

Preparation of Composite Reverse Osmosis Membranes by Plasma Polymerization.

II. Copolymerization of Unusual Comonomers

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Synopsis

Preparation of composite reverse osmosis membranes by plasma polymerization of 4-picoline, 3,5-lutidine, benzene, and acetylene with unusual comonomers such as H₂O and N₂ is investigated using the flow system of the monomers and an electrodeless glow discharge with 13.5 MHz radio frequency. These comonomers are incorporated into the plasma polymers and change their properties. Consequently, relatively hydrophilic polymers are formed from rather hydrophobic monomers such as benzene and acetylene by the copolymerization. The addition of H₂O and N₂ also improves the reverse osmosis characteristics of plasma polymers from hydrophilic monomers such as 4-picoline and 3,5-lutidine. The reverse osmosis characteristics of plasma polymers are influenced by the ratio of H₂O and N₂ to the basic monomer as well as by the total pressure of the monomers.

INTRODUCTION

In part I of this series of studies,¹ an extensive search of candidate monomers which might yield good reverse osmosis membranes was carried out. Because of the fragmentation of monomer molecules that occurs during plasma polymerization, many hydrophilic organic compounds having oxygen-containing groups (such as OH and carbonyls) do not polymerize well in plasma, and the polymers formed are too hydrophobic to be used as reverse osmosis membranes, which require high water throughput. Consequently, only nitrogen-containing compounds such as amines, aromatic amines, and hetroaromatic amines are found to be easily converted to reverse osmosis membranes.

In a series of studies on plasma polymerization of hydrocarbons,² amines, and nitriles,³ it is also found that nitrogen is easily incorporated into plasma polymers regardless of the chemical nature of nitrogen in monomers and that triple bond and aromatic structure contribute in a comparable manner to the plasma polymerization, which incorporates nitrogen efficiently.

In this study, the effects of nitrogen and water vapor, which essentially copolymerize with triple-bond, aromatic, and hetroaromatic compounds, on the reverse osmosis characteristics of the polymers are investigated.

EXPERIMENTAL

Plasma polymerization is carried out by the apparatus previously described in reference 4, which utilizes inductive coupling of 13.5 MHz radio frequency. Monomers are used as supplied, without further purification; however, liquid monomers are carefully degassed before they are used.

The condensibility of the monomer used in an experiment is checked by condensing a known amount of monomer by surrounding a cold finger (located in the monomer inlet system) with liquid nitrogen. Since the largest impurity in a vacuum system is caused by the leak of air, this condensibility test is found to be a very satisfactory means of checking the purity of monomers.

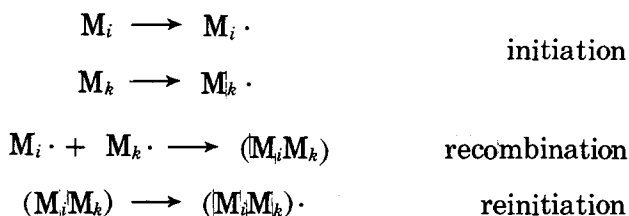
The procedure of membrane preparation is essentially the same with method I described in part I,¹ which uses the flow system of the monomer.

Reverse osmosis test is carried out with 3.5% NaCl solution at 1500 psi pressure using a high flow system. Test cells used for reverse osmosis test are similar to Millipore XX 44 04700 high-pressure 47-mm filter holder, but they are machined out from 316 stainless steel stock with modification according to McKinney's design.⁵ The details of the test cell can be also seen in reference 6. Four test cells are employed in a test loop pressurized by a 5.1 gph capacity pump (Milroyal, Model A, Milton Roy Co.)

Copolymerization of N₂, H₂O, and CO With Some Monomers By Plasma

Recent studies^{2,3} on the production of hydrogen gas accompanied by polymer formation from various organic compounds by plasma indicate that the following reactions seem to contribute the formation of free radicals: (1) hydrogen detachment, (2) opening of cyclic structure and double bond, (3) opening of triple bonds such as C≡C and C≡N, and (4) opening or fragmentation of aromatic and hetroaromatic structures.

Although the polymerization mechanism based on the free-radical reactions is neither fully elucidated nor confirmed, the following scheme of radical plasma polymerization seems to provide a useful conceptual view of the nature of plasma polymerization and the characteristic properties of polymers formed under the influence of the plasma condition of monomers. The reactions can be schematically represented by



where i and k are numbers of repeating units, i.e., $i = k = 1$ for the monomer.

The main difference between the conventional free-radical addition polymerization and the plasma polymerization is that the propagation via addition of free radical onto the double bond of the monomer is not necessary (and perhaps play a relatively minor role) in plasma polymerization, and the recombination of two free radicals, which is one of the major steps of termination of the chain growth in the conventional addition polymerization, is the main step of forming polymers. This scheme can reasonably explain the fact that nearly all organic compounds can be polymerized in plasma.

This scheme can also account for the fact that plasma polymerization often occurs under the condition where the rate of formation of free radical is extremely high.⁷ Under such a condition, the conventional addition polymerization cannot proceed due to premature termination of the growing chain, and therefore the assumption that precursor structures which can undergo polymerization are formed in plasma is not only unnecessary but also useless to explain plasma polymerization.

This scheme also suggests that any gases and vapors can create intermediate species in the form of free radicals in plasma can be incorporated into the polymer. The incorporation of unusual comonomers (such as N_2 and H_2O) can be realized in the following observations: (1) The rate of polymer deposition increases with addition of these monomers. (2) The concentration of trapped free radicals, and the color of the polymer is altered by the addition of the comonomers. (3) The existence of some element which is absent in the main monomer is confirmed by elemental analysis, ESCA Spectra (e.g., N in acetylene polymers). (4) IR spectra and surface properties (such as contact angle) are significantly altered by the addition of the comonomers.

The details of copolymerization of acetylene are presented in a separate paper, and only practical aspects in the membrane preparation is presented in this paper. Because of the fragmentation of aromatic and hetroaromatic compounds, benzene may be equivalent to three molecules of acetylene, and pyridine may be equivalent to two acetylene and one $HC\equiv N$ in plasma polymerization. Based on this viewpoint, preparations of reverse osmosis membranes from hetroaromatic amines, acetylene, and benzene with the addition of H_2O and N_2 are investigated in this paper.

RESULTS AND DISCUSSION

The addition of N_2 to 4-picoline greatly changes the reverse osmosis characteristics of plasma polymers. In Figure 1, the change of reverse osmosis characteristics with deposition time is shown in plot of log water flux versus salt rejection for 4-picoline (20 μm Hg), 4-picoline (50 μm Hg), 4-picoline (20 μm Hg) + N_2 (60 μm Hg), and 4-picoline (50 μm Hg) + N_2 (50 μm Hg). Without addition of N_2 , better reverse osmosis results are obtained by employing low pressure, although this procedure requires a longer deposition time. With addition of N_2 , reverse osmosis characteristics are improved at both vapor pressure levels evidenced by the shift of curves toward upper right-hand sides. The improvement is more pronounced at higher vapor pressure (i.e., 50 μm Hg), and better membranes are obtained with considerably shorter deposition time. (Note that results shown in Fig. 1 are obtained with 1.2% NaCl and 1200 psi, whereas the rest of results are with 3.5% NaCl and 1500 psi.)

Reverse osmosis results obtained with various amounts of N_2 at various 4-picoline and water vapor pressure are shown in Table I. The ratio of 4-picoline to H_2O is maintained at 4:1. There seems to be a trend that, whenever the total pressure of the system exceeds a certain level, the reverse osmosis characteristics deteriorate. This trend is more evident in results shown in Table II where argon is added to increase the total pressure. The addition of nonpolymerizing argon is thought to dilute the monomers and reverse the

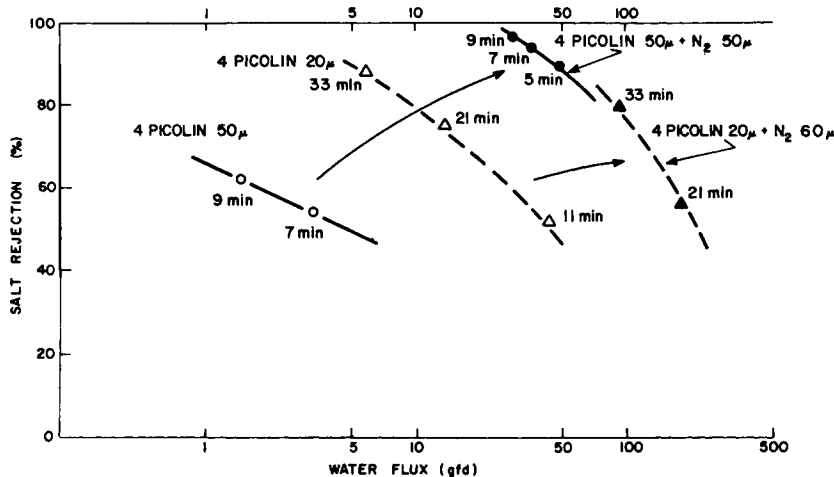


Fig. 1. Reverse osmosis characteristics of composite membranes prepared by plasma polymerization of 4-picoline with and without N_2 at two vapor pressures (porous polysulfone film as the substrate; 1.2% NaCl at 1200 psi).

trend found as the ceiling pressure. Since addition of an additional gas would change many other aspects of plasma, the result may not be attributed to a single factor. Nevertheless, results shown in Tables I and II indicate that the total pressure could be an important factor in preparation of membranes by plasma polymerization.

Results obtained by plasma polymerization of 3,5-lutidine are shown in Table III. Comparison of Table III with Table I indicates that there is little

TABLE I
Reverse Osmosis Results^a of Composite Membrane Prepared by Plasma Polymerization of 4-Picolin- H_2O-N_2 Series with Porous Polysulfone Film as the Substrate

Run no.	Vapor pressure 4P/ H_2O/N_2 , μ m Hg	Time, min	Salt rejection, %	Flux, gfd
121	20/5/0	7	93.5	2.6
122	20/5/20	7	97.2	8.2
123	20/5/40	7	97.2	16.0
124	20/5/60	7	84.1	20.1
126	30/7.5/0	5	95.6	1.2
127	30/7.5/20	5	93.3	3.2
128	30/7.4/40	5	72.7	4.4
160	30/7.5/60	5	67.7	11.0
130	30/7.5/80	6	42.1	13.6
161	40/10/0	3.5	61.9	4.4
131	40/10/20	3.5	93.1	3.5
132	40/10/40	3.5	93.9	3.5
133	40/10/62	3.5	12.0	30.2
135	40/10/80	3.5	28.0	18.5
140	10/2.5/0	15	97.2	4.8
162	10/2.5/10	15	94.6	12.5
136	10/2.5/20	15	77.4	35.6
137	10/2.5/40	15	28.6	75.6

^a 3.5% NaCl, 1500 psi.

TABLE II
Effect of Addition of Ar to Increase the Total Pressure of the System on Reverse Osmosis Characteristics of Plasma Polymer of 4-Picolin-H₂O-N₂^a

	Partial pressure, $\mu\text{m Hg}$	Time, min	Salt reject, %	Flux, gfd
<u>Without Ar</u>	4-P/H ₂ O/N ₂ = 20/5/20	7	97.2	8.2
<u>With Ar</u>	4-P/H ₂ O/N ₂ /Ar = 20/5/20/10	7	96.0	4.9
	20/5/20/40	7	90.6	12.1

^a Membranes are made with porous polysulfone as the substrate; 3.5% NaCl, 1500 psi.

TABLE III
Reverse Osmosis Results^a of Composite Membranes Prepared by Plasma Polymerization of 3,5-Lutidine with Porous Polysulfone Film as the Substrate

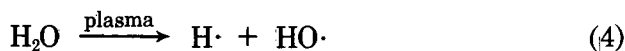
Vapor pressure Lu/H ₂ O/N ₂ , $\mu\text{m Hg}$	Time, min	Salt rejection, %	Water flux, gfd
10/2.2/10	15	93.6	4.3
10/2.2/10	25	93.7	4.0
18/4.7/21	8.5	91.0	19.0
18/4.7/21	15.0	77.6	14.6
18/4.7/21	20.0	88.1	16.8
8/6/50	10	93.0	9.8

^a 3.5% NaCl, 1500 psi.

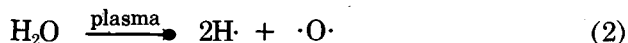
difference between 3,5-lutidine and 4-picoline as the monomer of plasma polymerization to prepare reverse osmosis membranes.

Some results obtained with membranes formed from acetylene/H₂O/N₂ series are shown in Table IV. Here again, addition of N₂ and H₂O seems to improve reverse osmosis characteristics, particularly water flux; however, excess amount (especially H₂O) tends to damage the salt rejection.

In plasma, water seems to be broken into two or three species. This is determined by observing the pressure changes that occur in a flow system of water vapor as the plasma is initiated. With the initiation of the plasma, the steady-state pressure reached is observed to be almost three times the initial preplasma pressure. Over a series of runs, an average increase of 2.8 times the initial pressure was observed. A reaction scheme compatible with these observations may be proposed:



and



It was conjectured that water may serve as a source of atomic hydrogen or oxygen. To further investigate this idea, alternate sources of these, namely, molecular hydrogen and molecular oxygen, were substituted in varying amounts for water in the acetylene/water/nitrogen system. The results are shown in Table V.

TABLE IV
Reverse Osmosis Results^a of Composite Membranes Prepared by Plasma
Polymerization of Acetylene-H₂O-N₂ Series with Porous Polysulfone
Film as the Substrate

Vapor pressure Acet/H ₂ O/N ₂ , μm Hg	Time, min	Salt rejection, %	Flux, gfd
20/5/20	10		
20/5/20	7	78.0	47.9
20/5/20	15	85.1	25.0
20/5/20	25	88.3	20.4
30/7.5/20	10	97.1	4.5
30/7.5/20	15	95.0	14.2
40/10/40	15	96.5	3.4
Effect of Water			
20/5/20	15	85.1	25.0
20/10/20	15	82.4	44.9
20/15/20	15	75.8	48.7
30/7.5/30	15	95.0	14.2
30/10/30	5	88.9	37.0
30/27.5/0	7	98.6	4.4
Effect of N ₂			
30/7.5/20	10	97.1	4.5
30/7.5/30	15	95.0	14.2
30/7.5/40	7	79.8	60.0
30/7.5/50	7	64.3	78.3

^a 3.5% NaCl, 1500 psi.

TABLE V
The Effect of Replacing H₂O in Acetylene-H₂O-N₂ System by O₂ and H₂ on the
Reverse Osmosis Characteristics of Membranes^a

System	Ratio	Time, min	Salt rejection, %	Water flux, gfd
C ₂ H ₂ /H ₂ /N ₂ ^b	40/5/25	5	33.6	29.2
C ₂ H ₂ /H ₂ /N ₂	40/15/25	5	12.8	68.1
C ₂ H ₂ /O ₂ /N ₂	40/15/25	5	17.2	90.7
C ₂ H ₂ /O ₂ /N ₂	40/30/25	5	17.6	89.7
C ₂ H ₂ /H ₂ O/N ₂ **	40/13/28	5	92.1	19.1
C ₂ H ₂ /H ₂ O/N ₂	40/14/28	5	94.8	1.2

^a Porous polysulfone as the substrate; 3.5% NaCl, 1500 psi.

^b N₂ plasma pretreatment 1 min.

An increase in the amount of molecular hydrogen appears detrimental to membrane formation, quite possibly by inhibiting hydrogen abstraction processes. The role of oxygen is unclear; doubling the amount of oxygen has little effect on membrane properties. It is concluded that the action of water in the acetylene system is complex and probably not a simple source of atomic hydrogen or atomic oxygen. The effect of hydrogen and oxygen on the reverse osmosis characteristics may not be properly evaluated by those experiments, since the rate of polymerization might be reduced to yield insufficient

TABLE VI

Effect of Heat, Hydrogenperoxide, and Chlorine on Reverse Osmosis Characteristics of Composite Membrane Prepared by Plasma Polymerization of Acetylene-H₂O-N₂ with Porous Polysulfone Film as the Substrate

Treatment of R. O. membrane	Salt rejection, %	Water flux, gfd
None (control)	96.2	1.2
Heat (80° C, 30 min)	96.2	2.3
H ₂ O ₂ (0.5% solution, 30 min)	95.2	1.4
50 ppm NaOCl, 30 min	93.7	7.3
0.5% NaOCl, 30 min	86.4	10.2

deposition. Nevertheless, it is clear that water is preferred in a practical sense.

As mentioned earlier, N₂ is participating in the polymerization, though the exact chemical formula is not known. Infrared spectrum of plasma polymer of acetylene/H₂O/N₂ is very much similar to those of allylamine and acrylonitrile.⁸ Therefore, it seems likely that plasma polymer membranes obtained from allylamine, acetylene/H₂O/N₂, benzene/H₂O/N₂, and 4-picoline/H₂O/N₂ are very much alike, and the relatively small difference in reverse osmosis characteristics is possibly due to the difference in plasma conditions employed.

It might be worth noting here, however, that the reverse osmosis characteristics of plasma polymers from acetylene/H₂O/N₂ are very stable and that no deterioration of performance is observed with test time (in contrast to the phenomena observed with allylamine membranes by Bell et al.⁹). The effects of heat and some oxidizing agents on the reverse osmosis characteristics are shown in Table VI.

It is further confirmed by ESCA that nitrogen in acetylene/H₂O/N₂ membranes is much more stable than that in allylamine membranes. Membranes of allylamine and acetylene/H₂O/N₂ are prepared, and half of each membrane is kept in air and the remaining half is kept in water for a few days before ESCA analysis is carried out. ESCA peak for N 1s for allylamine membranes kept in water is considerably smaller (approximately one half) than that for one kept in air, whereas no appreciable difference is observed with acetylene/H₂O/N₂ membranes. This observation is in accordance with that made by Bell et al. and more or less confirms the postulated mechanism of hydrolysis of aldimine- and ketimine-type structures for the deterioration of allylamine membranes. The details of the study by ESCA will be presented elsewhere.

The proposed mechanism of plasma polymerization of benzene via fragmentation into three acetylene is supported by the results obtained with membranes prepared from benzene/H₂O/N₂ series, in which a mole of benzene is regarded as three moles of acetylene. Results are shown in Figure 2 as plot of salt rejection versus log water flux.

The results indicate that the benzene series favorably compares with the acetylene series. As far as the polymerization is concerned, it is evident that benzene is equivalent to three acetylene; however, the significance in the membrane preparation may be in the interaction of the monomers with sub-

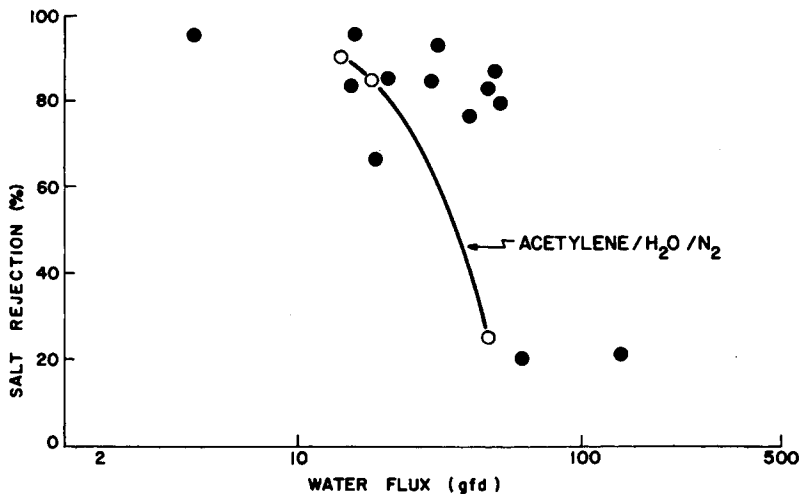


Fig. 2. Reverse osmosis characteristics of composite membranes prepared by plasma polymerization of benzene/H₂O/N₂ compared with those from acetylene/H₂O/N₂ represented by the solid line (porous polysulfone film as the substrate; 3.5% NaCl at 1500 psi).

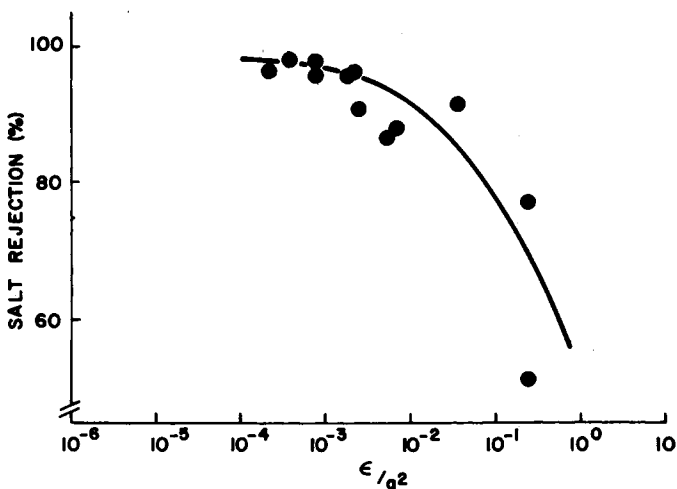


Fig. 3. The correlation between salt rejection and the effective porosity ϵ/q^2 of dry composite membranes.

strate polymer; i.e., benzene would be more typical solvent (or nonsolvent) to the substrate polymer, whereas acetylene may be a (nonsolvent) gas for most polymeric substrates. Thus, the similar behavior of benzene and acetylene may provide an additional degree of freedom in selecting a proper combination of monomer and substrate.

The aspect of hole filling by plasma deposition can be demonstrated by the change of water transport from the flow mechanism in porous membrane to the diffusive transport in nonporous homogeneous membrane due to the deposition of homogeneous polymer layer which fills the pore.

First, the porosity as porous media calculated from the gas permeability dependence on the applied pressure¹⁰ can be correlated to the salt rejection of the composite membrane as shown in Figure 3. The effective porosity ϵ/q^2 ,

where ϵ is the porosity and q is the tortuosity factor, is measured in dry state and may not directly correlate to the porosity of the membranes in wet state. Nevertheless, the decrease of porosity (as porous media) is clearly reflected in the increase in salt rejection in reverse osmosis.

It can be also done by analysis of reverse osmosis properties of a membrane as a function of the effective driving pressure according to the relationship developed by Yasuda and Lamaze.¹¹

Salt rejection R_s is a result of transport depletion of salt in relation to water flux and can be expressed as

$$R_s = \omega + [P_2 RT / P_1 V_1 (\Delta p - \Delta \pi)]^{-1}$$

where $\omega = RTK_1 / P_1 V_1 - 1$ is a parameter to describe the extent of flow; K_1 = hydraulic permeability; P_1 = diffusive water permeability; V_1 = molar volume of water; P_2 = diffusive salt permeability; $\Delta p - \Delta \pi$ = effective pressure, p_{eff} ; Δp = hydrostatic pressure change; and $\Delta \pi$ = osmotic pressure change.

Reverse osmosis membranes can be characterized simply by observing salt rejection as a function of effective pressure. Figure 4 is a plot of $1/p_{eff}$ versus $1/R_s$ of three plasma-polymerized reverse osmosis membranes. The membranes vary only in the treatment time, 4, 6, and 7 minutes as indicated.

It is desirable to minimize the y-intercept

$$\omega = \frac{RTK_1}{P_1 V_1} = \alpha \frac{K_1}{P_1}$$

thereby maximizing the diffusive water permeability and minimizing the hydraulic water permeability.

Membranes can be classified according to mode of transport⁴: (1) diffusion membranes for which $\omega = 1$; (2) diffusion-flow membranes, $\omega > 1$; and (3) flow membranes $\omega \gg 1$. In Figure 4, the 7-min line represents a diffusion membrane; all others are best described as diffusion-flow type.

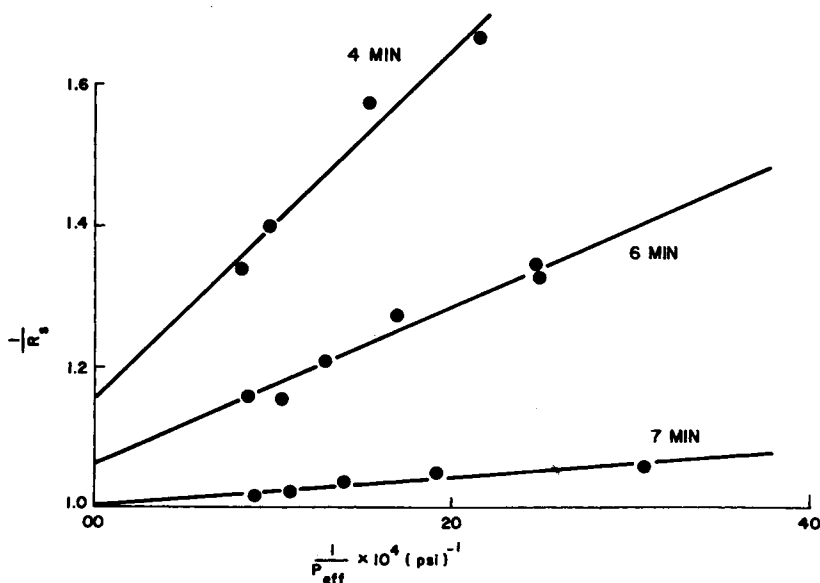


Fig. 4. The change of $1/R_s$ vs. $1/(\Delta p - \Delta \pi)$ dependence as a function of plasma deposition time.

The slope should also be minimal:

$$\text{slope} = \frac{P_2 RT}{P_1 V_1} = \alpha \frac{P_2}{P_1}$$

minimizing salt diffusive permeability P_2 for best rejection and again maximizing the diffusive water permeability for best flux.

Figure 4 shows an improvement in membrane with increased treatment time. The 7-min membrane is the best, having the smallest intercept, $\omega = 1$, and smallest slope, 20 (psi)⁻¹. Indeed, reverse osmosis tests gave fairly good results for this membrane with 99.0% salt rejection and 4.2 gfd water flux with 3.5% NaCl at 1500 psi. This result supports the importance of hole filling and of forming homogeneous diffusion-type membranes by plasma polymerization.

It may be concluded that the preparation of composite reverse osmosis membranes by plasma polymerization can be achieved with varieties of monomers and monomer mixtures. The addition of nitrogen gas into the plasma of monomer(s) which does not contain nitrogen atom produces the plasma polymer which is similar to the plasma polymers formed from the nitrogen-containing monomers. The addition of water vapor into the monomer systems increases the stability of the membrane formed, which seems to coincide with the remarkable reduction of free radicals⁸ found with those polymers formed with water vapor in the monomer systems. The utilization of new monomer systems seems to increase the versatility of the method to prepare reverse osmosis membranes that may have high degree of stability against severe conditions, in which commercially available membranes might be found unsatisfactory.

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