compounds, aliphatic amines, and nitriles) were found to yield excellent reverse osmosis membranes by plasma polymerization directly onto porous substrates such as Millipore filters, porous polysulfone filters, and porous glass tubes. Factors involved in the preparation of reverse osmosis membranes by plasma polymerization were investigated and discussed. The plasma polymerized membranes have the following unique features: (1) very stable performance independent of salt concentration and applied pressure (practically no water flux decline was observed with many membranes); (2) salt rejection and water flux both increase with time in the initial stage of reverse osmosis (consequently, the performance of the membrane improves with time of operation); (3) very high salt rejection (over 99%) with high water flux (up to 38 gfd) can be obtained with 3.5% NaCl at 1500 psi (membranes perform equally well under conditions of sea water conversion and brackish water treatment).

INTRODUCTION

The reverse osmosis properties of (ionic and nonionic) polymer membranes have recently been investigated based on the free volumes of membranes which allow passage of water and salt.¹⁻³ The results indicated that salt rejection and water throughput of a homogeneous polymer membranes are related and that good salt rejection can be obtained only with a water flux constant which is below a certain threshold value. Accordingly, there seems to be a limit to improving the characteristic water flux constants of polymers at a high salt rejection. Practical improvement, therefore, should depend heavily on the improvement of geometric factors of membranes such as (1) the reduction of effective thickness by asymmetric or composite membranes, (2) improvement of the surface/volume ratio by using tubular or hollow fiber membranes, and (3) combination of (1) and (2). A polymer which has good reverse osmosis characteristics may have no practical value unless the polymer can be formed into a functional membrane which has favorable geometric factors.

The aim of this study was the preparation of a composite membrane that would consist of an ultrathin salt-rejecting layer and a porous supporting layer made by the plasma deposition of polymer directly onto an appropriate substrate. In this approach, a polymer is formed into an ultrathin membrane intimately bonded to an appropriate porous substrate during the process of polymerization, instead of preparing a thin membrane from a polymer. A highly crosslinked ultrathin membrane is formed on the surface of a porous substrate; accordingly the final shape of the composite membrane depends on the shape of the porous substrate, i.e., flat sheet, tubular, and hollow fibers.

In this study, flat sheets and tubes of relatively large diameter (12-mm O.D.) were used to investigate important basic factors involved in the preparation of membranes by an electrodeless glow discharge of organic compounds.

Glow discharge polymerization can be achieved by a number of methods, e.g., d.c. and a.c. discharge with electrodes, and electrodeless discharge with radiofrequency (RF) and microwave. The majority of the studies that have appeared in the literature are concerned with polymer deposition onto an electrode. Buck and Davar⁴ have used glow discharge polymerization of monomer vapor using 40-kHz RF to prepare reverse osmosis membranes, by depositing polymer onto the surface of a porous support membrane (Millipore filter) fixed tightly on the surface of the electrode.

The size and shape of a membrane which can be prepared by the glow discharge deposition onto the electrode are limited by the size and shape of the electrode. For this reason, an electrodeless glow discharge seems to be a better way to prepare membranes, since polymer deposition occurs on any surface exposed to the glow discharge.

Connell and Gregor⁵ and Smolinsky and Heiss⁶ have used an electrodeless glow discharge to form a thin film on various kinds of substrate. The method used in this study is close to that of Smolinsky and Heiss, except that all polymer depositions were carried out in the glow region and that polymers were deposited onto nonconducting substrates such as organic polymers and glass. It seems very likely that properties of polymer formed in the glow region and in the nonglow region differ considerably, so that the best method and monomers found in this study may not necessarily apply to the deposition in nonglow region deposition. Therefore, all findings and discussions presented in this paper, in the quantitative sense, are confined to the particular sets of conditions used in this work.

EXPERIMENTAL

Apparatus

The apparatus used in this study is illustrated schematically in Figure 1. The discharge vessel consists of glass tubes with standard taper joints. The sample-holding unit has an inside diameter of 40 mm and a length of 300 mm; the discharge unit is tapered from a 50-mm to a 22-mm inside diameter

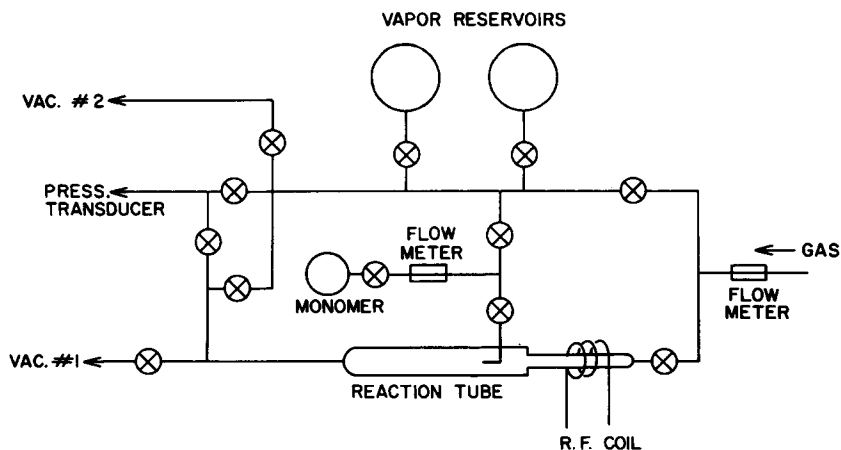


Fig. 1. Schematic representation of an electrodeless glow discharge system.

section which is inserted into the coil and has an overall length of 350 mm. The volume of the discharge vessel is 960 cc. The discharge unit has a monomer inlet placed in the center of the tube.

Since all parts are glass and are assembled by means of ground-glass joints, the reaction vessels are interchangeable for cleaning and degassing steps. All glass parts are cleaned by immersing in chromic acid cleaning solution for several hours, followed by rinsing, scrubbing with Alconox solution, and a final copious deionized-water rinse. The small amount of deposition occasionally left behind by this process is removed by baking in an annealing oven. Because of the standard taper joints and stopcocks used, the reaction vessels loaded with a sample can be degassed first on an auxiliary vacuum system and then transferred to the plasma apparatus vacuum system, thereby increasing the number of samples prepared within a given time.

The discharge vessel, when mounted in the plasma apparatus, is connected to a McLeod gauge and to a differential pressure transducer (the MKS Baratron pressure meter). The McLeod gauge is used to check the reference vacuum for the differential pressure transducer (less than 10^{-5} mm Hg) and also to calibrate the pressure gauge. Since the pressure of monomer vapor cannot be measured by a McLeod gauge due to the condensation of vapor during the compression process of the measurement, all pressure readings in either closed or flow systems are taken with the pressure transducer.

The apparatus can be evacuated to less than 10^{-5} mm Hg by a mercury diffusion pump backed by a rotary pump. However, for most experiments, the diffusion pump was bypassed and the system pumped down to a level of 0.2μ Hg before monomer vapor was introduced. The reference vacuum for the pressure transducer was always connected to the diffusion pump and kept at the level of less than 10^{-5} mm Hg.

An electrodeless radiofrequency discharge was used to initiate the plasma. The RF power supply is a radiofrequency transmitter, Heathkit Model DX60B. The output is fed into a linear amplifier, Heathkit SB-200, having a 500-watt capacity. The amplifier output is connected to the RF coil through a network of tunable capacitors. A Bendix coupler Model 262, 0.5–225 mc/sec, was used to measure the RF power. The RF power supply operates at 13.56 MHz and delivers continuously variable output power from 0 to 200 watts. A tuning circuit, located between the generator coil and the coupler, is used to match the impedance of the discharge vessel and the impedance of the amplifier output. The tuning circuit is adjusted so that the reflected power is maintained at the minimum.

Substrates

The substrates used include Millipore filters, porous polysulfone films, and porous glass tubes. The Millipore filters (VSWP-250 Å pore) were used as received from the Millipore Corporation, Bedford, Massachusetts. The porous polysulfone films were cast from a 20% polymer in N,N-dimethylformamide solution of polysulfone P-3500, provided by courtesy of Union Carbide. Cast films (5 mils casting thickness) were coagulated by water at 13°C. The casting and coagulation were carried out by a moving Mylar film-casting device traveling at a speed of approximately 50 cm/min.

The porous glass tubes (50 Å pore) were generously supplied by special courtesy of Corning Glass Works, along with invaluable information pertaining to the properties and proper processing of the tubes. The tubes could be recycled after each use by washing in deionized water, vacuum drying, then heating in a high-temperature oven slowly to 200°C (3 hr), and then more rapidly to 600°C (2 hr), where they were baked clean in 1 hr. The oven was then cooled to 200°C and the tubes stored until used in the oven at this temperature to avoid sorption of water, organic vapors, etc., by the highly porous tubes.

The polysulfone and Millipore substrates were mounted in the chamber by placing them tightly against the wall of the reaction tube using a Mylar film mask. The porous glass tubes were mounted in the center of the reaction tubes by inserting them onto glass tube extensions which are connected to the monomer inlet tubes by ground glass joints.

For each sample, the chamber is evacuated to less than 0.2 μ Hg and then checked (to make sure no leaks or further significant degassing occur) by isolating the chamber from the pump and determining that the pressure rise in the chamber is below 0.5 μ Hg for a 10-min period. The substrate is then ready for introduction of monomer, etc.

Monomers

The monomer is placed in a reservoir needle-valve flowmeter assembly that is connected to the reaction vessel by ground-glass joints. The pre-distilled monomer is degassed in the reservoir and thereafter kept under

vacuum. All monomers used to prepare reverse osmosis samples were previously characterized by determining flow rates in the system and deposition rates onto glass slides of polymer produced during specified glow discharge conditions.

Experimental Conditions

The various operational methods that can be used to prepare reverse osmosis samples will be described in detail in a later section (methods I–VII) and are summarized in Table I. The choice of one of the methods in the preparation of a particular sample is made on the basis of certain known characteristics of the monomer–substrate combination being employed (i.e., whether the monomer pressure increases or decreases in glow discharge, whether a monomer-saturated substrate or monomer flow system is being used, the rate and amount of sorption and/or adsorption by the substrate of the monomer, and the plasma susceptibility of the substrate).

TABLE I
Operational Factors Involved in Methods of Reverse Osmosis Membrane Preparation by Glow Discharge

Method	Monomer feed-in during glow discharge	Pumping during glow discharge	Sorption of monomer by substrate	Vapor pressure cited represents pressure of
I	+	+	–	steady-state flow before glow discharge
II	–	–	+	pseudosaturation ^a
III	–	–	–	monomer vapor reservoir
IV	+	–	+	pseudosaturation ^a
V	+	–	–	monomer vapor reservoir
VI	+	+	+	pseudosaturation ^a
VII	–	+	+	pseudosaturation ^a

^a Monomer is fed into a system with a porous substrate by a constant flow rate until the pressure of the system reaches a predetermined level. A substantial amount of monomer is sorbed by a substrate when the pressure reaches a given value; however, the substrate is not saturated, in a strict sense, at the monomer pressure cited.

The time of treatment needed, once the glow discharge is initiated, to deposit a sufficient amount of material is predicted from the deposition rate determined for each monomer. The wattage of the run is chosen as the lowest power that will maintain a full glow discharge in the entire reaction vessel once the glow discharge is initiated. The full-glow discharge region, instead of the nonglow discharge region, was chosen because in this system the amount of polymer deposition was very small and quite erratic in the nonglow region as compared to the full-glow region.

At the end of the specified treatment, the plasma discharge is stopped; if applicable, the monomer feed-in is discontinued and the reaction chamber is pumped out for 5 min to remove any residual monomer, etc. The sample is then exposed to air and is ready for testing.

POLYMER DEPOSITION BY AN ELECTRODELESS GLOW DISCHARGE

The rate of polymer deposition has recently been studied using the same system used for the membrane preparation for styrene,⁷ various olefinic monomers,⁸ and unconventional monomers⁹ which do not polymerize by conventional means of polymerization. Some important factors found in these studies are briefly presented here in order to present a general picture of a glow discharge polymerization used in this approach. The deposition rate R , (g/cm²-min) measured in the glow region of a steady-state flow of monomers is proportional to the weight basis flow rate F_w (g/min),

$$R = k F_w. \quad (1)$$

F_w is related to the monomer flow rate based on the volume F_v (cc(S.T.P.)/min), which can be easily measured by the pressure-volume relationship as follows:

$$F_w = \frac{M}{2.24 \times 10^4} F_v \quad (2)$$

where M is the molecular weight of a monomer. When the flow rate is controlled by changing monomer flow-in rate with constant pumping rate, F_v is generally given by

$$F_v = \alpha p_M^2 \quad (3)$$

where p_M is the monomer vapor pressure in a steady-state flow. Hence, the polymer deposition rate R is related to the monomer vapor pressure p_M as follows:

$$R = k \cdot \frac{M}{2.24 \times 10^4} \cdot \alpha p_M^2 \quad (4)$$

$$= a p_M^2. \quad (5)$$

As seen in eq. (4), the polymer deposition rate is a function of the characteristic rate constant k , molecular weight of monomer, the flow rate constant α , and the vapor pressure of the monomer. The constant α is dependent on how the steady-state flow of the monomer is maintained. Once conditions are set for a series of experiments and α values are measured in a consistent manner, the characteristic polymer deposition rate of monomers can be expressed by the constant k , in units of 1/cm², and is characteristic of a specific system.

The polymer deposition in an electrodeless glow discharge used in this study was found to be (1) linearly proportional to the discharge time and

(2) nearly independent of discharge wattage. As seen in eq. (4), the polymer deposition rate is dependent on the molecular weight of the monomer. Consequently, the higher the molecular weight of monomer, the higher the rate at which polymer deposits from a flow system of a given pressure.

The double bond of vinyl compounds (olefinic double bonds) was found not to play a major role in polymer deposition in an electrodeless glow discharge, and many organic compounds which do not contain olefinic double bonds have, by and large, similar k values according to the molecular weight.

It seems most probable that glow discharge polymerization proceeds via a unique polymerization mechanism of ionized molecules and the primary radicals formed from ions, and is completely different from conventional addition polymerization. It was found that many monomers which have plasma-susceptible groups and structures tend to decompose in a glow discharge and that polymers deposited from these monomers have considerably different properties from what would be expected from the structure of the original monomers. For this reason, many vinyl and acrylic esters were found not suited for this type of application. This is in strong contrast to the results of Buck and Davar⁴ (deposition onto an electrode by 40 kHz RF) in which a mixture of vinylene carbonate and acrylonitrile gave the best results. At least two major factors can be responsible for this difference.

One is the difference between the two mechanisms of polymer deposition onto an electrode and that onto the wall in an electrodeless glow discharge. In the former case, the adsorption of monomer plays an important role¹⁰⁻¹⁵ and the polymer deposition seems to be a consequence of simultaneous plasma polymerization and plasma-initiated adsorbed monomer (conventional polymerization). In the latter case, the polymerization in plasma (vapor phase) seems to play the major role.^{8,9}

Another factor is the difference in frequency. Perhaps in a low-frequency discharge, the plasma-initiated polymerization of adsorbed monomer is more significant due to the relatively slow cycle of excitation as compared to the lifetime of the excited species and the rate of supply of new monomer.

It is interesting to note that better reproducibility in the preparation of a reverse osmosis membrane by an electrodeless glow discharge was obtained with unconventional monomers which do not polymerize by other means, indicating that the absence of plasma-initiated polymerization of sorbed monomer simplifies the procedure.

The values of the polymer deposition rate constant a for some monomers are listed in Table II as a comparison of vinyl and unconventional monomers.

In order to prepare a reverse osmosis membrane by plasma polymerization, the polymer formed should be moderately hydrophilic so that a reasonable water throughput can be obtained.¹⁻³ Many hydrophilic organic compounds, however, contain structures and groups which cause decomposition of monomer in glow discharge and do not remain in the resultant polymer deposition.⁹ Therefore, a very hydrophobic polymer deposition is

TABLE II
Polymer Deposition Rate Constants a for Various Monomers^a

Vinyl monomers		Unconventional monomers	
Monomer	$a \times 10^4$, g/(cm ² · min· torr ²)	Monomer	$a \times 10^4$, g/(cm ² · min· torr ²)
4-Vinylpyridine	16.4	4-Methylbenzylamine	14.4
Styrene	12.1	4-Ethylpyridine	10.0
5-Vinyl-2-methylpyridine	11.9	Ethylbenzene	9.4
2-Vinylpyridine	10.4	3,5-Lutidine	8.8
N-Vinylpyrrolidone	9.7	N-Methylpyrrolidone	8.3
Acrylonitrile	7.2	Pyridine	7.5
Glycidyl methacrylate	4.0	Benzene	6.0
Methacrylic acid	1.9	Propionitrile	4.9
Vinyl acetate	1.3	<i>n</i> -Hexane	2.7
Vinylene carbonate	1.2	Cyclohexane	2.7
Acrylic acid	0.7	Dimethylsulfoxide	0.6

^a Polymer deposition rate R in g/(cm²·min) is given by $R = ap_M^2$, where p_M is the pressure of monomer in a flow system (before a glow discharge is initiated).

often obtained from a very hydrophilic organic compound. Accordingly, the choice of monomer should be based on the plasma polymerization characteristics as well as the hydrophilicity of organic compounds. Many nitrogen-containing organic compounds, particularly heteroaromatic amines and aromatic amines, were found to form polymer depositions which have excellent reverse osmosis characteristics.

POLYMER DEPOSITION ONTO POROUS SUBSTRATES

Polymer deposition onto a porous substrate is considerably different from that onto a nonporous inert surface such as a glass slide used in the investigation of polymer deposition rates described in the previous section. At least three major factors, described below, are found to play important roles in the preparation of reverse osmosis membranes by an electrodeless glow discharge of a monomer vapor.

Effect of Glow Discharge onto the Porous Substrate

This factor is particularly important when polymeric porous substrates are used. All polymers degrade and lose weight when samples are exposed to a glow discharge. The dependence of polymer degradation (manifested by the weight loss rate) on the experimental factors has recently been studied using the same system used in this study.¹⁶

It was found that (1) the weight loss is proportional to the exposure time, (2) the pressure of plasma has little effect, (3) the rate of weight loss is highly dependent on the discharge wattage (the higher the wattage, the higher the rate of weight loss), and (4) the deposition of polymer from vapor of monomer plasma onto a (nonporous) polymeric substrate does not com-

pletely shield the substrate polymer from degradation, and particularly at higher wattage the weight loss often exceeds the weight increase due to polymer deposition.

For the preparation of reverse osmosis membranes, the plasma susceptibility of porous polymeric substrate and the discharge wattage necessary to maintain a glow discharge of a monomer play a very important interrelated role.

Adsorption (or Sorption) Characteristics of Porous Substrates

Another important factor that is encountered in polymer deposition onto porous substrate is the adsorption or sorption characteristics of a porous substrate. This factor influences the polymer deposition in the following manner.

Porous substrates, in general, have a large internal surface area and are good adsorbing material. Consequently, the degassing of the substrate to maintain a desired vacuum level is dependent on how much and how strongly gases and vapors (particularly water vapor) are held by a porous substrate. Some of the vapors, particularly water vapor in a hydrophilic porous substrate, are difficult to degas by pumping. Thus, they will be evolved when

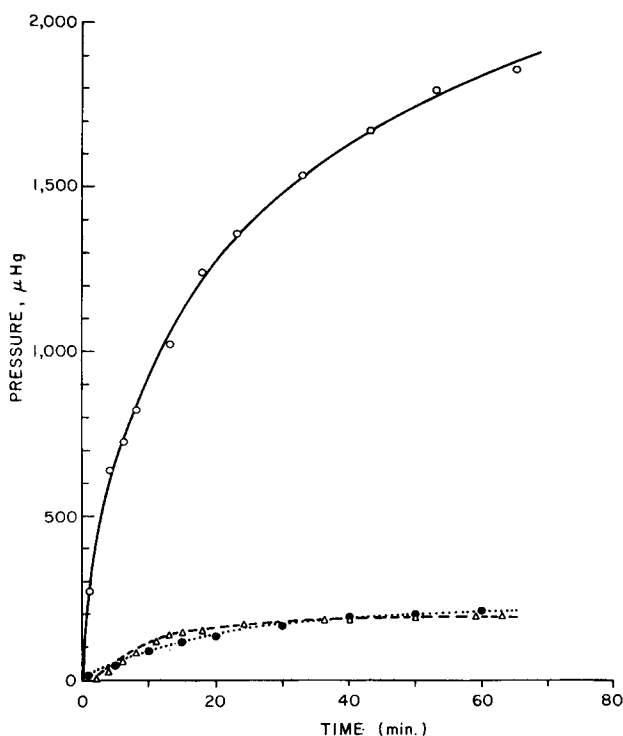


Fig. 2. Change of pressure in a chamber which contains a substrate in a glow discharge (under vacuum): (O) Millipore filter; (●) glass slide; (Δ) porous polysulfone film.

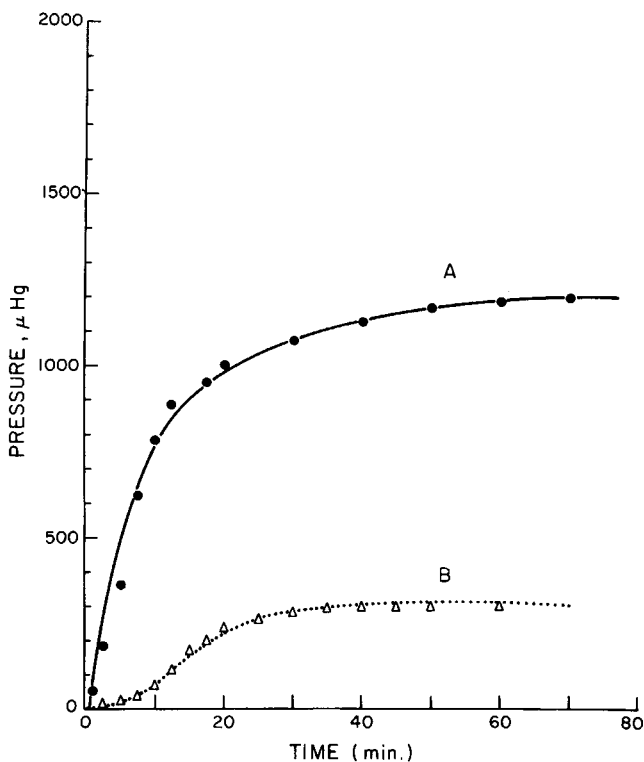


Fig. 3. Change of pressure in a chamber which contains a porous glass tube in a glow discharge (under vacuum): (A) porous glass tube stored in a dust-free container after the tube is baked at 600°C; (B) same tube used in A, but immediately after the tube is baked at 600°C.

the plasma is initiated, causing an uncontrollable effect due to this additional vapor plasma. In this respect, the hydrophilicity of the porous substrate plays a significant role in determining the reproducibility of polymer deposition.

When monomer vapor is introduced into the reaction system, some monomers will be adsorbed or sorbed by a porous substrate. The partition between vapor phase and sorbed phase is dependent upon the adsorbing capability of a porous substrate. For instance, when a porous glass tube is used as a substrate, nearly 100% of the monomer fed into a closed system is adsorbed, and it is difficult to establish a steady-state flow of monomer vapor until the substrate is saturated with the monomer, which takes several hours at the flow rates used in this study.

The measurement of pressure change in a reaction chamber which contains a well-degassed substrate in a glow discharge under vacuum will provide information on the combined effects of plasma susceptibility and desorption characteristics of a porous substrate. In Figure 2, plots of pressure versus time of plasma treatment are presented for Millipore filter

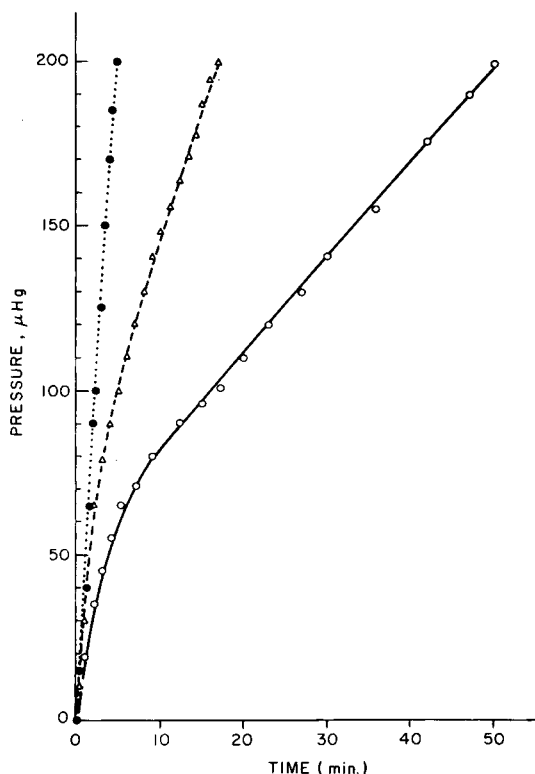


Fig. 4. Pressure buildup in a chamber containing a substrate when 4-vinyl pyridine is introduced at constant flow rate: (O) Millipore filter; (●) glass slide; (Δ) porous polysulfone film.

and porous polysulfone film. The results indicate that porous polysulfone is very stable against glow discharge and behaves similarly to glass tubes alone. The increase of pressure with a Millipore filter is most likely due to the degradation of polymers since a Millipore filter disappeared when it was exposed to prolonged glow discharge.

The pressure changes with nondegradable porous glass are shown in Figure 3 as plots similar to those of Figure 2. A porous tube, which was baked at 600°C and kept in an airtight glass-tube container for over several weeks, was placed in the reaction tube and degassed by vacuum. After the overnight degassing, the pressure of the reaction tube reached below the $0.5 \mu\text{Hg}$ level, and the leakage rate (including the degassing rate from the porous glass tube) was confirmed to be below the acceptable level. As seen by curve A in Figure 3, this tube showed marked increase of pressure in a glow discharge, but with a clear indication of leveling off with exposure time. When the same tube was baked again at 500°C and used immediately after cooling, the pressure was reduced to nearly the same level as that of the plain reaction tube (considering the increase in total surface area with the porous glass tube in the reaction chamber).

The pressure increase in a reaction chamber which contains a porous substrate when a monomer vapor is introduced by a given flow rate can be utilized to calculate the sorption capability of the porous substrate. The pressure buildup curves are shown in Figure 4 for Millipore filter and porous polysulfone film. The pressure buildup curve with a porous glass tube is too slow to be presented in the same time scale. From the slope of the linear portion of the pressure buildup curve, the ratio of monomer sorbed/monomer fed into the system are estimated as 0.636 for the polysulfone film, 0.926 for Millipore filter, and 0.9987 for the porous glass tube.

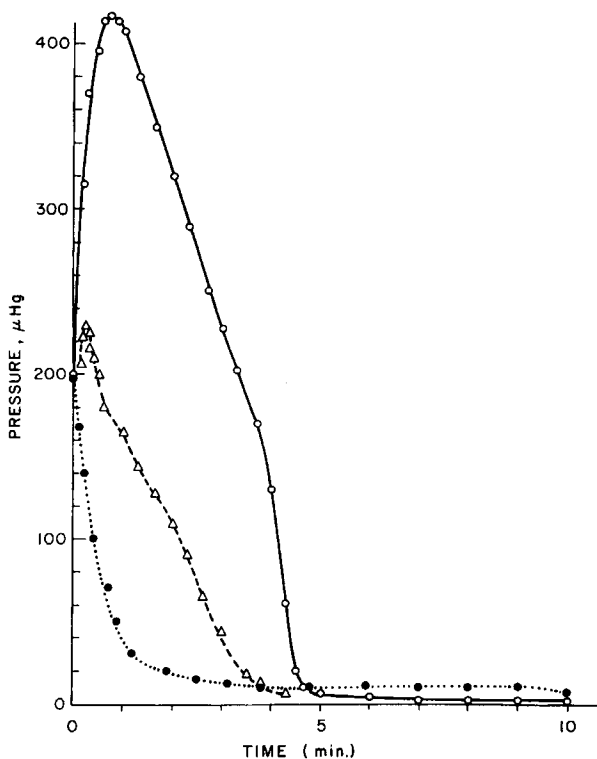


Fig. 5. Pressure change observed in a chamber containing a substrate pseudosaturated to an initial pressure of $200 \mu \text{ Hg}$ of 4-vinylpyridine, during glow discharge: (○) Millipore filter; (●) glass slide; (Δ) porous polysulfone film.

The sorption capability of a porous substrate and the effect of sorbed monomer on the polymerization of monomer vapor by glow discharge can be visualized by the pressure change in the similar system with a monomer (4-vinylpyridine), as shown in Figure 5. The monomer was introduced by a constant feed-in rate into a closed system which contains a porous substrate until the pressure of the system reached $200 \mu \text{ Hg}$. Consequently, the total amount of monomer introduced and the amount of monomer sorbed by a porous substrate are different depending on the sorbing capability of

the substrate. Without a porous substrate, the pressure of the system decreases as soon as a glow discharge is initiated. With a porous substrate which contains a certain amount of sorbed monomer, the pressure of the system increases at the initial stage, indicating that desorption rate of monomer exceeds the monomer consumption rate owing to polymerization.

The addition of nitrogen gas and water vapor changes the pattern of monomer adsorption, release of sorbed monomer, and polymerization of monomer vapor considerably, as seen in the similar plots shown in Figures

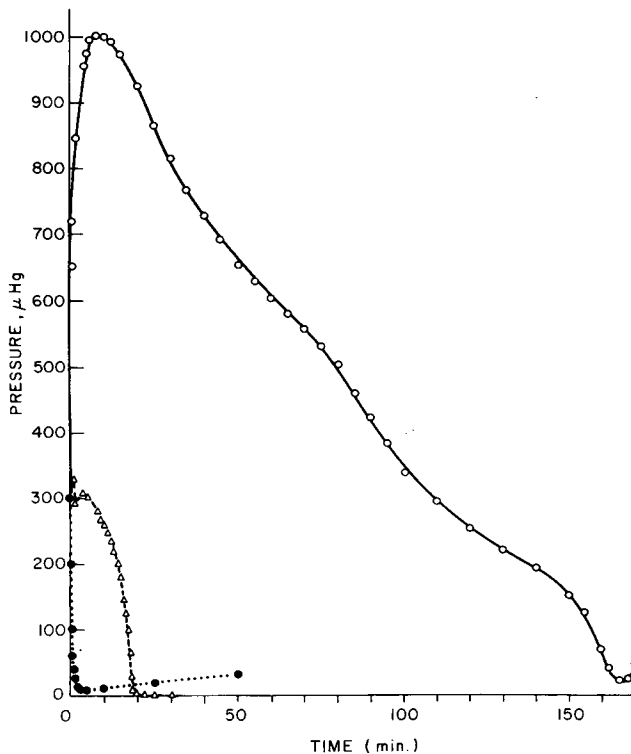


Fig. 6. Pressure change observed during glow discharge in a chamber containing a substrate pseudosaturated to $100 \mu \text{ Hg}$ of nitrogen and $200 \mu \text{ Hg}$ of 4-vinylpyridine ($300 \mu \text{ Hg}$ total pressure): (O) Millipore filter; (●) glass slide; (Δ) porous polysulfone film.

6, 7, and 8. With the addition of water vapor, the hydrophilicity of the porous substrate plays an important role which can be seen in the difference of pressure change observed when reversing the order of exposure to monomer and to water vapor. Namely, the amount of water vapor sorbed by hydrophilic Millipore filter is greater when water vapor is introduced first, whereas hydrophobic polysulfone sorbs more water when relatively more hydrophilic 4-vinylpyridine monomer is introduced first. Results shown in Figures 7 and 8 indicate that an excessive amount of water vapor prevents vapor-phase polymerization of 4-vinylpyridine.

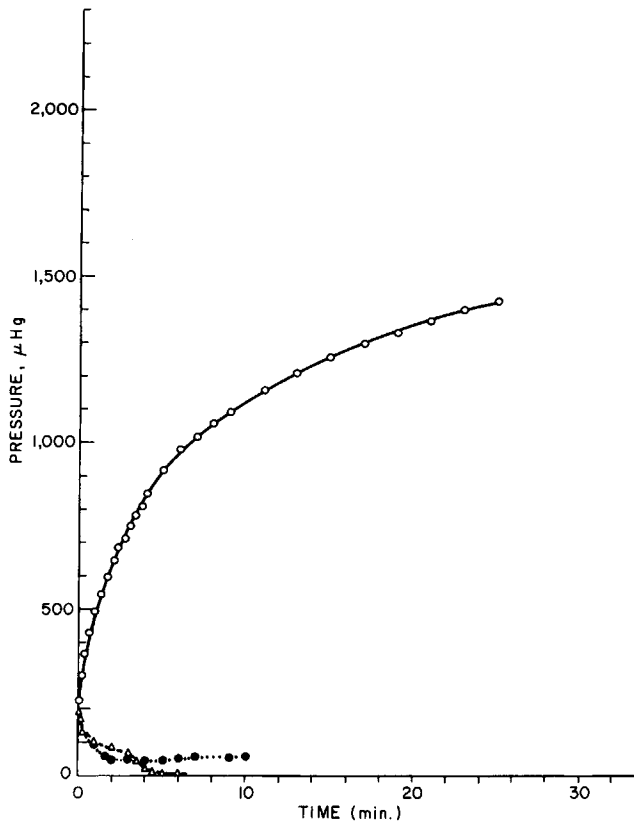


Fig. 7. Change of pressure observed during glow discharge in a chamber containing a substrate pseudosaturated first with water (to 20 μHg) and then with 200 μHg of 4-vinylpyridine (to 220 μHg total pressure): (O) Millipore filter; (●) glass slide; (Δ) porous polysulfone film.

Pore Size of Porous Substrate

The minimum thickness of polymer deposition needed to form a homogeneous flawless membrane is the radius of the pore it must bridge. Consequently, the reverse osmosis property of a composite membrane is greatly dependent on the pore size of a porous substrate.

TABLE III
Reverse Osmosis Characteristics of Porous Substrates^a

Porous substrate	Thickness, μ	Pore size, \AA	Water flux, gfd	Salt rejection, %
Millipore filter VS	48	250	400-500	0
Polysulfone	13	—	300-400	2-4
Porous glass	1100	50	0.6-1.0	5-10

^a Water flux and salt rejection were measured with 1.2% NaCl solution at 1200 psi applied pressure. Figures cited were taken after the initial drop of water flux which generally occurred in 2-3 hr were observed and the flux was stabilized.

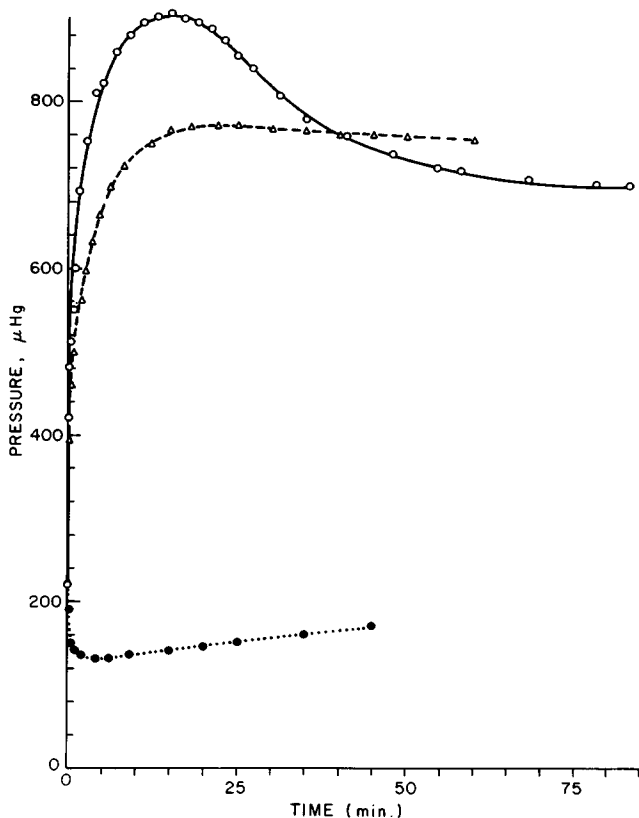


Fig. 8. Pressure change during glow discharge in a chamber containing a substrate pseudosaturated first with 4-vinylpyridine (to 200 μ Hg) and then with 20 μ Hg of water (to 220 μ Hg total pressure): (O) Millipore filter; (●) glass slide; (Δ) porous polysulfone film.

Reverse osmosis characteristics of porous substrates used in this study are summarized in Table III. The use of Millipore filter VC (nominal pore size 1000 \AA) as a substrate failed to produce good reverse osmosis membranes. It is estimated that a pore size of approximately 300 \AA or less is preferred in this application.

METHODS OF POLYMER DEPOSITION ONTO POROUS SUBSTRATES

The method to be used in depositing polymer membrane onto a porous substrate depends on the combination of the following factors: (1) available vapor pressure of a monomer, (2) characteristic polymerization rate of a monomer in a glow discharge, (3) the pressure change of a monomer in glow discharge (plasma susceptibility of the monomer), (4) plasma susceptibility of a porous substrate, (5) breakdown wattage necessary to initiate a glow discharge of a monomer, and (6) sorption characteristics of a

porous substrate. Using a vacuum RF discharge system described by Figure 1, the preparation of reverse osmosis membranes was carried out by the following methods:

Method I: Flow System. Monomer is fed in from the liquid monomer through an injection tube placed in the center of the reaction tube while the system was kept pumping.

Method II: Closed System with Sorption of Monomer by a Porous Substrate. Monomer is fed into a closed system at a constant flow rate until the pressure of the system reaches a predetermined level. No monomer feed-in and no pumping during the glow discharge.

Method III: Closed System without Sorption of Monomer by a Porous Substrate. Monomer vapor is stored in a reservoir without exposing the substrate to the monomer. As soon as the monomer vapor is introduced from the reservoir into a reaction tube which contains a porous substrate glow discharge is initiated.

Method IV: Semiclosed System with Sorption of Monomer by a Substrate. The procedure is similar to method II, except that monomer vapor is continuously fed into a closed system from a liquid monomer source during glow discharge.

Method V: Semiclosed System without Sorption of Monomer by a Substrate. Monomer vapor is allowed to build up in a reservoir from a liquid monomer source without exposing a substrate to the vapor. As soon as the monomer vapor is introduced into the reaction tube, glow discharge is initiated. Monomer vapor is continuously fed into a closed system from a liquid monomer source during glow discharge.

Method VI: Semiclosed System Connected to a Monomer Flow. The procedure is the same as method V, but as soon as glow discharge is initiated, the system is connected to a pump. This method is used when the pressure of a reaction tube rises due to either the decomposition of monomer or the plasma susceptible substrate.

Method VII: Semiclosed System Connected to Pump. The procedure is the same as method II, but as soon as glow discharge is initiated, the system is connected to a pump.

Operational factors in these methods are summarized in Table I. Some factors of porous substrates are compared in Table IV using 4-vinylpyridine as a monomer. The sorption capability of these porous substrates may vary with different monomers; however, it is expected that the variation due to type of monomer is small, since the major portion of monomer sorbed is by adsorption rather than sorption by solution of monomer in polymer of porous substrate.

The best method of polymer deposition from a monomer depends on the type of substrate; i.e., the best method for Millipore filter is not necessarily best for porous polysulfone. Due to many complicated factors which cannot be singled out, the best method for each substrate has to be established experimentally. In Table V, relatively good results obtained from 4-vinylpyridine with different substrates and by different methods are summarized.

TABLE IV
Some Factors of Porous Substrates in Preparation of Glow Discharge Deposition of 4-Vinylpyridine

Substrate	Pressure in-crease observed when substrate is exposed to plasma in vacuum, ^a μ Hg/30 min	Adsorption capability	Solvent power of monomer	Total sorption, ^b %	Remarks
Millipore VS	1500	moderate	swell	92.6	hydrophilic
Porous polysulfone	180	low	dissolve	63.6	hydrophobic
Porous glass	180	extremely high	no effect	99.9	hydrophilic

^a Substrate was well degassed prior to plasma exposure (pressure <0.5 Hg). The pressure increase may be caused by decomposition of substrate material and/or by degassing of strongly held gases and vapors by plasma exposure.

^b Total amount of monomer sorbed by physical adsorption on surface of pores and chemical sorption into material of porous substrate. Values are given by ratio in per cent of (amount of monomer sorbed)/(amount of monomer fed into the system) when the monomer is introduced by a constant flow rate until pressure of the system reaches 200 μ Hg.

TABLE V
Reverse Osmosis Results of Glow Discharge-Polymerized 4-Vinylpyridine Membranes
with Various Porous Substrates*

Substrate	Salt rejection, %	Water flux, gfd	Method of preparation
Porous glass			
13	70	0.46 ^b	III, 1000 μ Hg, 100 w, 20 m
16	87	0.51	VII, 130 μ Hg, 60 w, 13 m
17	90	0.49	VII, 130 μ Hg, 60 w, 35 m
7b	83	0.52	V, 36 μ Hg, 100 w, 10 m
24	71	0.51	IV, 130 μ Hg, 100 w, 10 m
23c	96	0.81	VII, 170 μ Hg, 60 w, 6 m
19d	80	0.78	VII, 130 μ Hg, 60 w, 16 m
Polysulfone			
Ro 165	79	9.9	IV, 380 μ Hg, 100 w, 5 m; 30 w, 5 m
Ro 169	89	4.0	V, 20 μ Hg, 30 w, 50 m
EPS 1	86	26.4	II, 200 μ Hg, 60 w, 10 m
EPS 17	80	2.0	II, 200 μ Hg, 60 w, 6 m
EPS 25	98	7.0	II, 200 μ Hg, 60 w, 7 m
Millipore VSW			
Ro 11	90	40.0	VI, 380 μ Hg, 150 w, 2 m; 30 w, 5 m
Ro 12	83	17.0	VI, 240 μ Hg, 150 w, 2 m; 30 w, 5 m
Ro 14	99	38.0	VI, 30 μ Hg, 150 w, 2 m; 30 w, 5 m
Ro 24	98	4.0	VI, 380 μ Hg, 150 w, 2 m; 30 w, 5 m
Ro 25	85	24.0	VI, 150 μ Hg, 100 w, 5 m
Ro 32	74	3.9	VI, 200 μ Hg, 80 w, 5 m
Ro 37	95	24.0	II, 200 μ Hg, 100 w, 5 m
Ro 91	89	2.0	VI, 100 μ Hg, 30 w, 3 m
Ro 98	96	1.1	VII, 1300 μ Hg, 150 w, 1 m; 30 w, 1 m
Ro 105	97	7.4	VII, 880 μ Hg, 100 w, 1 m

* 1.2% NaCl at 1200 psi.

^b The maximum water flux of porous glass tube (untreated) is approximately 1.0 gfd.

The results indicate that these three types of substrate can be utilized in the preparation of reverse osmosis membranes by glow discharge polymerization of 4-vinylpyridine, though the best method for each substrate has to be determined.

The following trends were repeatedly observed with 4-vinylpyridine as the monomer and may be worth mentioning here as general trends:

1. High monomer flow-in rate tends to cause less coherent, dark-colored deposition which yields poor salt rejection.
2. A good salt rejection with high water flux is obtained by polymer deposition which has a very light color regardless of the method involved.
3. Porosity of less than 300 Å is preferred for high salt rejection at high water flux. Millipore filter with a 1000-Å pore size failed to yield good reverse osmosis membranes.
4. Relatively low wattage, e.g., 30 watts, is sufficient to produce a good salt-rejecting membrane.

5. A certain amount of monomer sorbed by a substrate seems to help yield a good result, but an excessive amount of sorption seems to damage the reverse osmosis property of a glow discharge-polymerized polymer.

The sorbed monomer seems to behave in the following manner: (1) as a monomer reservoir which supplies monomer vapor, (2) as a solvent which alters the permeability characteristics of a substrate, (3) as a monomer which will undergo plasma-initiated (liquid phase) conventional polymerization, (4) as a monomer which may graft onto the substrate polymer, if a monomer is capable of polymerizing by addition polymerization in cases (3) and (4).

Since 4-vinylpyridine has a relatively low vapor pressure at ambient temperature, the feed-in rate from the liquid reservoir is rather low. A reasonable flow rate can be maintained in a flow system if the substrate does not sorb an appreciable amount of the monomer vapor, such as in the case of deposition onto slide glass. With a porous substrate, however, the sorption (or adsorption) rate of monomer vapor by a substrate is very high, and a flow of monomer cannot be maintained from a liquid monomer source, unless a glass tube of relatively large diameter without any constriction (such as flowmeter or needle valve) is used to connect the liquid reservoir to the reaction tube. Therefore, it is necessary either to store the monomer vapor in a large flask or to let a substrate sorb a substantial amount of monomer by continuous monomer feed-in in order to deposit a sufficient amount of polymer on the substrate.

A similar situation may be encountered with monomers which have a high boiling point and a relatively high rate constant a .

REVERSE OSMOSIS CHARACTERISTICS OF POLYMERS FORMED BY ELECTRODELESS GLOW DISCHARGE

Some reverse osmosis results of glow discharge polymer membranes obtained with porous polysulfone film as substrate are shown in Table VI. These results are not the best or optimized results obtainable with those monomers, since the method and time of treatment were deduced from the kinetic data and behavior of a monomer in a glow discharge. The best method for a combination of monomer and substrate can be found only by experimentation. Therefore, these data should be taken as an indication of the potentiality of glow discharge polymers as reverse osmosis membranes. The reverse osmosis membranes of glow discharge polymers have quite unique features which are completely opposite to generally found trends. These are: (1) steady increase of salt rejection and water flux with time of reverse osmosis run; (2) very stable water flux after the initial incline is stabilized (practically no water flux decline is observed with many membranes); (3) excellent performance at high salt concentration and under high pressure.

Buck and Davar⁴ reported that water flux increased steadily for the first eight days with glow discharge-polymerized membrane of vinylene car-

TABLE VI
Reverse Osmosis Results of Glow Discharge-Polymerized Polymers from Various Monomers with Porous Polysulfone Films as Substrates^a

Run no.	Monomer	Salt re- jection, %	Water flux, gfd	Method of preparation
3a	4-Vinylpyridine	95	1.6	II, 360 μ Hg, 60 w, 7 m
4b	N-vinylpyrrolidone	82	7.4	VI, 40 μ Hg, 30 w, 30 m
4h	N-vinylpyrrolidone	91	10.6	I, 20 μ Hg, 30 w, 30 m
5g	5-vinyl-2-methylpyridine	82	14.6	II, 500 μ Hg, 30 w, 3.5 m
6d	4-picoline	98	6.4	II, 540 μ Hg, 30 w, 8 m
6e	4-picoline	95	13.6	II, 560 μ Hg, 30 w, 3 m
6f	2-vinylpyridine	88	3.2	II, 380 μ Hg, 30 w 2.5 m
6k	pyridine	62	10.4	II, 560 μ Hg 30 w 5 m
6l	1-methyl-2-pyrrolidone	60	26.0	I, 28 μ Hg, 60 w, 30 m
6m	4-ethylpyridine	98	9.6	II, 520 μ Hg, 30 w, 7 m

^a 1.2% NaCl at 1200 psi.

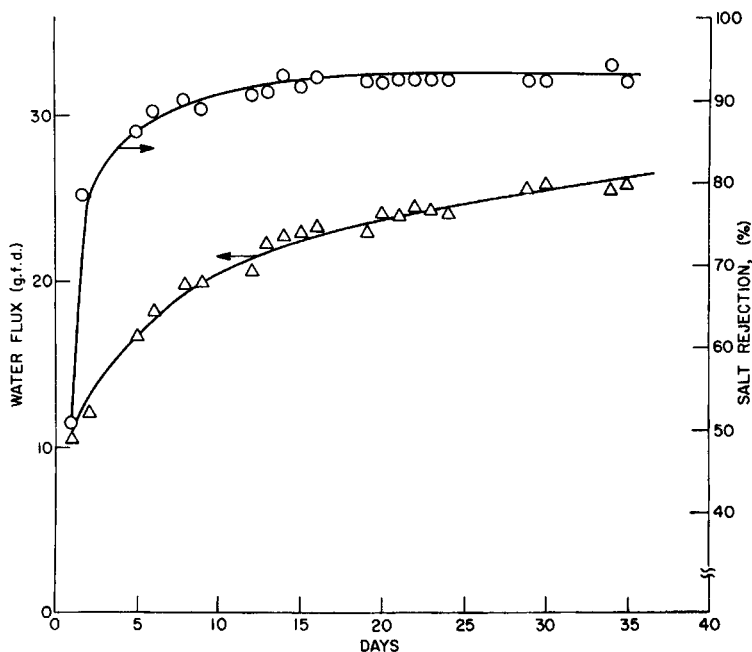


Fig. 9. Change of salt rejection and water flux with time (1.2% NaCl, 1300 psi). Membrane of plasma-polymerized 4-vinylpyridine on Millipore VS filter.

bonate and acrylonitrile mixture (deposited onto a Millipore VS filter fixed to an electrode at 40 kHz). Membrane prepared in this study showed more pronounced increases in both water flux and salt rejection, and some examples are shown in Figures 9 and 10. These trends (i.e., increases in water flux and salt rejection with time) are found regardless of type of substrate, type of monomer used, concentration of salt, and pressure. There-

TABLE VII
Effect of NaCl Concentration and Applied Pressure

Membrane		1.2% NaCl at 1200 psi		3.5% NaCl at 1500 psi	
Monomer	Substrate	S.R., %	gfd.	S.R., %	gfd
4-Picoline	polysulfone	97.7	7.7	96.0	7.6
4-Methylbenzylamine	polysulfone	89.6	2.0	96.0 ^a	2.2
<i>n</i> -Butylamine	polysulfone	93.1	2.3	93.7	2.7
4-Vinylpyridine	polysulfone	96.5	3.7	96.7	4.9
		0.3% NaCl at 1000 psi		3.5% NaCl at 1500 psi	
4-Vinylpyridine	porous glass tube	95.5	0.72 ^b	96.4	0.80 ^b
3,5-Lutidine	polysulfone	81.1	6.2	99.0	12.0

^a Membrane was beginning to increase S.R. and water flux when feed solution was changed.

^b Water flux of untreated porous glass tube is approximately 1.0 gfd.

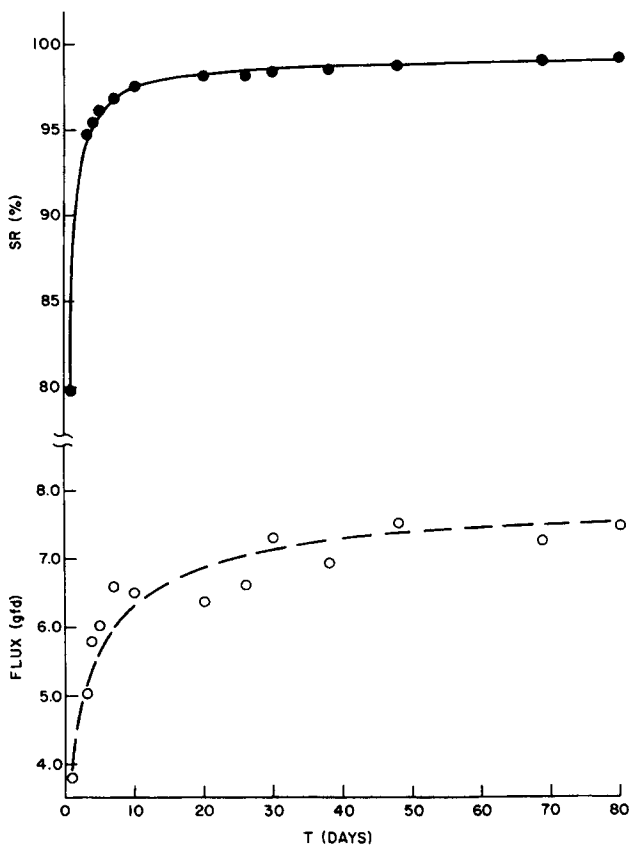


Fig. 10. Change of salt rejection (SR) and water flux with time (3.5% NaCl, 1500 psi). Membrane of plasma-polymerized 4-vinylpyridine on porous polysulfone film.

fore, this feature is a unique characteristic of glow discharge polymer and is probably due to chemical changes in the membrane as suggested by Buck and Davar.⁴ The water flux of many conventional polymers declines with time owing to compaction of the membrane, and the trend is more pronounced with high salt concentration and high pressure. In this respect, the glow discharge polymers have an excellent suitability for sea water conversion by reverse osmosis. The composite membranes prepared by glow discharge showed equally good performance under conditions for sea water conversion and brackish water treatment, as shown in Table VII.

CONCLUSIONS

It may be concluded that an electrodeless glow discharge as described in this paper can be effectively utilized to prepare reverse osmosis membranes using appropriate porous substrates, and that reverse osmosis membranes so prepared have unique features which make the glow discharge polymer particularly suited for sea water conversion, and for other applications under severe conditions.

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