

Reverse Osmosis with Dynamically Formed Membranes from Water-Soluble Polymers

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Synopsis

Membranes were dynamically formed from poly(acrylic acid), poly(1-methyl-2-vinylpyridinium iodide), and methylcellulose on a Millipore filter. The effects of the conditions of membrane formation on reverse osmosis performances and the membrane structure were investigated. The primary factors that affect membrane performance were ascertained to be the kind and concentration of salts and the pH of the preparing solutions, the concentration and the polymerization degree of the membrane materials, the pore size of filters, and the pressure and circulation velocity during membrane formation. Two types of dynamically formed membranes, the membranes inside the filter and the membranes on the filter, were distinguished.

INTRODUCTION

Reverse osmosis with the dynamically formed membrane has been reported,¹ and recently the running result of a pilot plant of reverse osmosis with dynamically formed membranes was reported.²⁻⁵ A dynamically formed membrane has three advantages over membranes formed by the usual casting method: (1) the membrane formation is very easy, so that regeneration and removal of the membrane are feasible; (2) the dynamically formed membrane ensures a very high flow rate in general; and (3) membrane materials that are difficult to use in the casting method can be easily utilized. For example, inorganic colloids and water-soluble polymers could be formed into a reverse osmosis membrane by the dynamic method. Some characteristic membranes, such as the hydrous Zr(IV) oxide-polyacrylate membrane,⁶ have been proposed for special uses.

The conditions of membrane formation have not been investigated in detail except for the dual membrane.⁶ It is therefore possible that membranes with good performance can be formed dynamically from characteristic materials. In this paper the factors controlling the performance of dynamically formed membranes were investigated by using some water-soluble polymers.

EXPERIMENTAL

Measurements of Membrane Performance

The reverse osmosis apparatus used in this study has a desalting cell of the flat type and was described previously.⁷ The porous supports were Millipore filters with 0.025- μm pores. After the solution of the membrane material was passed through the porous support at high pressure for 4-6 hr, the performance of the membrane formed on the porous support was tested. During the test, a small amount (10 ppm) of membrane material was added to the feed solution

to compensate its release from the porous support. The salt rejection was determined from measurements of electrical conductivities of the product and the feed solution.

Membrane Materials

Membrane materials in this investigation were poly(acrylic acid) (PAA), poly(1-methyl-2-vinylpyridinium iodide) (PVP), and methylcellulose (MC). These were chosen as typical representatives of polyanion, polycation, and neutral polymer, respectively. Unless stated otherwise, the polymerization degree of PAA is about 3000. PVP was prepared by refluxing poly(2-vinylpyridine) with methyl iodide (molar ratio 1:6) in methanol for 24 hr. MC (2% aqueous solution) has a viscosity of 4000 cp at 20°C.

Scanning Electron Microscopy Studies

The membrane samples formed dynamically on the Millipore filters had been kept wet for some days and were fractured in a frozen state in liquid nitrogen to obtain fresh edges. The membranes were then shadowed with gold and palladium under vacuum, and the cross section was examined with a Hitachi S-550 electron microscope.

RESULTS AND DISCUSSION

Factors in Membrane Formation

Effect of pH During Membrane Formation

The effect of pH during PAA membrane formation is shown in Table I. As in the case of dual membrane,⁶ the stepwise pH increases or decreases were repeated till the neutral condition was obtained. The membrane performance was measured by using the feed solution of pH 7, because the salt rejection of PAA membranes is maximal at pH 7.^{8,9} The salt rejection increases and the flux decreases with lowered pH of the preparing solution; since the dissociation of carboxylic groups of PAA decreases and the shape of the PAA molecules becomes more compact in the solution at lower pH, it becomes difficult for PAA molecules to pass through the Millipore filter. The repulsion between PAA molecules becomes weak, and therefore a dense membrane is formed. The effect of pH during formation of PVP membranes and the result of reverse osmosis with the feed solutions of different pH are shown in Fig. 1. The increase in salt rejection is due to an increase in the dissociation of PVP. The effect of pH during the PVP membrane formation was examined by using the feed solution of pH 5.0, and the result shows that when the dissociation of PVP during membrane formation is depressed, the membrane becomes dense and the salt rejection is high. The dissociation of polyelectrolytes as membrane materials must be low during membrane formation in order to form a charged membrane of high rejection (Fig. 1 and Table I). In the case of formation of a neutral polymer membrane, the effect of pH of the preparing solution is less pronounced.

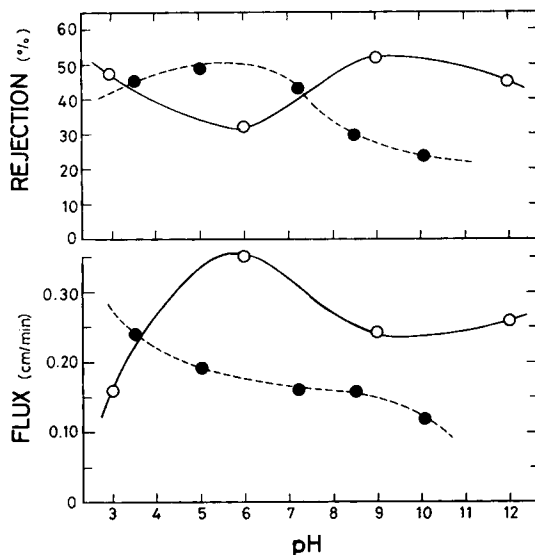


Fig. 1. Effects of pH during formation of PVP membrane and pH of feed solutions on reverse osmosis properties. (O) Effect of pH during membrane formation; conditions of membrane formation: PVP 100 ppm, NaCl 0.5M, 80 kg/cm²; conditions of measuring membrane performance: pH 5.0, PVP 10 ppm, NaCl 0.05M, 80 kg/cm². (●) Effect of pH of the feed solutions; conditions of membrane formation: PVP 100 ppm, pH 11.8, NaCl 0.5M, 80 kg/cm²; conditions of measuring membrane performance: PVP 10 ppm, NaCl 0.05M, 80 kg/cm².

TABLE I
Effect of pH on Formation of PAA Membrane^a

Membrane	Flux, cm/min	Rejection, %
A	0.090	80
B	0.15	62
C	0.20	35
D	0.18	28

^a Conditions of membrane formation: A—pH 2.0 (0.5 hr) → pH 3.5 (0.5 hr) → pH 5.0 (0.5 hr) → pH 7.0 (0.5 hr); B—pH 4.0 (1.5 hr) → pH 7.0 (0.5 hr); C—pH 7.0 (2.0 hr); D—pH 9.0 (1.0 hr) → pH 7.0 (1.0 hr). PAA 100 ppm, pH adjustment HCl–NaOH, pressure 80 kg/cm². Conditions of measuring membrane performance: NaCl 0.05M, PAA 10 ppm, pH 7.0, pressure 80 kg/cm².

Effect of Salt Concentration During Membrane Formation

Not only the pH but also the ionic strength determines the degree of dissociation of polyelectrolytes. Figure 2 shows the effect of sodium chloride concentration in the preparing solution on the PAA membrane performance. The PAA membrane was formed from solutions of varying NaCl concentrations at pH 4.0, and membrane performance was tested with a 0.05M NaCl solution of pH 7.0. Salt rejection increases with increasing salt concentration in the preparing solution. Since the degree of dissociation decreases with an increase of salt concentration, the result shows again that a depression in the dissociation of PAA during membrane formation results in high rejection.

The behavior of the PVP membrane was similar to that of the PAA membrane. When the membrane was formed from a solution containing 100 ppm PVP at pH 10 in the absence of salt, the flux was 0.20 cm/min and the rejection was 54%. When the membrane was formed in the presence of 0.05M sodium iodide, the

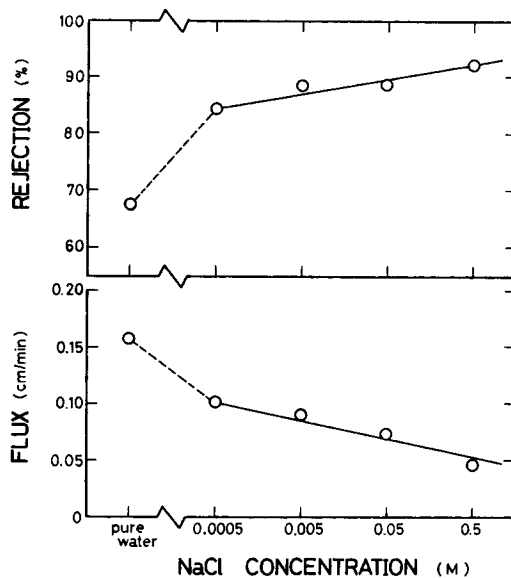


Fig. 2. Effect of NaCl concentration during membrane formation. Conditions of membrane formation: pH 4.0, PAA 100 ppm, 80 kg/cm². Conditions of measuring membrane performance: pH 7.0, NaCl 0.05M, PAA 10 ppm, 80 kg/cm².

flux was 0.11 cm/min and the rejection was 57% (pressure was 80 kg/cm² and the feed solution was 0.05M NaCl at pH 5.0 containing 10 ppm PVP).

Effect of Addition of Salts in Membrane Preparation

Aqueous methylcellulose solutions are sols at high and low temperatures and gels at medium temperature. The temperature of sol-gel transformation changes with addition of various salts in the solution. The temperature of sol-gel transformation (Table II) was measured according to the procedure of Heymann.¹⁰ The order of depression of sol-gel transformation temperature coincides with the lyotropic series. Table III shows the effect of addition of various salts at 30°C and the effect of temperature of membrane formation on the membrane performance. When the temperature is higher and sodium sulfate, which decreases the gel point, is added in the preparing solution, salt rejection of the membrane becomes higher.

The effect of addition of various salts during membrane formation was observed for the PAA membrane (Table 4) as well as the MC membrane. The effect of anions (coions) is slight, but the effect of cations (counterions) is great. The

TABLE II
Influence of Salts on Sol-Gel Transformation of Methylcellulose in Water^a

Salt	Melting point, °C
Na ₂ SO ₄	26.2-7.3
NaCl	30.0-25.3
NaI	43.9-30.7
None	35.0-29.6

^a Conditions of measurement: MC 1.6%, salt 0.2M.

TABLE III
Effects of Salts and Temperature on Formation of MC Membrane^a

Salt	Flux, cm/min	Rejection, %
Na ₂ SO ₄ (0.05M)	0.031	68
NaCl (0.05M)	0.037	57
NaI (0.05M)	0.033	59
None (30°C)	0.037	61
None (40°C)	0.028	70
None (50°C)	0.028	77

^a Conditions of membrane formation: MC 1000 ppm, 80 kg/cm². Conditions of measurement of membrane performance: NaCl 0.05M, MC 10 ppm, pressure 80 kg/cm², 30°C.

TABLE IV
Effects of Salts During PAA Membrane Formation^a

Salt	Flux, cm/min	Rejection, %
NaCl	0.051	89.0
Na ₂ SO ₄	0.050	89.4
CH ₃ COONa	0.052	88.7
NH ₄ Cl	0.049	91.3

^a Conditions of membrane formation: PAA 100 ppm, pH 4.0, salt 0.05M, pressure 80 kg/cm². Conditions of measurement of membrane performance: NaCl 0.05M, pH 7.0, pressure 80 kg/cm².

addition of ammonium ions imparts the membrane with high rejection. Poly(acrylic acid) is coagulated by the addition of divalent or trivalent cations, and membranes with good performance were not formed.

Effect of Concentration of Membrane Material

Rejection increases and flux decreases with an increase in the concentration of PAA membrane material; this effect is larger for the MC membrane (Figs. 3 and 4).

Effects of Polymerization Degree and Pore Size of Porous Supports

Table V shows the effects of the polymerization degree of PAA and the pore size of porous supports. Rejection increases with a decrease in pore radius; flux does not change significantly in a range of pore size from 0.10 to 0.025 μm . Rejection increases and flux decreases with an increase of polymerization degree in the range investigated. This trend is not general, inasmuch as it was reported that dual membranes with maximum rejection are prepared of PAA having a molecular weight of about 50,000.⁶ The result suggests that the dimension of membrane-forming molecules requires porous supports of suitable pore size for obtaining the best membrane performance. The performance of the MC membrane, like that of the PAA membrane, changes with the pore size but the dependence on pore size is smaller (Table VI).

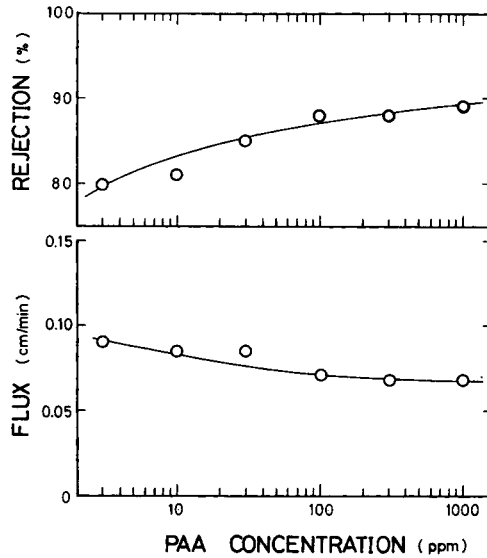


Fig. 3. Effect of PAA concentration during membrane formation. Conditions of membrane formation: pH 4.0, NaCl 0.05M, 80 kg/cm². Conditions of measuring membrane performance: pH 7.0, NaCl 0.05M, PAA 10 ppm, 80 kg/cm².

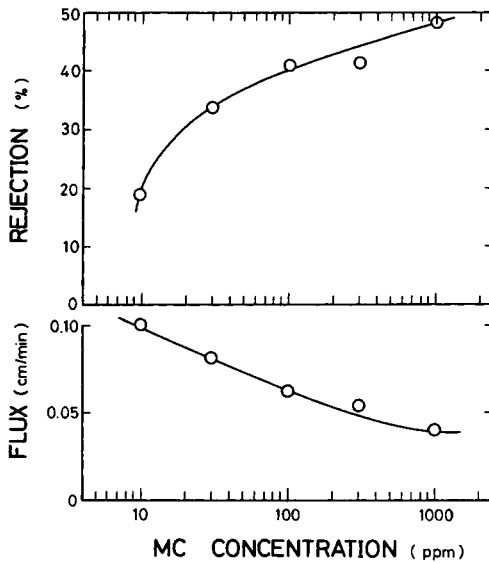


Fig. 4. Effect of MC concentration during membrane formation. Conditions of measurement of membrane performance: MC 10 ppm, NaCl 0.05M, 60 kg/cm².

Effect of Pressure During Membrane Formation

Figure 5 shows the effect of pressure during membrane formation on the PAA membrane performance. Rejection increases and flux decreases with increasing pressure. Since the PAA membrane is regarded as a charged membrane, then the charge density X may be estimated from the rejection R according to the equation proposed by Kraus¹¹:

TABLE V
Effects of Pore Size of Porous Support and Polymerization Degree of PAA^a

Pore size, μm	Polymerization degree	Flux, cm/min	Rejection, %
0.025	ca. 3000	0.071	88
0.050	ca. 3000	0.11	82
0.10	ca. 3000	0.079	80
0.22	ca. 3000	0.70	4
0.025	ca. 350	0.19	60
0.025	ca. 90	0.18	64

^a Conditions of membrane formation: PAA 100 ppm, NaCl 0.05M, pH 4.0, pressure 80 kg/cm². Conditions of measurement of membrane performance: NaCl 0.05M, PAA 10 ppm, pH 7.0, pressure 80 kg/cm².

TABLE VI
Effect of Pore Size of Porous Support for MC Membrane^a

Pore size, μm	Flux, cm/min	Rejection, %
0.025	0.034	49
0.050	0.029	46
0.10	0.026	47
0.22	0.029	33

^a Conditions of membrane formation: MC 1000 ppm, pressure 80 kg/cm². Conditions of measurement of membrane performance: NaCl 0.05M, MC 10 ppm, pressure 80 kg/cm².

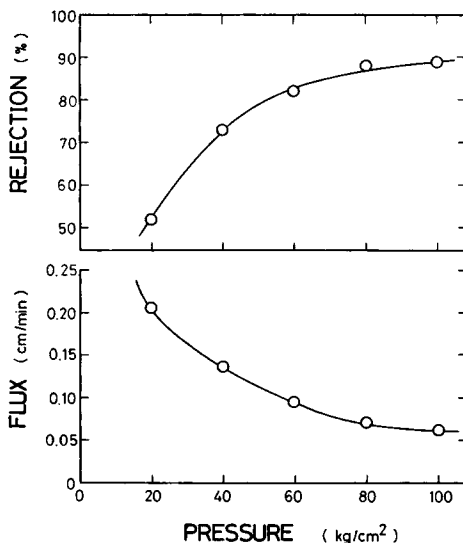


Fig. 5. Effect of pressure during PAA membrane formation. Conditions of membrane formation: pH 4.0, PAA 100 ppm, NaCl 0.05M. Conditions of measuring membrane performance: pH 7.0, PAA 10 ppm, NaCl 0.05M, 80 kg/cm².

$$X = C_0 \left[\frac{1}{1 - R} - (1 - R) \right]$$

where C_0 is the salt concentration in the feed solution. The charge density calculated from the equation has been plotted versus the pressure during

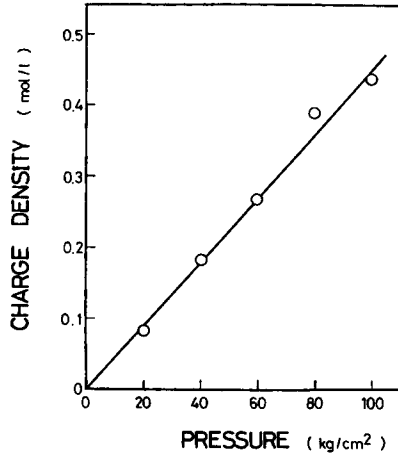


Fig. 6. Charge density of dynamically formed PAA membrane vs pressure during membrane formation.

membrane formation in Figure 6, which shows that the charge density is proportional to the pressure. Since the charge density is proportional to the density of the membrane, this result means that the density of the membrane increases proportionally with pressure. Figure 7 shows the effect of pressure on MC membrane performance. Rejection increases and flux decreases with increase in pressure. Figure 8 is a logarithmic plot of flux J_v versus pressure P during membrane formation. The relationship is expressed as follows for both membranes:

$$J_v = a \cdot P^{-n} \quad n \doteq 0.80$$

The coefficient a changes with the membrane material and the conditions of membrane formation, whereas n is nearly constant.

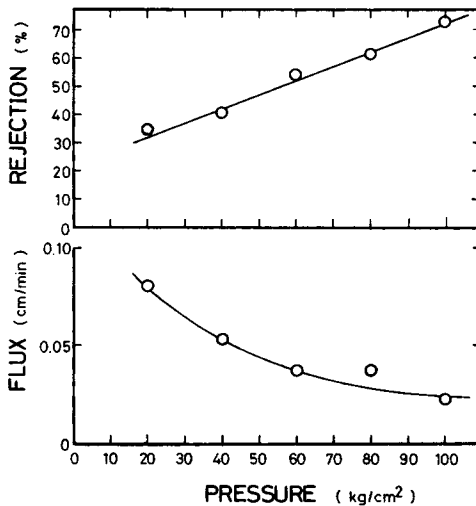


Fig. 7. Effect of pressure during MC membrane formation. Conditions of membrane formation: MC 1000 ppm. Conditions of measurement of membrane performance: MC 10 ppm, 80 kg/cm², NaCl 0.05M.

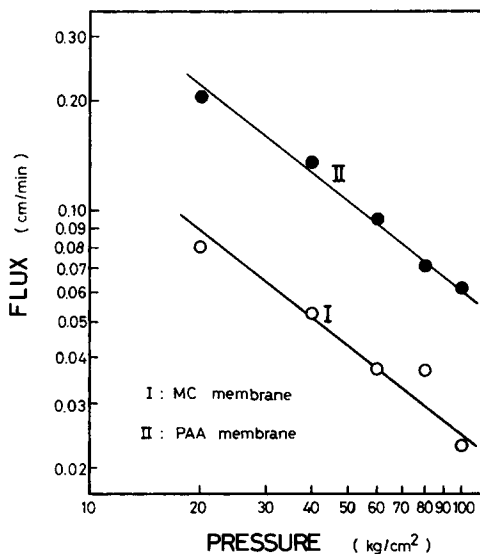


Fig. 8. Effect of pressure during membrane formation on flux across dynamically formed membranes.

Effect of Circulation Velocity During Membrane Formation

The circulation velocity during membrane formation affects membrane performance. The salt rejection of the PAA membrane formed at 28 l./hr was 88% from a 0.05M NaCl solution at a flux of 0.071 cm/min, and that formed at 7 l./hr was 88% at a flux of 0.077 cm/min. The MC membrane formed at 28 l./hr rejected 49% at a flux of 0.034 cm/min, and that formed at 7 l./hr rejected 56% at a flux of 0.022 cm/min. This slight effect is considered to be due to the change in membrane thickness with circulation velocity. The effect is larger for the MC membrane than for the PAA membrane. The difference occurs because the PAA membrane is formed inside the filter and the MC membrane is formed *on* the filter, as observed by electron microscopy.

Observations by Scanning Electron Microscopy

A scanning electron micrograph ($\times 5000$) of the dynamically formed PAA membrane (rejection 92.8% and flux 0.055 cm/min for 0.050M NaCl at 80 kg/cm²) and a micrograph ($\times 25,000$) of the MC membrane (rejection 57.0% and flux 0.037 cm/min under the same conditions) are shown in Figures 9 and 10, respectively. The pores of the Millipore filter were packed with PAA in the upper half of the photograph (Fig. 9). The MC layer was formed on the Millipore filter (Fig. 10). It has been reported that a hydrous oxide dynamic membrane was formed on the filter,¹² but it is clear from these photographs that the PAA membrane is formed inside the Millipore filter, whereas the MC membrane is formed on the filter.

This difference in the site of membrane formation can be attributed to the difference in size of the molecules involved in membrane formation. When the dimensions of the membrane-forming molecules are larger than the pore size

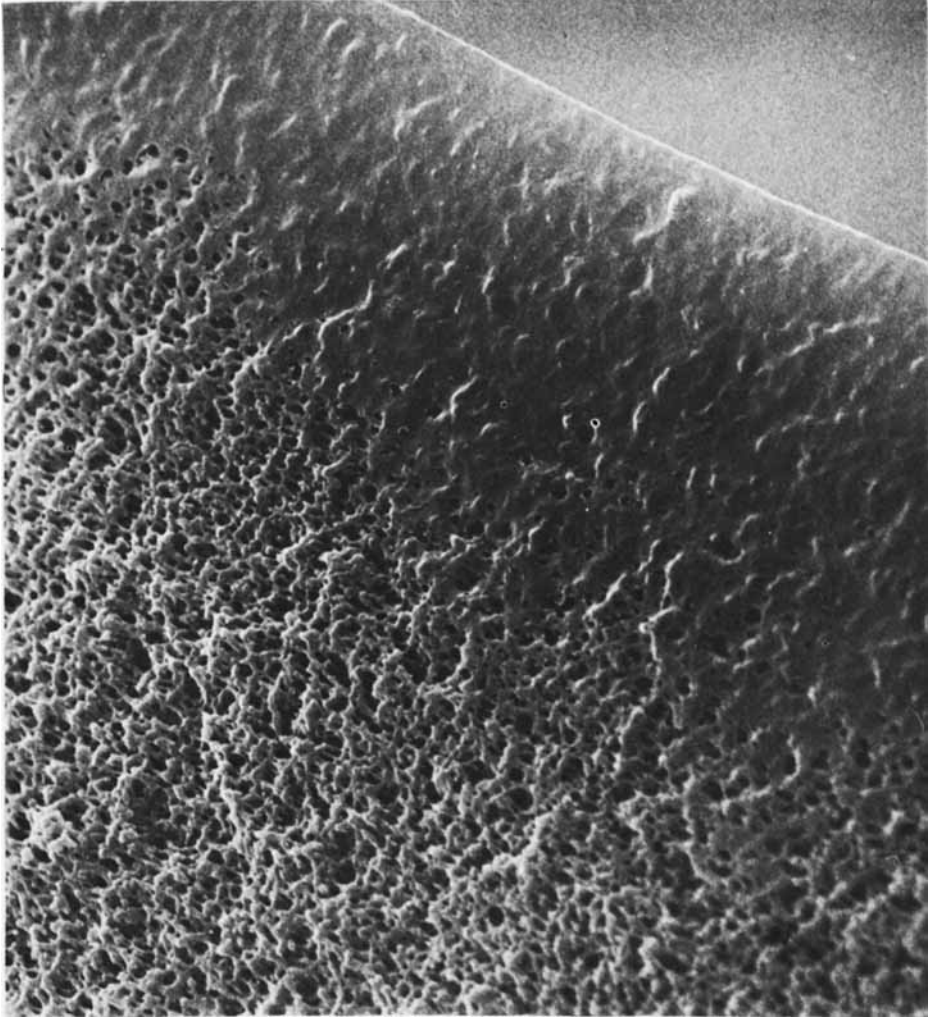


Fig. 9. Cross section of dynamically formed PAA membrane ($\times 5000$).

and/or attractive interaction between the molecules occurs, the molecules do not penetrate the filter, and therefore the membrane is formed *on* the filter. This is the case with the MC membrane. However, when the dimensions of the membrane-forming molecules are smaller than the pore size and a repulsive interaction occurs between the molecules, the molecules can penetrate the filter in the initial period of membrane formation. They are then adsorbed on the surface of the pores *in* the filter, leading to membrane formation inside the filter. This situation applies to the formation of the PAA membrane.

CONCLUSIONS

This investigation reveals that, in order to obtain dense membranes with good performance, the following conditions are required: The dissociation of ionizable

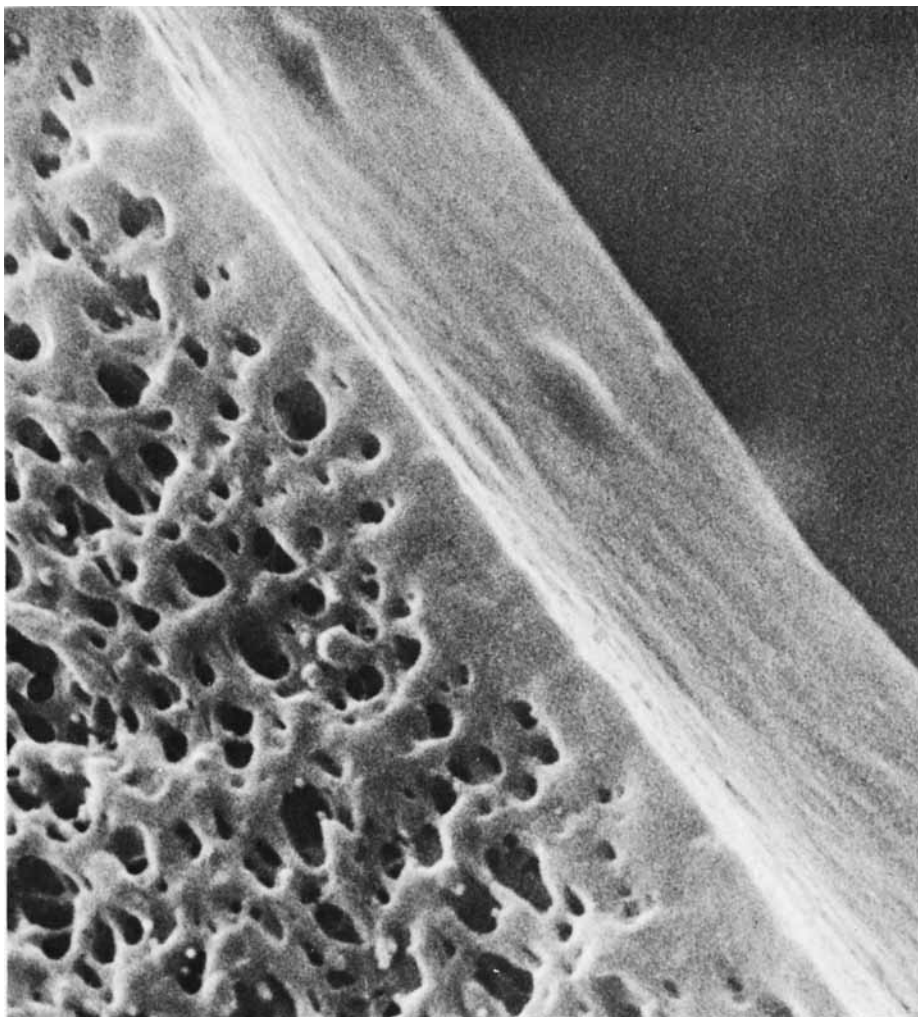


Fig. 10. Cross section of dynamically formed MC membrane ($\times 25,000$).

groups is low during membrane formation, and the concentration of sol-gel transformation of polymers is lowered by the addition of salt; it is desirable that the concentration of the membrane material be high and that pressure during membrane formation is high. A suitable pore-size range of the filter is required in order to obtain good performance. Two types of membranes, membranes inside and membranes on the filter, were distinguished by electron microscopy.

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