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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Cadotte, J. E. , King, R. S. , Majerle, R. J. and Petersen, R. J.(1981) 'Interfacial Synthesis in the Preparation of Reverse Osmosis Membranes', *Journal of Macromolecular Science, Part A*, 15: 5, 727 — 755

To link to this Article: DOI: 10.1080/00222338108056764

URL: <http://dx.doi.org/10.1080/00222338108056764>

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Interfacial Synthesis in the Preparation of Reverse Osmosis Membranes

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ABSTRACT

Reverse osmosis membranes are currently finding increasing use in the production of potable water from salt-laden water sources, and in the purification and recycle of industrial process waters. Most reverse osmosis membranes are comprised either of polyamide hollow fibers or cellulose acetate sheet films. A new type of reverse osmosis membrane, made by the interfacial synthesis of ultrathin membranes directly on microporous support media, is being explored. Two types of interfacially formed membranes are specifically described. One is based on an ultrathin polyamide barrier layer made by interfacial reaction of polyethylenimine with isophthaloyl chloride. The barrier material is supported by a heat-polymerized intermediate zone of polyethylenimine, supported in turn by a microporous polysulfone substrate. The second membrane consists of a polyamide formed from piperazine and a mixed acyl halide reagent. This nonpolymeric amine leads to a different surface texture and the absence of an intermediate zone between the barrier film and the microporous polysulfone substrate. This latter membrane exhibits excellent water fluxes (as high as $4.0 \text{ m}^3/\text{m}^2\text{-day}$ at 100 atm) under seawater reverse osmosis test conditions, and shows very high rejection (99%) of inorganic salts containing polyvalent anions. Differences in the morphology of the salt barrier layers for these two cases are described, and the resulting effects on membrane desalination properties are discussed.

INTRODUCTION

Reverse osmosis is a process whereby water is forced by pressure through a semipermeable membrane counter to the normal direction of osmotic flow. In the case of water desalination, the semipermeable membrane must possess a particularly dense barrier layer to reject dissolved solutes in the water, such as sodium chloride. Rather low diffusive permeabilities for water through such dense structures are the expected norm.

Reverse osmosis became a commercially feasible process upon the development of the asymmetric, or anisotropic, membrane by Loeb and Sourirajan.⁽¹⁾ This membrane was formed from a solution of cellulose acetate having about 39 percent acetyl content. It was cast in such a fashion as to develop a dense surface skin about 0.25 μm thick on top of a porous structure 50 to 150 μm thick. The bulk of the membrane contained about 55 to 60 percent void space, with pores ranging from greater than 1000 \AA on the bottom (coarse) side of the membrane to less than 100 \AA in the zone immediately underlying the surface layer. Considerable variation in these parameters occurs, however, depending upon the method of membrane fabrication. Kesting⁽²⁾ has provided an excellent review of the various routes to asymmetric cellulose acetate membranes and their resulting physical structures.

Although asymmetric cellulose acetate membranes find broad commercial application today, these reverse osmosis membranes suffer severe drawbacks. These include limited pH stability, susceptibility to biological attack, compaction at high pressures (which reduces water flux), wet-dry irreversibility (in most but not all types), and an upper temperature operating limit at about 35°C (95°F).

One approach toward improved membrane performance was to fabricate the surface skin and the porous support layer as two separate entities, then combine them to achieve maximum performance. By this method, each layer could be optimized separately, the surface layer

for reverse osmosis properties and the porous underlayer for durability and compaction resistance. This approach was successfully developed for cellulose acetate barrier layers deposited on microporous polysulfone (poly[oxy-1,4-phenylenesulfonyl-1,4-phenylene]) substrates.^(3,4) Qualities of increased water flux and decreased sensitivity to compaction were achieved by this approach, but the other drawbacks of cellulose acetate membranes remained.

Interfacial synthesis appears to be a promising method for deposition of ultrathin barrier films in situ on microporous polysulfone substrates. This paper describes several reverse osmosis membrane compositions that have been successfully prepared by interfacial methods. Also described are results of scanning electron microscopy studies on thin-film polyamide composite membranes, with particular attention to piperazine-based polyamide compositions.

Various thin-film composite membranes can be prepared by interfacial deposition of ultrathin polymeric barrier films on microporous polysulfone substrates. To be functional in water desalination, however, the interfacially formed barrier layers must have a balance of hydrophilic and hydrophobic groups. They must also consist of a fairly rigid chemical structure overall to resist compaction under high pressure.

Table 1 illustrates several types of such membranes.^(5,6) Aromatic polyamines and polyphenolics can be prepared by a gas-liquid interfacial reaction, using formaldehyde vapor. An acid catalyst in the resorcinol solution is needed. These membranes were simply prepared by exposing the impregnated polysulfone supports to formaldehyde vapor in closed Petri dishes. Similarly, aromatic polyester and polyamide membranes can be prepared by exposure to heated vapors of acid chlorides, as illustrated in the case of sorbitol.

Where aromatic polyester and polyamide membranes are involved, however, the best results are generally realized through use of hexane

TABLE I. Examples of Experimental Semipermeable Membrane Compositions Prepared by Interfacial Methods

Membrane Type	Aqueous Reactant	Crosslinking Agent	Reverse Osmosis Properties*	
			Salt Rej. (%)	Water Flux (m^3/m^2 -day)
polyamine	1,3-diaminobenzene	formaldehyde vapor	97	1.8
polyester	resorcinol	isophthaloyl chloride in hexane	40	1.8
polyphenol	resorcinol	formaldehyde vapor	75	1.7
polyamide	piperazine	isophthaloyl chloride in hexane	98	1.1
polyester	sorbitol	terephthaloyl chloride in hexane	97	0.9
polyester	sorbitol	trimesoyl chloride vapor	60	4.0

* Data from 16 hour tests with 3.5% synthetic seawater at 100 atm pressure and 25°C.

solutions of the corresponding aromatic acyl halides. Examples of these are also illustrated in Table 1.

From related work in reverse osmosis, it was apparent that polyamides possessed particularly promising semipermeability characteristics necessary for water production and salt rejection.⁽⁷⁾ Interfacial formation of polyamides upon porous substrates to produce reverse osmosis membranes has also been described, although salt rejections greater than 85 percent were not achieved.⁽⁸⁾ To be commercially useful, reverse osmosis membranes should exhibit salt rejections of at least 95 percent for brackish water treatment and 98.5 percent

for seawater desalination, while providing water throughput rates (fluxes) of at least $0.40 \text{ m}^3/\text{m}^2\text{-day}$ (about 10 gallons per square foot of membrane area per day) at normal use pressures.

In our research effort, the interfacial formation of ultrathin polyamide membranes was investigated, using microporous polysulfone as a preferred microporous support layer. Table 2 contains data obtained in initial trials of this approach. These data (which actually pre-date the data in Table 1) reveal the difficulty involved in preparing salt-retentive membranes by interfacial polyamide membrane synthesis. In all cases involving monomeric diamines, salt rejections were far below useful levels. Only in the case of a polymeric amine, polyethylenimine, was a membrane obtained showing promise for reverse osmosis desalination.

The findings in Table 2 for membranes made from monomeric diamines were not particularly surprising, however. Morgan, in his review of condensation polymers,⁽⁹⁾ stated that washed but undried

TABLE II. Reverse Osmosis Performance of Membranes Prepared by Interfacial Reaction of Terephthaloyl Chloride with Various Amines

Amine	Reverse Osmosis Performance*	
	Salt Rejection (%)	Water Flux ($\text{m}^3/\text{m}^2\text{-day}$)
hydrazine	**	**
1,2-ethanediamine	**	**
1,3-propanediamine	30	9.5
1,6-hexanediamine	8	4.2
1,3-diaminobenzene	12	1.1
1,4-diaminobenzene	38	2.2
piperazine	74	2.4
polyethylenimine	96	1.2

* Test conditions 100 atm, 3.5% synthetic seawater, 25°C.

** Too brittle to test.

films of 6/10 polyamide prepared by unstirred interfacial synthesis were readily permeable to inorganic salts and small dye molecules. At first glance, therefore, membranes with poor salt rejection capabilities are to be expected via interfacial polyamide synthesis.

The last two cases in Table 2, piperazine and polyethylenimine, have been examined in detail, and conditions have now been developed that provide high salt rejection membranes in both cases. Studies on the polyethylenimine case have been reported by us in recent years.⁽¹⁰⁻¹²⁾ Piperazine polyamide reverse osmosis membranes have been studied of late by us, and are the main subject of this paper. Differences in the manner of their behavior (piperazine vs. polyethylenimine) in regard to interfacial formation, membrane morphology, and subsequent properties are discussed in this presentation.

EXPERIMENTAL METHODS

To prepare the microporous polysulfone substrate, a 15-percent solution of polysulfone (Union Carbide Corporation, Grade P-3500) in dimethylformamide was drawn out on a flat glass plate using a 175 μ m knife gap. The plate was immediately immersed in a water bath at room temperature in one smooth motion. Within 30 seconds, a white microporous sheet formed and spontaneously lifted away from the glass surface. After five minutes, the polysulfone support was removed, rinsed with fresh water, then stored in deionized water until used. The top surface (air side) was used as the support surface for membrane formation.

Interfacial membrane synthesis was accomplished using unstirred, nondispersion methods. Starting with polyethylenimine, interfacial polyamide membranes were made using isophthaloyl chloride. This reactant gave higher water fluxes than terephthaloyl chloride (Table 2) while providing equivalent salt rejections. The polyethylenimine used in this study was Tydex 12, made by Dow Chemical Company. It

is no longer available from this source, but an equivalent grade may be obtained from Cordova Chemical Company, Sacramento, California, or purchased from laboratory chemical supply houses. A microporous polysulfone support was immersed in a solution of 0.67% by weight of polyethylenimine in deionized water for two minutes, then drained for an equal time. The support film was then covered with a solution of 0.5% isophthaloyl chloride in hexane. After removal from the hexane solution, the coated substrate was heat-cured in an oven at 110°C for 15 minutes.

Piperazine polyamide membranes were formed by similar methods. In one version, a microporous polysulfone substrate was saturated with an aqueous solution of 1.0% piperazine, 1.0% of an inorganic acid acceptor, and 0.5% dodecyl sodium sulfate. Excess reagent was either drained off or was "squeezed" off by means of a low durometer rubber roller. A suitable squeeze roller was fashioned from a length of glass tubing inserted through latex rubber tubing. The impregnated polysulfone substrate was then covered with 0.1 to 1.0 percent by weight isophthaloyl chloride in hexane for 20 seconds. The resulting thin-film composite membrane was drained and air-dried at room temperature. Variations of this membrane were also made wherein part or all of the isophthaloyl chloride was replaced by trimesoyl chloride (benzene-1,3,5-tricarboxylic acid chloride). Potential acid acceptors include sodium hydroxide, sodium carbonate, and sodium phosphate. In one case, N,N'-dimethylpiperazine was used as an acid acceptor. In the absence of any such additive, piperazine was used as an acid acceptor itself.

In a second version, the polysulfone support was coated with a 1:1 water: isopropanol solution containing 2.0 percent sulfonated polysulfone, 1.0 percent piperazine and 2.0 percent N,N'-dimethylpiperazine. The sulfonated polysulfone was prepared by treatment of ten parts Udel P-3500 resin in dichloromethane with five parts chlorosulfonic acid, decanting, washing the precipitated polymer

with additional dichloromethane, then neutralizing with aqueous triethylamine. The coated support film was interfacially reacted with isophthaloyl chloride as before to produce a piperazine polyamide membrane, followed by a heat-cure at 110°C for 15 minutes. This version contained a hydrophilic sulfonated polysulfone sub-layer between the support film and the polyamide barrier layer.

These membranes were tested in a high pressure reverse osmosis test loop, described elsewhere.⁽¹³⁾ Test conditions were 100 atm (1500 psi) feedwater pressure and 25°C temperature, and 3.5 percent by weight synthetic seawater (made with "Sea-Salt", Lake Products Company, St. Louis, MO), except as otherwise stated. Crossflow was maintained at about 1000 fold greater than membrane flux to avoid concentration polarization effects at the membrane surface. Membrane specimens were run under test conditions for 16 to 24 hours before taking flux and salt rejection measurements.

For scanning electron microscopy studies, samples 4 cm² were obtained from polysulfone supports both without membrane and with interfacial membranes deposited upon them. The samples were stored 24 hours in a vacuum dessicator prior to mounting to insure evaporation of any surface moisture; critical point drying was not necessary. A specimen 8 mm in diameter was cut from each sample and mounted, with the glossy (air or membrane) surface facing up, using conductive silver paint. The mounted specimens were again vacuum dessicated to allow the paint to dry thoroughly. Eight inches of wire with a 1:1 ratio of gold to gold:palladium (60:40) were then evaporated onto the specimens at 40 V in a vacuum of 1.8×10^{-5} torr using a Denton Vacuum Evaporator. Specimens were subsequently observed using a Hitachi Model 450 scanning electron microscope.

REVERSE OSMOSIS TEST RESULTS

Table 3 contains reverse osmosis test data on these various membranes. Polyethylenimine interfacially crosslinked by isoph-

TABLE III. Reverse Osmosis Performance of Membranes from Polyethylenimine and Piperazine Interfacially Reacted with Isophthaloyl Chloride

Amine Reagent	Acyl Chloride Concentration	Water Flux ($\text{m}^3/\text{m}^2\text{-day}$)	Salt Rej. (%)
0.67% polyethylenimine	0.5%	1.0	99.3
1.0% piperazine, 0.93% NaOH	1.0%	0.37	96
1.0% piperazine, 0.93% NaOH	0.1%	0.86	98
2.0% sulfonated polysulfone, 2.0% piperazine, 2.0% N,N'-dimethylpiperazine	0.1%	0.81	98.4

thaloyl chloride was found to give salt rejections in excess of 99 percent when tested with synthetic seawater. These salt rejections could be obtained routinely as skill developed in their preparation. Water fluxes for this membrane averaged $1.1 \text{ m}^3/\text{m}^2\text{-day}$ under the test conditions stated.

The poly(piperazine isophthalamide) thin-film composite membrane could be made to give seawater salt rejections in excess of 95 percent under carefully controlled conditions. These included using fresh reagents and making sure that the isophthaloyl chloride was pure. Quality of the microporous polysulfone support was also important. The support film had to be fresh, free of pinholes and other defects, and cast from fresh, clear polysulfone solutions. Even so, salt rejections above 97 percent were very difficult to obtain.

Use of selected water-soluble polymers as additives in the membrane synthesis improved membrane salt rejections to as high as 98.5 percent, which represented the lower limit for single-pass seawater desalination. The case in Table 3 involving the use of sulfonated polysulfone is the best example of the phenomenon.

At its best, the piperazine isophthalamide membrane gave fluxes of $1.0 \text{ m}^3/\text{m}^2\text{-day}$. This was considered to be a marginal performance for commercial application. When trimesoyl chloride was substituted for isophthaloyl chloride, however, membrane fluxes were enhanced dramatically. Yet, peculiar salt rejection results were observed. Results are illustrated in Figures 1 and 2. In simulated seawater performance tests, the flux, initially at $1.0 \text{ m}^3/\text{m}^2\text{-day}$ for the piperazine isophthalamide membrane, increased to $3.4 \text{ m}^3/\text{m}^2\text{-day}$ for the piperazine trimesamide membrane with a peak flow of about $4.0 \text{ m}^3/\text{m}^2\text{-day}$ for the 50:50 blend. Salt rejection of the synthetic seawater by the barrier layer dropped immediately at low levels of trimesoyl chloride addition to the isophthaloyl reagent, falling into the range of 60 to 70 percent for most of the membrane combinations.

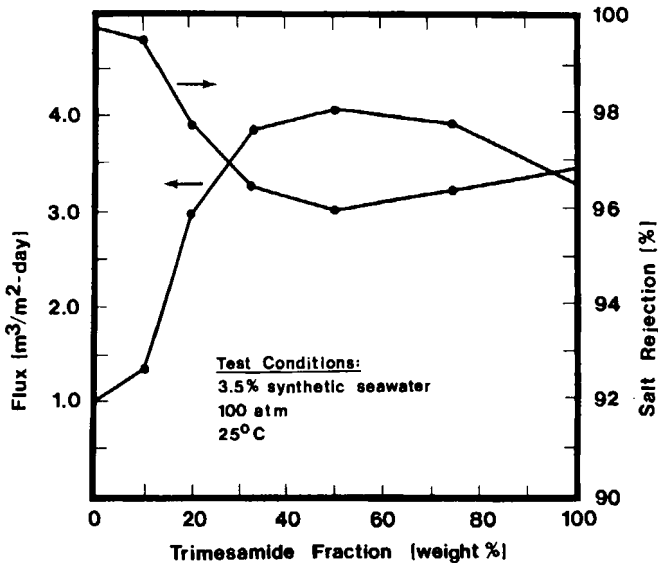


FIGURE I. Seawater Desalination Flux and Salt Rejection as a Function of Isophthaloyl and Trimesoyl Content in Piperazine Polyamide Membranes.

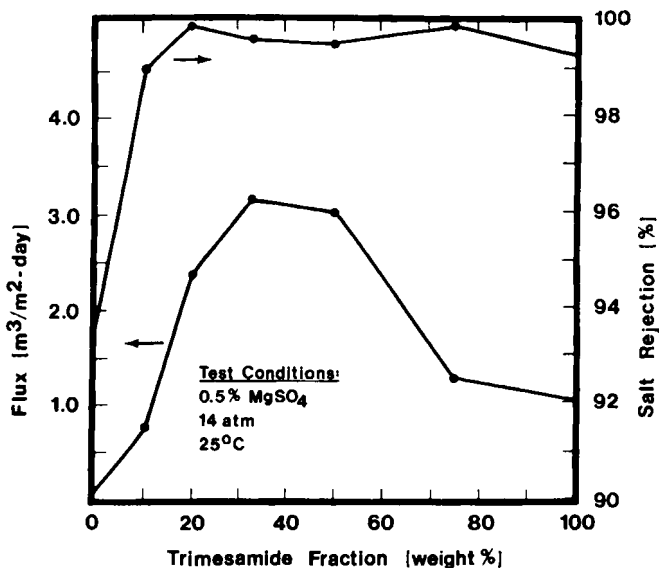


FIGURE II. Brackish Water Desalination Flux and Salt Rejection as a Function of Isophthaloyl and Trimesoyl Content in Piperazine Polyamide Membranes.

Simulated brackish water tests with 0.5 percent magnesium sulfate at 14 atm (200 psi) exhibited the same type of flux curve, showing a maximum of 3.1 m³/m²-day flux at a weight ratio of 2:1 isophthaloyl chloride: trimesoyl chloride in the hexane solution. Salt rejections, initially good at about 94 percent for the piperazine isophthalamide thin-film composite membrane, actually increased to the 99 percent level upon the substitution of ten percent of isophthaloyl chloride by trimesoyl chloride in the interfacial reactant solution. At greater addition levels of trimesoyl chloride, the magnesium sulfate rejection remained above 99 percent, in direct contrast to the seawater rejection data. Thus, while greatly enhancing flux, trimesoyl chloride also caused an unexpected divergence in salt barrier properties toward simulated seawater versus simulated brackish water.

In a subsequent experiment, a single disc of piperazine trimesamide membrane was sequentially tested toward a series of inorganic salt solutions under reverse osmosis conditions at 14 atm and 25°C. Results of these tests are shown in Table 4. These data show that the salt rejection is highly dependent on the valence charge of the anion. Divalent anions (e.g. sulfate) are rejected by the barrier layer very effectively. Monovalent anions (e.g. chloride) are rejected poorly. The cation charge has little or no effect on the salt rejection of this membrane.

These results implied that the polypiperazineamide barrier layer in these interfacially formed membranes contained pendant carboxylate groups when trimesoyl chloride was used as an interfacial reactant. Subsequently, a 1.0 percent solution of trimesoyl chloride in hexane was stirred rapidly with water for 30 minutes. Hydrolysis of acid chloride groups liberated hydrochloric acid, which was extracted into the water phase. Separation of the water and titration with base showed the presence of 83 percent of

TABLE IV. Rejection of Various Solutes by a Piperazine Trimesamide Interfacial Membrane

Solute Used in Test Loop	Reverse Osmosis Test Data*	
	Salt Rejection (%)	Flux (m^3/m^2 -day)
0.1% $MgSO_4$	98.0	1.4
0.1% NaCl	70	1.3
0.5% NaCl	50	1.7
0.5% Na_2SO_4	97.8	1.7
0.5% $MgCl_2$	46	1.3
0.5% $MgSO_4$	97.9	1.3

* Test conditions: 14 atm, 25°C.

one equivalent of hydrochloric acid. The diacyl chloride form remained soluble in hexane, maintaining a clear solution, and this solution was active in the preparation of interfacially-formed piperazine polyamide films. It appears, therefore, that facile hydrolysis of one of the acyl halide groups on the trimesoyl chloride ring occurs, but that further hydrolysis is slowed thereafter. Hydrolysis as a competing reaction with polyamide formation in the interfacial contact zone could occur and result in carboxylate ion formation in the piperazine trimesamide membranes.

Table 5 shows the effect of acid acceptors in the aqueous piperazine phase upon reverse osmosis properties of resulting membranes. When trimesoyl chloride was reacted interfacially with piperazine, the tightest membranes with the highest salt rejections occurred as a function of the following acid acceptor order: none > sodium carbonate > sodium hydroxide. For isophthaloyl chloride under identical conditions, this order was reversed. Acid acceptors appeared to promote the hydrolysis side reaction on trimesoyl chloride, leading to poorer salt rejections in the final interfacial membrane as the basicity of the acid acceptor increased.

TABLE V. Effect of Acid Acceptors on Properties of Polypiperazineamide Membranes Formed with Trimesoyl or Isophthaloyl Chloride

Acyl Halide	Acid Acceptor	Reverse Osmosis Test Data*	
		Salt Rejection (%)	Flux ($\text{m}^3/\text{m}^2\text{-day}$)
trimesoyl Chloride	none	88	1.5
	Na_2CO_3	54	2.3
	NaOH	28	1.2
isophthaloyl chloride	none	55	2.3
	Na_2CO_3	80	0.69
	NaOH	97	0.29

* Test conditions: 68 atm (1000 psi), 3.5% synthetic seawater, 25°C.

Addition of sodium dodecyl sulfate surfactant to the aqueous piperazine solution did not significantly change any of the performance data of the membrane formed from trimesoyl chloride and piperazine. For the isophthaloyl chloride-piperazine series, addition of 0.5 percent to 1.0 percent of the surfactant improved salt rejections significantly, but at about a 40 percent loss in membrane flux. Thicker membranes appeared to result.

If carboxylic acid groups are present in polypiperazineamide membranes containing the trimesoyl group, then such membranes should show a pH dependence relating to the ionization state of these pendant groups. Table 6 shows the effect of feedwater pH

TABLE IV. Effect of Feedwater pH on the Reverse Osmosis Properties of the 9:1 Isophthaloyl:Trimesoyl Polypiperazineamide Membrane

		Reverse Osmosis Test Data*			
		Salt Rej. (%)	Flux ($\text{m}^3/\text{m}^2\text{-day}$)	Salt Rej. (%)	Flux ($\text{m}^3/\text{m}^2\text{-day}$)
	pH	Example 1		Example 2	
Increasing pH	7.9	93	0.66	96	0.46
	8.8	92	0.65	94	0.45
	9.9	92	0.63	94	0.56
	11.0	91	0.66	94	0.44
	11.9	89	0.67	94	0.45
		Example 3		Example 4	
Decreasing pH	8.0	89	0.65	91	0.66
	6.8	90	0.31	91	0.34
	5.2	89	0.26	91	0.33
	2.6	90	0.22	91	0.30
	2.2	91	0.21	91	0.30

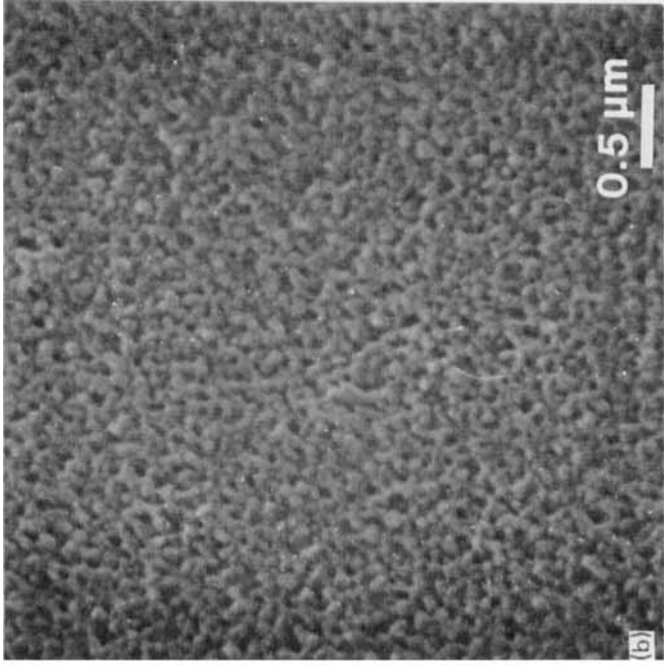
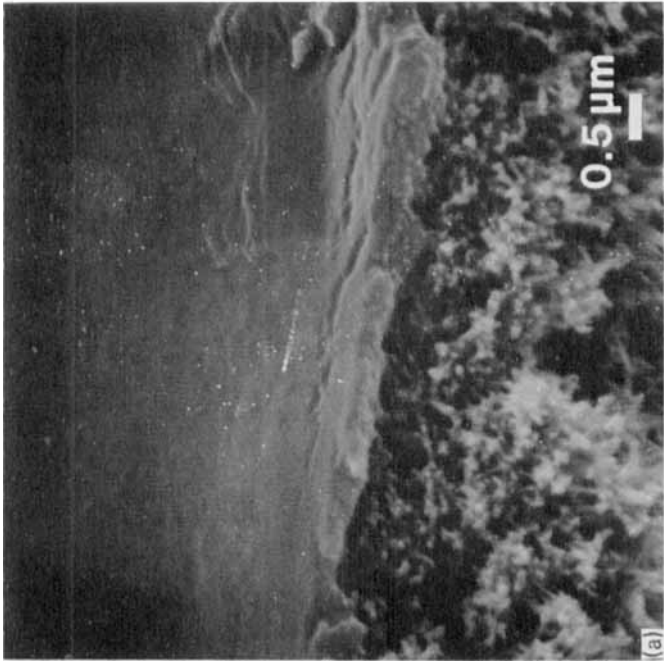
* Test conditions: 40 atm, 1% sodium chloride, 25°C.

on examples of a 9:1 copolyamide of piperazine with isophthaloyl and trimesoyl chlorides respectively. Two test samples were taken from neutral to pH 11.9; flux and salt rejection were essentially constant through this range. Two other samples were taken from pH 8.0 down to pH 2.2; flux dropped dramatically for both examples between pH 8.0 and 6.8, as the conversion of carboxylate salts to free carboxylic acid groups began to take place, reducing membrane swelling. Again salt rejections remained constant. In another, separate example of polypiperazineamide membrane containing higher carboxylate content (higher trimesoyl substitution), in which salt rejections were initially 60 to 70 percent, the same type of flux decrease occurred upon changing pH from 8.0 to 5.5, but salt rejection increased to 90 percent.

SCANNING ELECTRON MICROSCOPY

Both the polysulfone support and the polypiperazine membranes were examined in detail and characterized by scanning electron microscopy. Figure 3 shows different aspects of the microporous polysulfone support layer. Figure 3a consists of a cross-section of the upper layers of a thin-film composite reverse osmosis membrane made by interfacial polymerization. In this example the surface barrier layer is about 3000 Å thick. The surface of the polysulfone is indistinguishable from the membrane coating in this photomicrograph, but the porous substructure of the polysulfone can be seen.

Figure 3b is a photograph of the top surface of the polysulfone support material itself, magnified 20,000 X. This surface resembles a layer of spherical particles fused together. Micropores present in this surface layer were measured by both scanning and transmission electron spectroscopy and were found to average about 330 Å diameter. Figure 3c illustrates the porous structure underlying this dense surface layer. This cross-section reveals a macroreticular polysul-



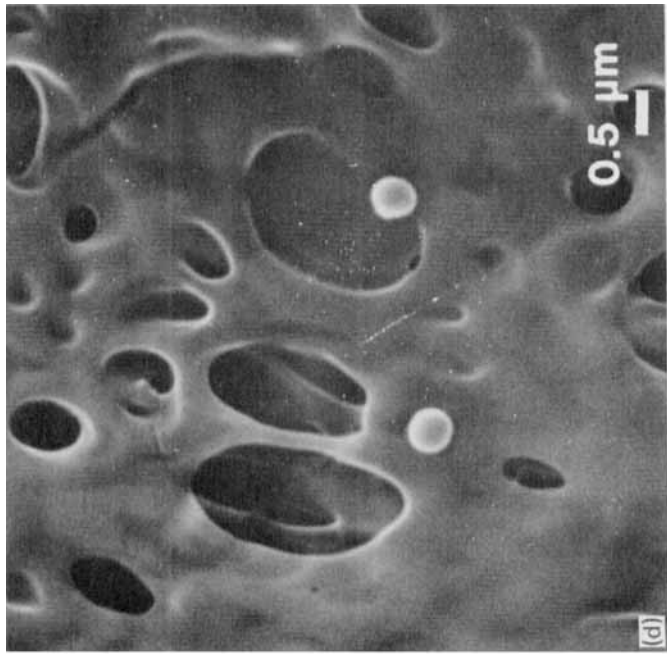
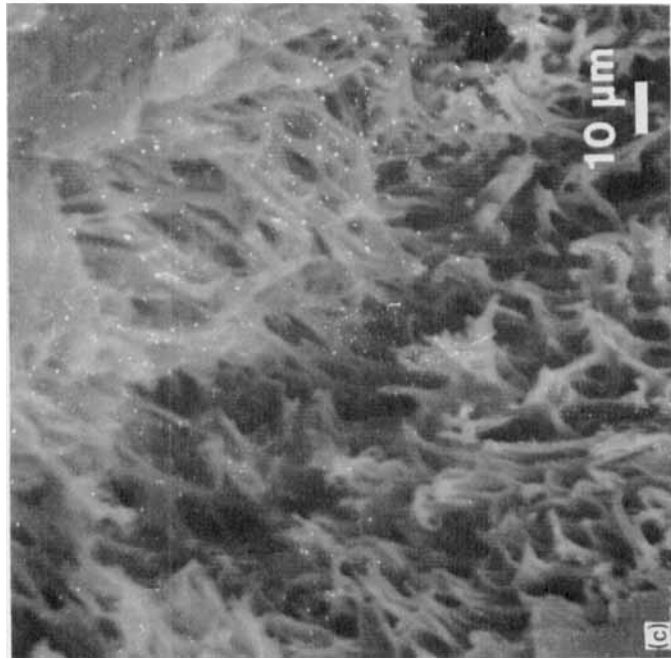


Figure III. Scanning Electron Photomicrographs of Microporous Polysulfone Support Films. a) Cross-section of the upper zone of a thin-film composite reverse osmosis membrane depicting a 300A-thick interfacial membrane deposited upon a microporous polysulfone substrate. b) Top surface of a microporous polysulfone support film showing an array of 330A micropores which support the interfacial membrane. c) Cross-section of the polysulfone support film showing a microporous reticular foam structure. d) Bottom surface of the polysulfone with typical large pores evident.

fone structure resembling an open cell foam. Accurate cross-sections like this were difficult to achieve without smearing or serious deformation. This specimen was prepared by tearing of the polysulfone material while immersed in liquid nitrogen. Figure 3d shows the bottom side of a microporous polysulfone support film. Large pores, diverse in dimensions and typically ranging from 20,000 to 40,000 Å, were present. This side of the film was in contact with a smooth glass plate during quenching of the film in water.

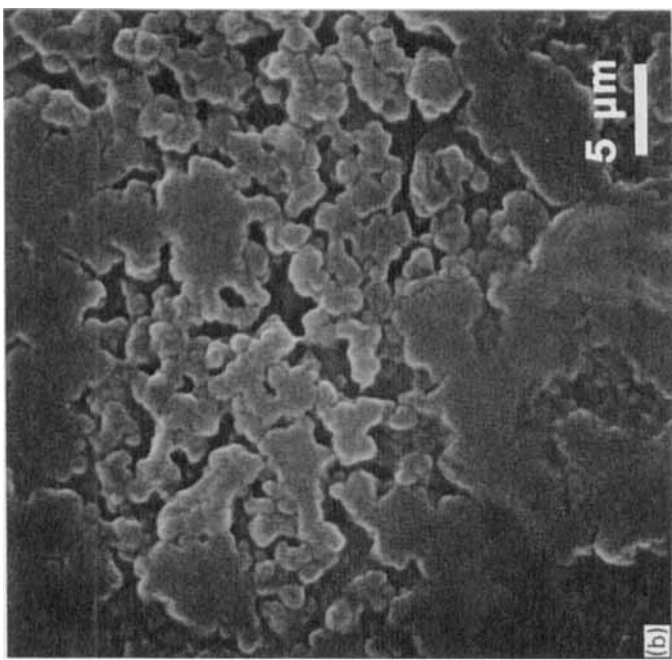
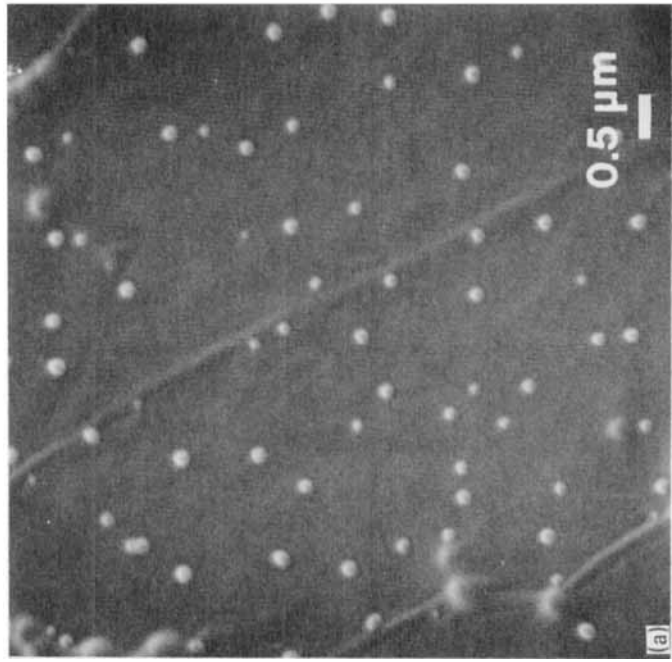
Microporous polysulfone supports for interfacially formed reverse osmosis membranes are observed, therefore, to be highly asymmetric films. The top surface with its 330 Å-diameter microporous proves very effective in supporting ultrathin, interfacially formed membranes. A 2000 Å-thick interfacial membrane can be supported to 100 atmospheres feedwater pressure by this microporous surface layer without breakthrough. The microporous sublayer supports this surface composite zone very adequately, while offering no restriction to the water flow that has come through the membrane. In commercial practice, this polysulfone support would be about 25 to 40 μm thick and backed by a nonwoven polyester web.

Figure 4 contains scanning electron photomicrographs of the surfaces of various piperazine polyamide membranes, along with a polyethylenimine isophthalamide membrane. These surfaces represent the side in contact with the hexane solution of the acyl chloride. The polyethylenimine isophthalamide membrane, Figure 4a, is basically smooth with some occasional longitudinal ridges. White beads of polysulfone detritus were accidentally deposited on the surface of this interfacial membrane during its preparation, and are artifacts in this figure. In Figure 4b, the piperazine isophthalamide membrane, in contrast, is very rugged in surface topography. Although interfacial formation takes place under quiescent conditions, the structure in Figure 4b suggests mixing at the interface, resulting in formation of polymer globules that become cemented together. Surfactant was

used in polypiperazineamide membrane preparations. Initial formation at the interface may have involved initially emulsified piperazine isophthalamide, which then became insoluble and fused together. This and the two remaining membranes in Figure 4 were prepared using a 1.0 percent aqueous piperazine solution containing 1.0 percent sodium hydroxide and 0.5 percent sodium dodecyl sulfate. The acyl chloride reagent was 1.0 percent reactant by weight in hexane.

Figure 4c, depicting the surface of the piperazine trimesamide interfacial membrane, shows a completely different surface structure. The membrane surface texture results from a swelling of the membrane during formation. This swelling results in an expansion of the interfacial membrane in the plane of its formation. For the specimen in Figure 4c, development of a bubbled surface pattern resulted. Other patterns such as a series of closely spaced ridges were also seen, each one being indicative of this membrane swelling phenomenon. Between the ridges this membrane presents a smooth surface not at all reminiscent of the piperazine isophthalamide membrane. Swelling is thought to occur via formation of pendant sodium carboxylate groups in the membrane structure, followed by subsequent water absorption. Further reaction apparently takes place within the swollen membrane, fixing it into this convoluted shape permanently. Thus, even though the membrane was desiccated in the preparation of specimens for scanning electron microscopy, the ridged structure remained extant.

Figure 4d shows an example of a 2:1 copolymer of piperazine isophthalamide-co-trimesamide respectively. This example resembled neither membrane of the respective homopolymers of Figure 4b and 4c, but was more like the polyethylenimine isophthalamide membrane. This copolymer membrane, which represents the case of peak water permeability under reverse osmosis conditions, apparently avoids the excess of carboxylate groups that cause the swelling in the piperazine trimesamide membrane.



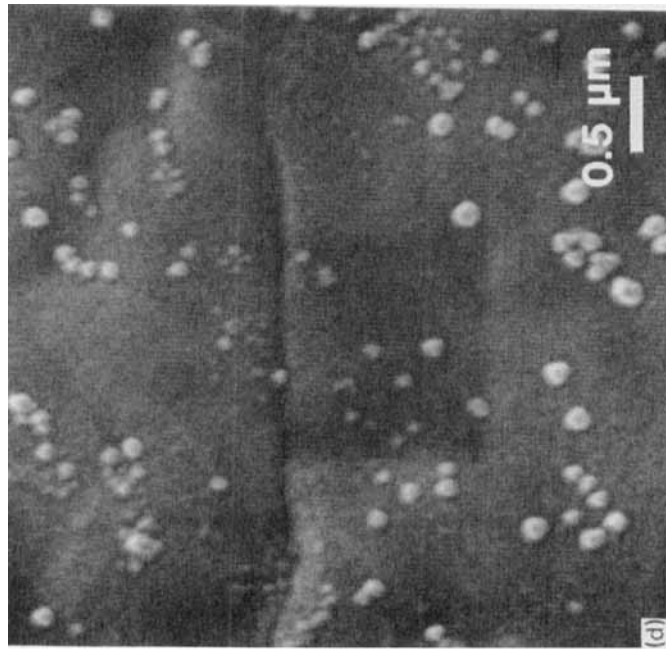
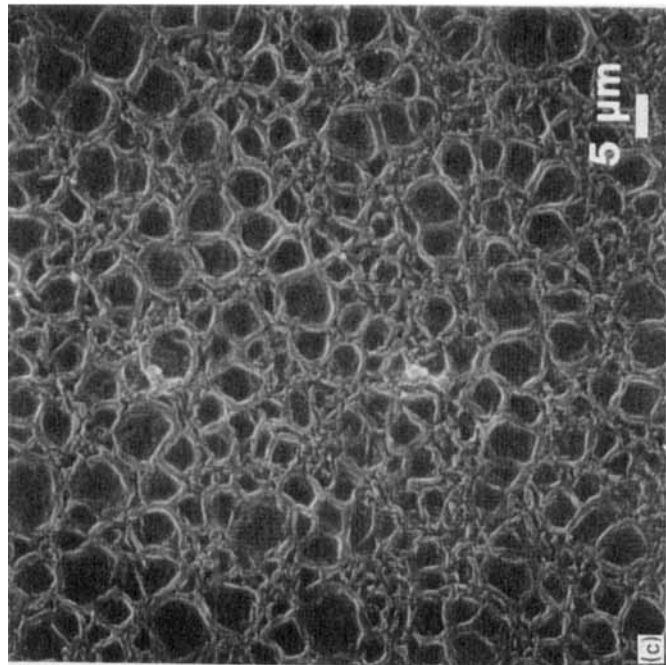


Figure IV. Scanning Electron Photomicrographs of the Surface of Interfacially Formed Polyamide Membranes.

- a) Polyethylenimine isophthalamide (white beads are artifacts -- colloidal polysulfone particles).
- b) Piperazine isophthalamide.
- c) Piperazine trimesamide.
- d) 2:1 piperazine isophthalamide-co-trimesamide (white beads are colloidal polysulfone particles).

The backside of the polypiperazineamide membranes, the side in contact with the aqueous piperazine solution impregnated into the surface of the polysulfone support film, was also examined. The polysulfone was dissolved away by playing dichloromethane solvent onto the composite membrane placed face down on a microscopy mounting grid. Figure 5a shows the back surface of the piperazine isophthalamide interfacial membrane. Surface projections corresponding to the size of the polysulfone surface micropores were noted. In Figure 5b, the back surface of the piperazine trimesamide membrane does not show this pattern; rather, a rippled structure was present. This structure was evidence of membrane swelling, and resembled one of the alternate types of ridged surface structures observed in addition to that of Figure 4c. The piperazine isophthalamide membrane as it formed remained in intimate contact with the polysulfone support surface, while the piperazine trimesamide membrane lifted away from the polysulfone surface as it swelled during the interfacial formation step.

DISCUSSION

A strong body of evidence has been developed in the field of interfacial polyamide synthesis to indicate that polymer formation takes place in the organic phase. Thus, the amine diffuses across the water-solvent interface and reacts with the acyl halide in the organic phase. A smooth polymer film initially forms at the interface. Further polymer formation takes place on the organic solvent side of the deposited film. This latter surface becomes increasingly rough as polymer formation proceeds. The polymer film is normally porous, allowing for the transport of amine reactant and the acid byproducts across the interfacial region. This accounts in part for the difficulty in obtaining high salt-rejecting membranes by interfacial synthesis.

In the case of polyethylenimine, however, the reaction of this polyamine with isophthaloyl chloride at the interface should result

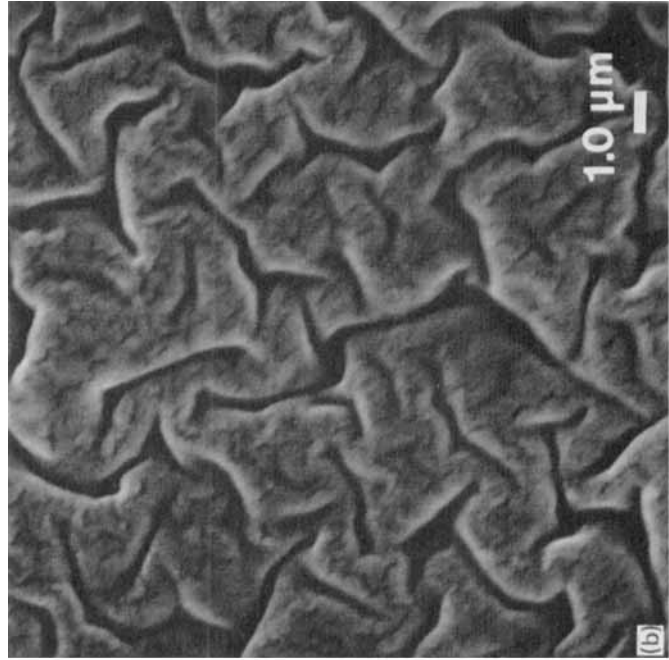
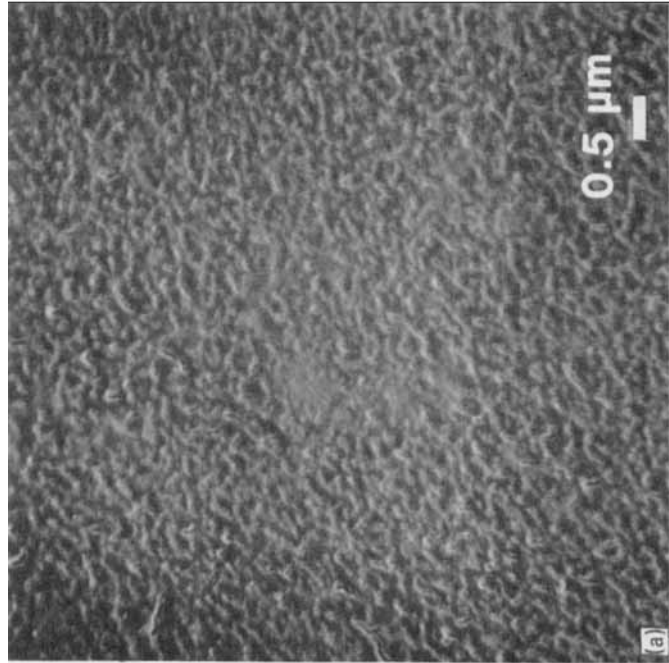


Figure V. Scanning Electron Photomicrographs of Interfacial Membrane Surfaces in Contact with Microporous Polysulfone.

- a) Piperazine isophthalamide membrane backside showing template of polysulfone surface micropores.
- b) Piperazine trimesamide membrane backside showing effect of swelling and absence of any patterning by the polysulfone surface originally in contact with it.

in the instantaneous formation of a barrier layer through which further polyamine, because of its high molecular weight, cannot penetrate. Thus, after the initial formation of a continuous film, further reaction must take place not in the organic phase but in the aqueous phase. Because of the low solubility of isophthaloyl chloride in the aqueous phase, a thin skin develops which only slowly increases in cross-section thereafter. A graded structure is also developed, ranging from complete acylation on the organic solvent side to the barest insolubilization on the aqueous face.

Actually a layer of unreacted polyethylenimine becomes entrapped between the interfacial polyamide deposit and the microporous support surface. Upon heating in air to greater than 100°C, this unreacted polyethylenimine is both dried and insolubilized. The insolubilization takes place mainly by the splitting out of ammonia, but also involves oxidation and generation of ketonic groups.^(10,11)

The final result is a three-layer structure that consists of a microporous substrate, an intermediate layer of insolubilized polyethylenimine, and a surface barrier layer of dense polyamide material. The intermediate layer serves as a transition zone between the polysulfone substrate and the polyamide barrier layer, providing additional support to this extremely thin barrier surface. The final composite thus withstands 100 atmospheres pressure without difficulty.

In contrast to this three layer structure, the piperazine isophthalamide membrane does not form an intermediate zone between the barrier layer and the polysulfone substrate. It is in direct contact with the polysulfone surface, as indicated in Figure 5a. Furthermore, the desalting zone will tend to be "buried" in the polyamide layer, being close to the polysulfone surface. Any significant discontinuities or defects in the polysulfone surface structure would therefore disrupt the salt barrier layer. This affects in a

major way the success or failure in achieving high salt rejections for piperazine isophthalamide interfacial membranes. In this respect, we have experienced considerable difficulty in fabricating poly-piperazineamide membranes by machine processes, and noted on several occasions that substandard polysulfone support material greatly lowered resulting membrane salt rejections.

An intermediate zone can be built into the polypiperazineamide membrane construction, as illustrated by the use of sulfonated polysulfone. When heated to 130°C, this sulfonated polysulfone polymer undergoes insolubilization by intramolecular sulfone formation. Thus, a three layer composite can be formed, consisting of microporous polysulfone as the base layer, insolubilized sulfonated polysulfone as the intermediate layer, and a piperazine isophthalamide interfacial membrane as the salt barrier overlay. This composite membrane exhibits salt rejections approaching the 99 percent level, as shown by the example in Table 3.

The large change in properties of the polypiperazineamide membranes as a function of trimesoyl content deserves comment. The scanning electron photomicrographs displayed a striking change in morphology as isophthaloyl chloride was replaced by trimesoyl chloride in the membrane preparation. Other conditions, which included use of sodium dodecyl sulfate as surfactant and sodium hydroxide as acid acceptor, remained constant. We believe that the results show a two-fold mechanism of action by trimesoyl chloride beyond that of isophthaloyl chloride -- its trifunctionality and the generation of free carboxylate groups in the final membrane.

The trifunctionality of trimesoyl chloride results in the instantaneous formation of a three-dimensional crosslinked polyamide structure at the interface upon exposure of the hexane solution of the acyl chloride to the aqueous piperazine solution. Thus, a smooth ultrathin membrane forms at the interface. Swelling and

thickening by further polyamide formation takes place on this interfacial membrane with further time exposure, leading to the convoluted structure shown in Figure 4b. This additional behavior, particularly the swelling, is promoted by the hydrolysis and salt formation of residual carboxylic acid chloride groups on the trimesoyl linkages in the polyamide, and by premature hydrolysis of unreacted trimesoyl chloride.

The formation of piperazine isophthalamide is not like this. Because isophthaloyl chloride is only difunctional, linear oligomers are formed in the first instant of exposure. These oligomers are partially soluble in the aqueous phase, especially those that are amine-terminated, (6) and will also be emulsified to some extent by the surfactant. When molecular weights of the oligomers exceed solubility limits and surfactant emulsification potential, precipitation and fusion of the polyamide particles takes place. The interfacial membrane at this point would be relatively rough and quite porous. Further diffusion of reactants through this structure would eventually produce a thick, dense membrane having satisfactory salt rejection characteristics. The resulting membrane would thus have the appearance of Figure 4a.

When trimesoyl and isophthaloyl chlorides are combined, the trifunctionality of the trimesoyl chloride contributes to instantaneous formation of a smooth, ultrathin interfacial film. The rugged texture of the piperazine isophthalamide membrane is essentially eliminated in the 2:1 copolymer of piperazine isophthalamide-co-trimesamide.

The fact that water flux reaches a peak in brackish water tests with the 2:1 copolymer (see Figure 2) is of interest. Two explanations seem plausible. First, the piperazine trimesamide homopolymer membrane may have too much carboxylate ion functionality, such that it begins to behave as a soft, compressible gel structure

when wet. Compaction of this gel structure under the hydrostatic pressure involved would limit water flux.

The second explanation is more complex. Hydrolysis and membrane swelling appears to take place concurrently with interfacial membrane formation in the piperazine trimesamide membrane. It is likely that reactants diffuse into this swollen membrane and react in situ in the membrane structure. Thus, although the piperazine trimesamide membrane was originally a swollen, permeable polymer network, it subsequently became dense by deposition of new polyamide within the swollen network. This explanation is supported by the fact that the convoluted surface texture of the membrane in Figure 4b remains fixed even after dessication. A flat film merely swollen with water would shrink back to a tight, stretched film upon drying. For the high flux copolymer, however, carboxylate anion formation presumably occurs at a slower rate, so that the membrane fabrication process is finished before this phenomenon begins to assert itself. Then, under reverse osmosis test conditions on the finished membrane, carboxylate salt formation and membrane swelling reaches a state of completion, generating a high flux membrane. We believe that this latter explanation fits the data better.

In summary, thin-film composite reverse osmosis membranes can be readily prepared by interfacial polymerization techniques. This approach behaves well in the preparation of polyethylenimine isophthalamide membranes. In fact, it has reached a commercial stage in the form of a polyetheramine isophthalamide membrane version, tradenamed "PA-300".⁽¹⁴⁾ The polypiperazineamide membrane system is more difficult insofar as fabrication of high salt rejection membranes is the goal. Large variations in both physical structure and reverse osmosis properties occur in this system as the content of the trifunctional trimesoyl chloride is increased. Piperazine trimesamide and its copolymers with the isophthalamide

behave like hybrid membranes, possessing both cation exchange character and reverse osmosis desalination properties. They may find usefulness in the treatment of waters containing polyvalent anions, or in the separation of larger constituents such as in the concentration of sugar solutions.

ACKNOWLEDGEMENT

Portions of this work were supported by the Office of Water Research and Technology, U.S. Department of the Interior, under Contract Numbers 14-34-0001-2883, 14-34-0001-6512 and 14-34-0001-8512. The research support by this agency is gratefully acknowledged.

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