

Aromatic Polyamide–Hydrazides for Water Desalination. I. Syntheses and RO Membrane Performance

M. D. SATRE and N. D. GHATGE,* *Research & Development Division (Polymer), Bharati Vidyapeeth, Erandwane, Pune-411 038, India*, and
M. P. S. RAMANI, *Head, Desalination Division, Bhabha Atomic Research Centre, Bombay-400 085, India*

Synopsis

Wholly aromatic polyamide–hydrazides (PAH) were synthesized by low-temperature solution polycondensation of *m*-amino benzhydrazide (MABH)/*p*-amino benzhydrazide (PABH) with isophthaloyl chloride (ICL)/terephthaloylchloride (TCI) in *N,N*-dimethyl acetamide (DMAC)/*N*-methyl-2-pyrrolidone (NMP). The polymers were characterized for their properties. Membranes were prepared from these (PAH) polymers under different casting conditions by varying the casting solution composition, evaporation time, post-annealing treatment, etc. The reverse osmosis (RO) tests for these membranes were performed with 5000 ppm aqueous sodium chloride feeds at 40 and 70 kg/cm² operating pressures. Addition of lithium chloride to casting solutions and annealing in hot water conferred optimum selectivity to RO membranes. Membranes showed rejections up to 98.5% at flux > 20 cm/day.

INTRODUCTION

Wholly aromatic polyamide–hydrazides (PAH) are a class of speciality polymers used in reverse osmosis (RO) applications.¹⁻¹² Polyamide–hydrazides polymers have been investigated extensively as potential high-performance materials with high thermal stability.¹³ The various properties of polyamide–hydrazides such as thermo-oxidative stability,¹² high mechanical strength and moduli,¹⁴ and the solute rejection capabilities^{2,10} were established. The membrane performances of these polymers in RO applications are influenced by several structural¹² and processing variables,¹⁵ such as primary polymer structure (*m/p*-phenylene units), casting solution composition, evaporation period, post-annealing treatment, etc.

In this communication, we present the synthesis and RO studies of (a) poly[3-(isophthaloylamino) benzoic acid hydrazide], (b) poly[3-(terephthaloylamino) benzoic acid hydrazide], (c) poly[4-isophthaloylamino) benzoic acid hydrazide], and (d) poly[4-(terephthaloylamino) benzoic acid hydrazide].

EXPERIMENTAL

Materials

Reagents. *m*-Aminobenzoic acid (Fluka), *p*-aminobenzoic acid (Loba Chemie, India), concentrated sulfuric acid (Glaxo, India), calcium hydride

* To whom correspondence should be addressed.

(Riedal-De-Haen AG), lithium carbonate (Thomas Baker, India), hydrazine 80% solution (BDH) (India), and sodium chloride (Loba Chemie, India) were of analytical grade and were used as received. Isophthaloyl chloride [ICl] (Fluka) and terephthaloyl chloride [TCI] (Fluka) were recrystallized from dry *n*-hexane. Lithium chloride (Loba Chemie, India) was dried at 120°C under vacuum. Sodium chloride feed solutions were prepared in deionized water.

Solvents. Methanol, acetone, chloroform, and *n*-hexane were purified by standard procedures. *N*-methyl-2-pyrrolidone [NMP] and *N,N*-dimethylacetamide [DMAC] (SRL, Bombay) were distilled over calcium hydride and stored over molecular sieves before use.

Monomers

(a) ***m*-Aminobenzhydrazide [MABH]:** *m*-Aminobenzoic acid was esterified to methyl 3-aminobenzoate (3-MABE) by use of sulfuric acid catalyst in methanol. This (3-MABE) on reaction with excess of hydrazine hydrate in methanol yielded MABH. Crude MABH was recrystallized from chloroform, mp 91–92°C.

(b) ***p*-Aminobenzhydrazide [PABH]:** *p*-Aminobenzoic acid was esterified to methyl 4-aminobenzoate [4-MABE] by use of hydrochloric acid gas as catalyst in methanol. This [4-MABE] was then reacted with excess of hydrazine hydrate in methanol to form PABH. Crude PABH was recrystallized from methanol, mp 223°C.

Methods

Polymer Synthesis

The polymers were synthesized by low-temperature polycondensation. A typical synthesis of poly[3-(isophthaloylamino) benzoic acid hydrazide] [PAH 1010] is as follows:

A 1000-mL four-necked round-bottom flask was equipped with halfmoon stirrer, nitrogen inlet tube, and thermowell. *m*-Aminobenzhydrazide [MABH], 12.094 g (0.08 mol), and 320 mL of dry *N,N*-dimethylacetamide [DMAC] were added and stirred under nitrogen atmosphere until complete dissolution. The contents were cooled to –10°C. After 20 min, 16.243 g (0.08 mol) of isophthaloyl chloride [ICl] was added slowly with constant stirring over a period of 1 h. After this period, the reaction was continued at –10°C for another 2 h. The reaction temperature was then raised to room temperature and maintained for 12 h with stirring under nitrogen atmosphere. The reaction mixture was then neutralized with 5.9 g (0.078 mol) of lithium carbonate, heated to 80°C, degassed under vacuum, and filtered through sintered glass funnel. The polymer solution was precipitated with 3 L of deionized water. The precipitated polymer was washed with cold and hot water, acetone, and dried at 75°C at vacuum for 6–7 h. The yield of polymer (PAH 1010) was 21.8 g (97%).

The polymerization procedure was repeated using *N*-methyl-2-pyrrolidone [NMP] as solvent instead of DMAC under similar experimental conditions to study the effect of solvent on molecular weight buildup.

Polymer Characterization

(a) Percent moisture regain (% MR): A dried polymer sample (at 70°C, 3 mm Hg, for 6 h) was allowed to absorb moisture for 24 h in a humidity chamber

maintained at 65% relative humidity (RH) at 22°C. Then a weighed amount of the moisture-absorbed sample was dried in an oven at 110°C to a constant weight. The percent moisture regain by the polymer sample was calculated on the basis of weight loss.

(b) Solubility: The solubility of polymers in DMAC was determined at room temperature (22°C). The saturated solutions of the polymers in DMAC were prepared at room temperature by equilibrating for 24 h. The solubilities of polymers were recorded as percent weight dissolution per hundred gram of solvent (% wt/wt).

(c) Viscosity: Relative viscosities of a 0.5% solution of polymers in DMAC were measured at 25°C using Ubbelohde viscometer. Inherent viscosities (η_{inh}) were calculated and expressed in deciliter per gram.

Asymmetric Membrane Casting

Flat sheet asymmetric RO membranes were prepared by the following solution casting technique. Lithium chloride (0–7 g) was dissolved in 100 mL of DMAC at room temperature (22–25°C) and the polymer (4–20 g) was dissolved in this mixed solvent system. Alternately, casting solution can also be prepared from the reaction mixture directly. The reaction mixture was neutralized with lithium carbonate and then filtered. An additional amount of lithium chloride was added to bring the salt concentration to the desired level.

The casting solution (at room temperature, 22°C) was poured onto a clean, dry glass plate (30 × 20 cm) and spread with the aid of a specially designed casting glass rod to form uniform thin film. The thickness of the cast solution was controlled between 200 and 450 μm . The glass plate was placed in an air-circulating electrically heated oven maintained at 110°C. All the membranes were cast at a constant temperature of 110°C. The evaporation period was varied between 10 and 300 min. The glass plates were cooled and immersed in a deionized water bath for at least 15 h at room temperature. This ensured the preservation of the anisotropic membrane structure. This operation completely removes the residual salt and solvent from the membrane. All the membranes were preserved in deionized water until testing at ambient temperature.

These membranes were tested either directly or after annealing for different times (from 1 to 15 min) in deionized water that was maintained at 60–90°C.

Membrane Characterization

(a) Specific water content (S): 4 × 4 cm² specimens of the membrane were cut. Water adhering to the surface of the membrane was removed by pressing it in between filter papers. The specimens were weighed and then dried to constant weights at 110°C. The specific water content determined was expressed in grams of water present per cubic centimetre (g/cm³) of membrane.

(b) RO performance evaluation:

(i) RO testing unit: The RO testing unit fabricated in house for this study is presented in Figure 1. It consists of a 40-L capacity feed reservoir (FR). The feed reservoir was connected to the pressure dosing pump (DP) with the constant capacity to pump 13 L of feed per minute. The dosing pump was connected to the water reservoir (WR₁); this reservoir in turn was connected to the feed inlet (FI) of the test cell (A) as well as air reservoir (AR). The outlet of the

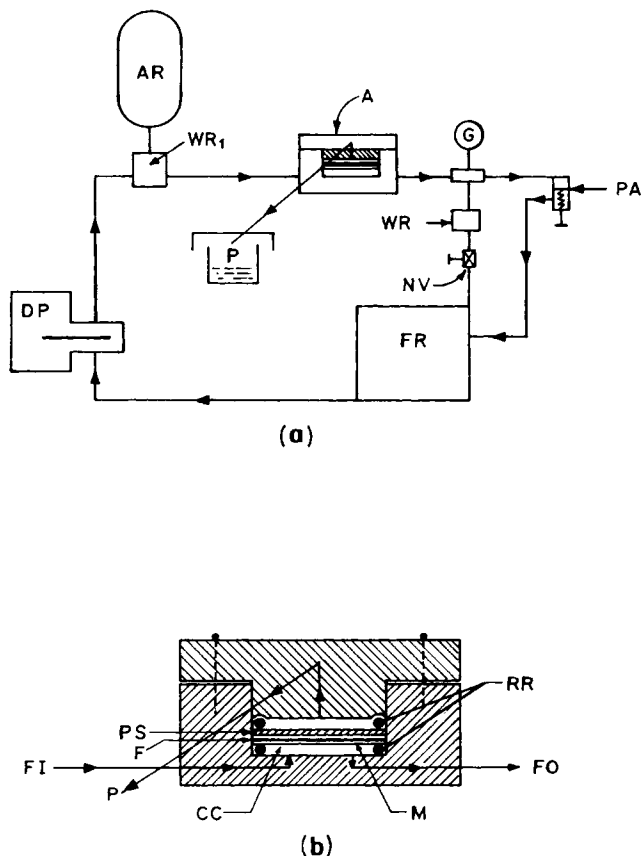


Fig. 1. (a) RO testing unit and (b) RO testing cell.

test cell (FO) for feed retentate was connected to a pressure gauge (G). The pressure gauge was connected to the feed reservoir through two arms. In one arm, pressure regulator valve (PA) and in the other arm water reservoir (WR₂) and needle valve (NV) were connected. The high-pressure line connections between DP, WR₁, AR, A, G, WR₂, and PA were made using $\frac{1}{4}$ -in.-diameter high-pressure stainless steel pipes with stainless steel unions. The low-pressure connections from FR to DP, RV to FR, and PA to FR were made with rigid PVC tubing of 0.5 cm internal diameter. The pressure gauge (G) recorded pressure in the range from 0 to 140 kg/cm² (0 to 2000 psi). WR₁, WR₂, and AR help in maintaining constant pressure. The test cell was with a test chamber (CC) diameter of 50 mm. The permeate (P) was collected from the upper half of the test cell at atmospheric pressure.

Circular membrane (M) of diameter 50 mm was placed in the test cell (A) with the skin layer facing the incoming feed. The membrane was supported on filter paper (F) and porous stainless steel plate (PS). Rubber O rings (RR) were used to seal the membranes and ensure leak-free operations. In all RO test experiments, the effective membrane area remained constant, i.e., 13.2 cm².

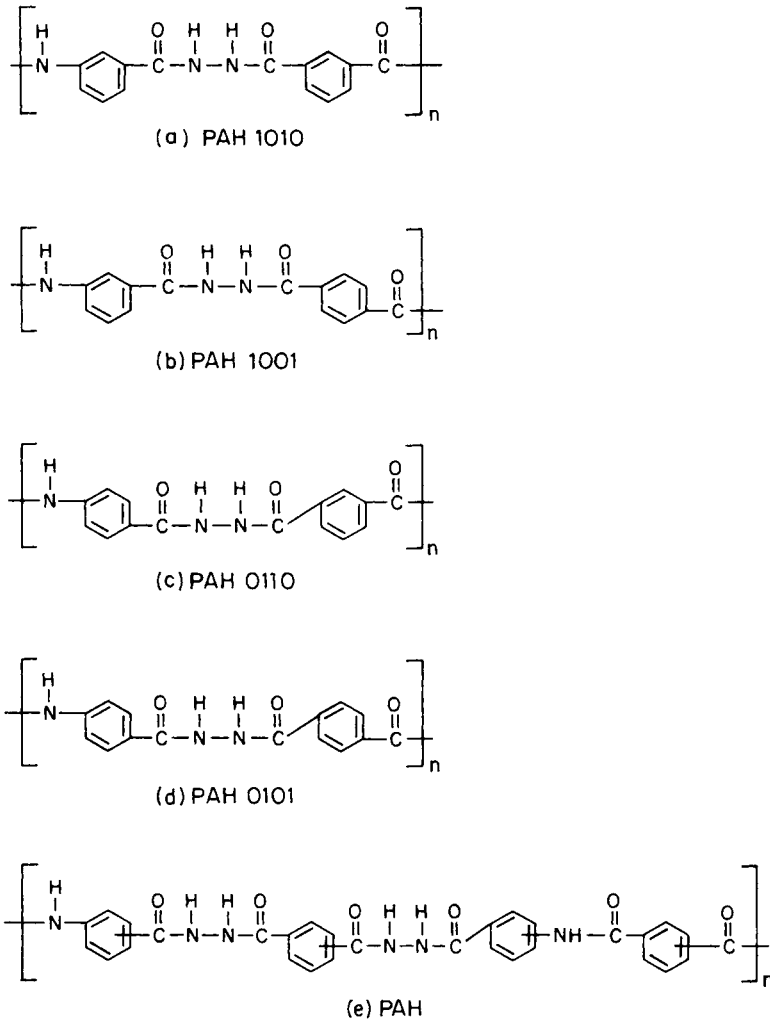


Fig. 2. Wholly aromatic polyamide-hydrazides.

(ii) RO tests: The water permeability tests were performed for deionized water and 5000-ppm aqueous sodium chloride feed solutions at room temperature. The feed concentration was kept constant in all the test experiments. The tests for deionized water were conducted for 2 h with an interval of 25 min. The tests for feed solution (5000 ppm NaCl/H₂O) were performed for 6 h with an interval of 30 min. The operating pressure was also kept constant at either 40 or 70 kg/cm². The permeate volumes (fluxes) were measured in milliliters. The concentration of electrolyte (NaCl) in the feed and in the permeate were measured using a standardized digital conductivity meter.

The pure water permeability constant (A) was expressed in g mol H₂O/cm² s atm. Permeate fluxes for 5000-ppm aqueous sodium chloride feed solutions were recorded as centimeters per day and salt rejections as percent salt rejection.

TABLE I
Monomer Compositions and Inherent Viscosities of Aromatic Polyamide-Hydrazides (PAH)^a

Polymer code	% Monomer				Reaction solvent	η_{inh}^b (dL/g)
	MABH	PABH	ICI	TCl		
PAH 1010	100	—	100	—	NMP	0.69
PAH 1001	100	—	—	100	DAMC	1.60
PAH 0110	—	100	100	—	NMP	1.01
PAH 0101	—	100	—	100	DAMC	3.35

^a Polymers prepared by low-temperature solution polycondensation method.

^b Determined in DMAC at 25°C.

RESULTS AND DISCUSSION

Polymer Preparation

The wholly aromatic polyamide-hydrazide polymers were prepared by the reactions of MABH/PABH with stoichiometric amounts of ICl/TCl in DMAC/NMP as illustrated in Figure 2. These four PAH polymers are as (a) poly[3-(isophthaloylamino) benzoic acid hydrazide] [PAH 1010], (b) poly[3-(terephthaloylamino) benzoic acid hydrazide] [PAH 1001], (c) poly[4-(isophthaloylamino) benzoic acid hydrazide] [PAH 0110], and (d) poly[4-(terephthaloylamino) benzoic acid hydrazide] [PAH 0101]. The structural compositions, solvents used, and inherent viscosities obtained are shown in Table I. The meta- and para-phenylene moieties were changed to incorporate 100% meta-, 50 : 50% meta : para, and 100% para-phenylene linkages in the polymers. Thus all polymers are structurally similar except for the mode of linking of phenylene groups in the polymer chain. The rate of reaction of hydrazide group with the acid chloride group is seven times faster than that of the amino group.¹⁶ Such polymers have partially ordered structures.^{14,16-19} From these studies it appears that the PAH polymers obtained in our studies may have predominantly the structure of partially ordered type [(e)-PAH] as given in Figure 2.

DMAC and NMP act as good acid acceptor solvents for polymerization. The liberated hydrogen chloride reacts with the solvent (DMAC/NMP) to form

TABLE II
Percent Moisture Regain (% MR) and Solubility of Aromatic Polyamide-Hydrazide Polymers

Polymer code	η_{inh}^a (dL/g)	Moisture regain ^b (%)	Maximum solubility ^c (% wt/wt)
PAH 1010	0.69	12.70	60
PAH 1001	0.62	13.81	50
PAH 0110	0.73	13.50	45
PAH 0101	3.35	14.83	17.5

^a Determined in DMAC at 25°C.

^b Determined at 22°C and RH 65%.

^c Determined in DMAC at 22°C.

TABLE III
Directional Performance of Membranes^a (on PAH 1010)

Skin facing to feed side		Skin facing to permeate side	
Flux (cm/day)	Salt rejection (%)	Flux (cm/day)	Salt rejection (%)
48.5	95.89	56.2	93.16
93.0	95.64	104.6	91.81
51.9	93.81	65.0	90.12

η_{inh} (PAH 1010): 0.69 dL/g
 Casting solution: Polymer 14%, LiCl 5%, and DMAC 81%
 Cast thickness: 200 μ m
 Evaporation period: 35–45 min
 Annealing: 70°C for 2 min (H₂O)
 Operating pressure: 70 kg/cm²

^a Evaporation temp.: 110°C, coagulation temp.: 22–25°C (H₂O), feed conc.: 5000 ppm NaCl/H₂O, effective membrane area: 13.2 cm², pump feed flow rate: 13 L/h.

salts (DMAC-HCl/NMP-HCl). The salts may enhance the solubility of the growing polymer, thereby assisting in molecular weight buildup. It was also observed that the type of reaction media affects the polymer molecular weight.

Viscosities

The inherent viscosities for polyamide-hydrazides are given in Table I. These polymers are of high molecular weights. The polymer chain rigidity in this series increases with an increase in para-linkages as observed from the increased values of inherent viscosities (DMAC, at 25°C) from 0.69 to 3.35 dL/g for PAH 1010 to PAH 0101. The polymers with all meta-linkages have low inherent viscosities, whereas those with para-linkages have high inherent viscosities. The polymers with 50 : 50 meta : para-linkages (PAH 1001 and PAH 0110) have intermediate inherent viscosities in between these two values. The higher inherent viscosities for PAH 1010 and PAH 0110 were obtained in NMP as the best reaction media; however, inherent viscosities for PAH 1001 and PAH 0101 were higher in DMAC. It was also observed that the polymerizations at small-scale (0.02 mol) reactions gave polymers of high inherent viscosities, but for the large-scale (0.08 mol) experiments, the viscosities obtained were invariably lower than those observed in Table I. This may be due to the effect of stirring and other factors that affect the large-scale reaction.

Percent Moisture Regain

All PAH polymers showed the percent moisture regain (% MR) between 10 and 15% (at 22°C, RH 65%) as shown in Table II. This high moisture uptake reflects the hydrophilic/polar character of these polymers. The presence of a hydrazide group enhances the moisture uptake relative to polyamides (5% MR) and cellulose acetate (6% MR).²⁰ In normal polyamides, there is one NHCO group per unit as against one CONHNHCO group per unit in the hydrazides.

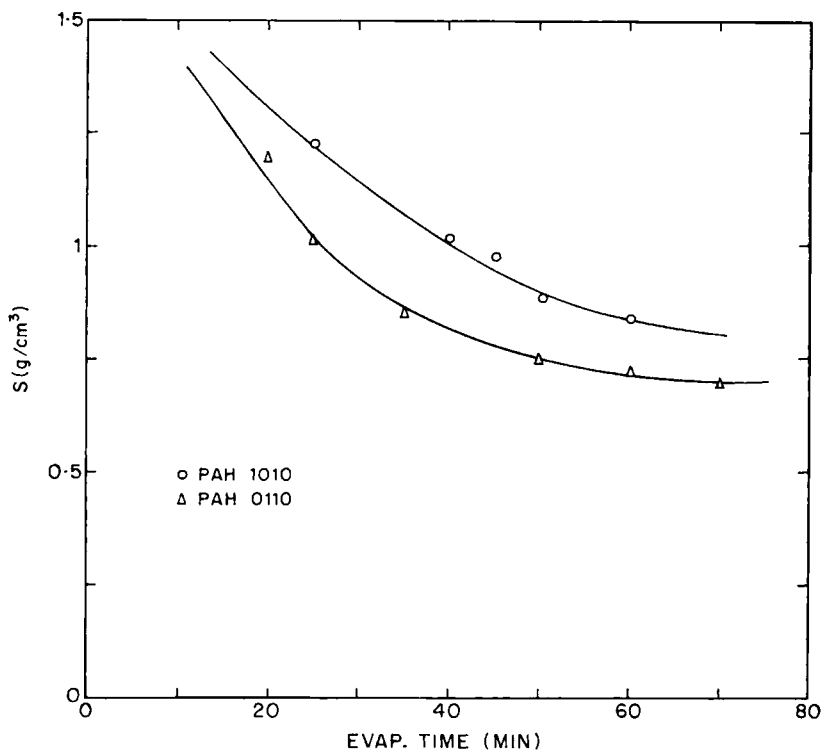


Fig. 3. Effect of evaporation period on specific water content of membranes.

As most of the polymer polarity is due to functional groups, the latter are more polar and hence attract larger water sorption. The moisture uptake of polyamide hydrazides is nearly similar to polybenzimidazoles (13% MR).²⁰ The high percent moisture uptake degree of these polymers guides us to select them as RO candidate materials.

Solubility

The polyamide-hydrazide polymers were highly soluble at room temperature in polar solvents such as DMAC, NMP, dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), hexamethylphosphoramide (HMPA), and concentrated sulfuric acid. The solubilities of PAH polymers in DMAC at room temperature are listed in Table II. The wt % solubility at 22°C for PAH 1010, PAH 1001, PAH 0110, and PAH 0101 were as 60, 50, 45, and 17.5, respectively. The PAH 0101 with all para-linkages forms very high viscous solutions even at lower concentrations; however, at higher concentrations these solutions appear as gels.

In general, high solubility is a desired requirement for membrane processing. The higher solubility of polyamide-hydrazides in comparison to Kevlar (polyterephthalamide) is due to the higher polarity of amide linkages as well as the weaker intermolecular hydrogen bonding.^{21,22} The polymers having para-linkages in this series are less soluble in DMAC than the polymers having meta-

TABLE IV
Effect of Evaporation Period on PAH 1010 Membranes^a

Evaporation period (min)	<i>S</i> (g/cm ³)	<i>A</i> × 10 ⁶ (g mol H ₂ O/cm ² s atm)	Flux (cm/day)	Salt rejection (%)
25	1.22	2.6	133.0	74.45
40	1.02	1.8	92.4	82.58
45	0.98	1.6	79.7	85.87
50	0.88	1.5	76.6	90.14
60	0.84	1.2	53.1	70.04

η_{inh} (PAH 1010): 0.69 dL/g

Casting solution: Polymer 14%, LiCl 5%, and DMAC 81%

Cast thickness: 200 μ m

Operating pressure: 40 kg/cm²

^a Same as in Table III. *S*, specific water content of membrane; *A*, pure water permeability constant.

linkages. This may be due to the increased rigidity, packing efficiency, and hydrogen bonding.

Membrane Evaluation

Membrane Anisotropy

Electron microscopic studies reveal that the cast membranes have anisotropic structures,^{8,9,23} i.e., a thin-skin layer (active layer) and supporting core type matrix structure. During the solvent evaporation step, the free surface exposed to atmosphere assumes a dense skin type of structure, and the surface in contact with the glass plate (substrate) retains a more porous structure. This structure was preserved by coagulation in water. A simple dye penetration test shows

TABLE V
Effect of Evaporation Period on PAH 0110 Membranes^a

Evaporation period (min)	<i>S</i> (g/cm ³)	<i>A</i> × 10 ⁶ (g mol H ₂ O/cm ² s atm)	Flux (cm/day)	Salt rejection (%)
20	1.20	1.11	62.5	86.32
25	1.01	1.08	56.7	88.83
35	0.85	1.03	48.9	89.06
50	0.75	0.90	37.5	91.99
60	0.72	0.69	26.4	92.56
70	0.70	0.26	15.1	91.00

η_{inh} (PAH 0110): 0.73 dL/g

Casting solution: Polymer 10%, LiCl 2%, and DMAC 88%

Cast thickness: 200 μ m

Operating pressure: 40 kg/cm²

^a Same as in Table III. *S*, specific water content of membrane; *A*, pure water permeability constant.

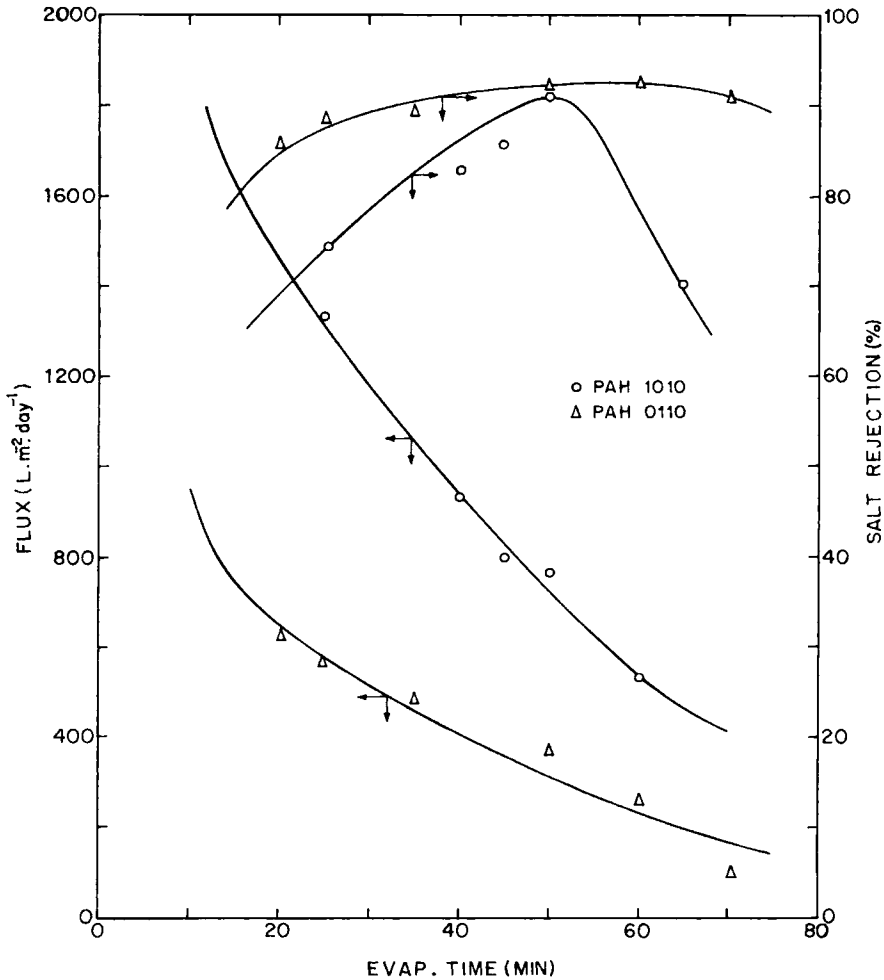


Fig. 4. Effect of evaporation period on flux and salt rejection.

the concentration of dye molecules on the skin side that is absent on the porous side due to passage of dye into the pores of the porous layer.

To understand the anisotropy (asymmetry) of membranes, both surfaces of the membranes were exposed for RO tests. These results are shown in Table III. The PAH 1010 membrane displayed a 95.89% salt rejection and 48.5 cm/day flux at 70 kg/cm² operating pressure. On reversing the membrane surface of the same membrane (skin facing the permeate side), 93.16% salt rejection and a flux of 56.2 cm/day was observed. This increase in flux characteristic is coupled to a loss in salt rejection that is typical of anisotropic membrane.¹⁵ The reduced selectivity during the reverse operation is partially attributed to the concentration polarization in the porous supporting matrix layer of the membrane.¹⁰

Specific Water Content

The specific water content (S) is a measure of the porosity of the membrane. It depends on the casting solution composition, casting conditions, annealing

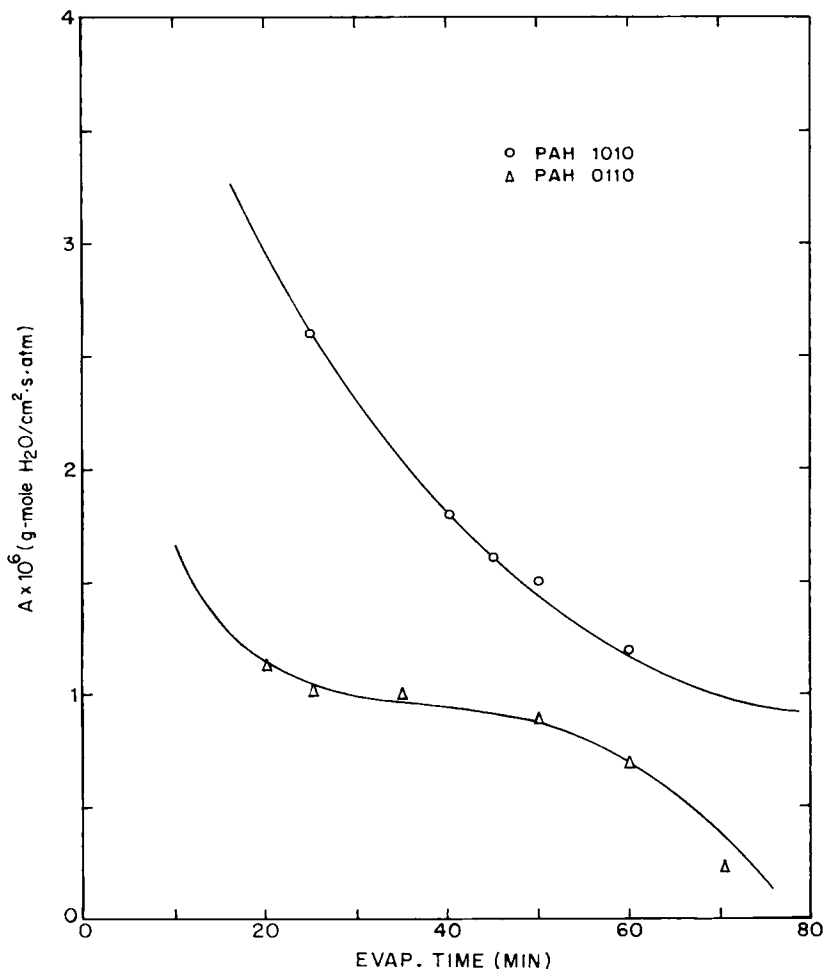


Fig. 5. Effect of evaporation period on pure water permeability constant.

temperature, and annealing time. The results obtained for PAH 1010 and PAH 0110 membranes are as shown in Figure 3. The values reported are for intact membrane as it was difficult to estimate the water content for dense skin alone. The higher values could be due to condensed water in the voids of the porous layer. The specific water content decreases with increase in evaporation period and is ultimately a measure of membrane characteristics. As seen from Table IV, the specific water content for PAH 1010 membranes decreased from 1.22 to 0.88 g/cm³, as the evaporation time was increased from 25 to 60 min. The same membrane on annealing at 70°C for 2 min observed specific water content between 0.98 and 0.70 g/cm³ (as shown in Table VIII), which is lower than observed before annealing. The specific water content also depends on the casting solution composition (as seen from Table VI) and on annealing temperature (as seen from Table X).

Effect of Evaporation Period

The effect of evaporation period on the RO performance of PAH 1010 and PAH 0110 membranes are shown in Tables IV and V, respectively. In case of

TABLE VI
Effect of Lithium Chloride (in Casting Solution) on PAH 1001 Membranes^a

Casting solution	Evaporation period (min)	S (g/cm ³)	A × 10 ⁶ (g mol H ₂ O/cm ² s atm)	Flux (cm/day)	Salt rejection (%)
I	40	0.9	0.9	43.5	93.44
II	40	1.1	1.3	51.9	94.04
I	45	0.7	0.7	31.1	95.04
II	45	0.75	1.1	48.8	96.95

η_{inh} (PAH 1001): 0.62 dL/g
 Casting solution: I II
 Polymer (%) 10 10
 LiCl (%) 1 2
 DMAC 89 88
 Operating pressure: 40 kg/cm²

^a Same as in Table III. S, specific water content of membrane; A, pure water permeability constant.

PAH 1010 membranes, an increase in evaporation period from 20 to 60 min at 40 kg/cm² operating pressure resulted in a decrease in the flux from 133.0 to 53.1 cm/day, while the salt rejection reaches a maximum of 90.14%, which corresponds to an evaporation period of 50 min (as shown in Fig. 4). The decrease in salt rejection after 50 min can be attributed to the onset of organization (crystallization) at higher evaporation times.¹⁰

Similarly, the PAH 0110 membranes cast between 20 and 70 min showed an increase in salt rejection with evaporation time up to 60 min (as shown in

TABLE VII
Effect of Casting Solution Composition on PAH 0101 Membranes^a

Cast solution	Evaporation period (min)	Flux (cm/day)	Salt rejection (%)
I	30	47.7	91.22
I	40	45.2	93.57
II	30	50.2	79.16
II	40	20.9	85.90
III	30	24.7	98.29
III	40	20.9	98.59

η_{inh} (PAH 0101): 3.35 dL/g
 Casting solution: I II III
 Polymer % 4 4 7
 LiCl % 1.5 2 2
 DMAC % 94.5 94 91
 Cast thickness: 450 μ m
 Annealing: 90°C for 5 min (H₂O)
 Operating pressure: 70 kg/cm²

^a Same as in Table III.

TABLE VIII
Effect of Annealing on PAH 1010 Membranes^a

Evaporation period (min)	<i>S</i> (g/cm ³)	<i>A</i> × 10 ⁶ (g mol H ₂ O/cm ² s atm)	Flux (cm/day)	Salt rejection (%)
25	0.98	1.7	78.3	90.89
40	0.88	1.4	64.2	92.70
45	0.85	1.2	56.7	93.77
50	0.79	1.1	53.1	95.76
60	0.70	1.0	43.5	78.00

η_{inh} (PAH 1010): 0.69 dL/g

Casting solution: Polymer 14%, LiCl 5%, and DMAC 81%

Cast thickness: 200 μ m

Annealing: 70°C for 2 min (H₂O)

Operating pressure: 40 kg/cm²

^a Same as in Table III. *S*, specific water content of membrane; *A*, pure water permeability constant.

Table V and Fig. 4). However, a small loss in rejection was noted due to morphological changes above 60 min. This decrease in rejection is less than that of PAH 1010 membranes and is due to the decrease in meta-phenylene content from 100 to 50% (50 : 50, meta : para). At less than 20 min evaporation period, the salt rejections for both the membranes were poor (< 70–80%). The pure water permeability constant (*A*) for PAH 1010 and PAH 0110 membranes was decreased from 2.6 to 1.2×10^{-6} and from 1.11 to 0.26×10^{-6} gm mol H₂O/cm² s atm when the evaporation period was increased from 25 to 60 and 20 to 70 min, respectively, as shown in Fig. 5.

The solvent type, temperature, time of evaporation, and casting solution composition determines the rate and extent of solvent evaporation. The residual solvent content indicates the porosity and pore size distribution of the membrane. At relatively short evaporation time a greater amount of solvent remains,

TABLE IX
Effect of Annealing on PAH 0110 Membranes^a

Evaporation period (min)	Membrane type	Flux (cm/day)	Salt rejection (%)
15	Unannealed	112.8	80.86
15	Annealed	68.0	93.38
25	Unannealed	56.6	88.77
25	Annealed	45.2	94.01

η_{inh} (PAH 0110): 0.73 dL/g

Casting solution: Polymer 10%, LiCl 2%, and DMAC 88%

Cast thickness: 200 μ m

Annealing: 70°C for 2 min (H₂O)

Operating pressure: 40 kg/cm²

^a Same as in Table III.

TABLE X
Effect of Annealing Temperature on PAH 1010 Membranes^a

Membrane type	<i>S</i> (g/cm ³)	<i>A</i> × 10 ⁶ (g mol H ₂ O/cm ² s atm)	Flux (cm/day)	Salt rejection (%)
Unannealed	1.20	1.57	127.3	79.00
Annealing at 70°C for 2 min	0.90	0.97	86.0	92.33
Annealing at 90°C for 2 min	0.79	0.49	45.5	96.37

η_{inh} (PAH 1010): 0.69 dL/g

Casting solution: Polymer 14%, LiCl 5%, and DMAC 81%

Cast thickness: 200 μ m

Evaporation period: 40 min

Operating pressure: 70 kg/cm²

^a Same as in Table III. *S*, specific water content of membrane; *A*, pure water permeability constant.

which gives rise to a more porous membrane structure (i.e., less permselectivity). Extended and longer drying times result in considerable loss of solvent, which on coagulation gives less porous membrane. Membranes were opaque in appearance when evaporation period was short (< 15 min) and turned transparent with the increase in evaporation period.

Effect of Casting Solution Composition

The casting solution compositions are very important in membrane casting. Lithium chloride was added to improve permselectivity of the membrane. The effect of lithium chloride concentration in casting solutions on the performance of membrane is presented in Table VI. For membranes of PAH 1001, with an increase in lithium chloride concentration from 1 to 2%, an increase in the flux was observed. For the membrane dried up to 40 min the flux was increased from 43.5 to 51.9 cm/day, and for the membrane dried at 45 min it increased from 31.1 to 48.8 cm/day at nearly similar rejections. For good RO performance the lithium chloride concentration was found to be 10–50 wt % of the polymer

TABLE XI
Effect of Inherent Viscosity on PAH 1001 Membranes^a

η_{inh} (dL/g)	Evaporation period (min)	Flux (cm/day)	Salt rejection (%)
0.62	35	40.4	90.62
0.39	35	41.6	71.93
0.62	45	28.1	97.44
0.39	45	29.6	76.30

Casting solution: Polymer 7%, LiCl 1%, and DMAC 92%

Cast thickness: 200 μ m

Operating pressure: 70 kg/cm²

^a Same as in Table III.

in casting solution. As shown in Table VII, the lithium chloride loading equal to 50 wt % results in the loss of membrane permselectivity. The PAH 0101 membrane cast from casting solution III (polymer 7%, LiCl 2%, and DMAC 91%) is preferable over the other two casting solutions (I and II).

Effect of Annealing

Electron microscopic studies revealed that the pore size of membrane skin decreases on annealing.^{10,23} The extent of decrease in pore size, i.e., membrane shrinkage, varies with annealing time and temperature. The pore size in the membrane skin decreases due to the consolidation of the skin region with little effect on the membrane interior matrix. Annealing decreases the flux level at increased salt rejection, as given in Tables VIII and IX. The effect of annealing temperature on flux and rejection is presented in Table X. Annealing of membrane at 70°C for 2 min results in increased salt rejection from 79.00 to 88.33% and with simultaneous reduction in flux from 127.3 to 86 cm/day at 70 kg/cm² operating pressure. The salt rejection of the same membrane was further enhanced to 96.37% with still lower flux of 45.5 cm/day on annealing at 90°C for 2 min. Thus, annealing of PAH membranes significantly influences their RO performance. The performance of PAH membrane annealed at 90°C appears to be better than cellulose acetate membranes.²⁴

Effect of Molecular Weight (Viscosity)

The membrane performance is dependent on the molecular weight of the polymer. The RO results for the two PAH 1001 polymers of inherent viscosities 0.62 and 0.39 dL/g are presented in Table XI. It seems that the polymers with inherent viscosity of 0.62 dL/g have better RO performance than the polymers having inherent viscosity of 0.39 dL/g. The polymers having higher inherent viscosity are more rigid and are associated with increased intermolecular hydrogen bonding. Hence they offer higher resistance to water and salt flow resulting in better RO performance.

CONCLUSIONS

The wholly aromatic polyamide-hydrazide polymers of high molecular weights (film forming viscosities) were synthesized for RO membrane preparation. DMAC and NMP were found to be the best solvents for polymerization reactions. All polymers exhibited high solubility in DMAC and a high degree of moisture uptake. The RO membrane performance was found to be dependent on casting solution composition (containing lithium chloride salt), evaporation time period, and annealing temperature.

One of us (M.D.S.) wishes to thank CSIR, New Delhi, for the award of Senior Research Fellowship, Dr. S. S. Kadam, Principal, Poona College of Pharmacy (Degree), Pune, for his keen interest and Mr. S. B. Dhumal for his assistance in the work.

References

1. J. W. Richter and H. H. Hoehn, *Ger. Offen.* 1,941,932 (1970); *Chem. Abstr.*, **73**, 26342v (1970).

2. L. E. Applegate and C. R. Antonson, in *Reverse Osmosis Membrane Research*, H. K. Lonsdale and H. E. Podall, Eds., Plenum, New York, 1972, p. 243.
3. R. A. Halling, U.S. Pat., 3,954,607 (1976); *Chem. Abstr.*, **85**, 47674t (1976).
4. N. W. Rosenblatt, *Proc. Int. Symp. Fresh Water Sea, 4th*, **4**, 349 (1973).
5. N. W. Rosenblatt, J. P. Agrawal, C. R. Antonson, D. C. Brandt, and D. M. Brethauer, *NTIS from Gov. Announce Index (U.S.)*, **76**(15), 69 (1976); *Chem. Abstr.*, **86**, 60330t (1977).
6. T. Matsura, P. Blais, L. Pageau, and S. Sourirajan, *Ind. Eng. Chem. Process Des. Dev.*, **16**(4), 510 (1977).
7. K. Chan, T. Matsura, and S. Sourirajan, *Ind. Eng. Chem. Prod. Res. Dev.*, **23**, 492 (1984).
8. R. McKinney, Jr., in *Reverse Osmosis Membrane Research*, H. K. Lonsdale and H. E. Podall, Eds., Plenum, New York, 1972, p. 253.
9. R. McKinney, Jr., *Se. Purif. Methods*, **1**(1), 31 (1972); *Se. Purif. Methods*, **3**, 87 (1974).
10. R. McKinney, Jr., and J. H. Rhodes, *Macromolecules*, **4**, 633 (1971).
11. P. Zschocke and H. Strathmann, *Angew. Makromol. Chem.*, **73**, 1 (1978) (Ger.); *Chem. Abstr.*, **90**, 122630j (1979).
12. P. R. Dvornic, *J. Polym. Sci. Polym. Chem. Ed. A1*, **24**, 1133 (1986).
13. B. M. Culbertson and R. Murphy, *J. Polym. Sci. Polym. Lett. Ed.*, **5**, 807 (1967).
14. J. Preston, W. B. Lack, and W. L. Hofferbert, Jr., *J. Macromol. Sci. Chem.*, **A7**, 67 (1973).
15. S. Sourirajan and T. Matsura, in *Reverse Osmosis and Ultrafiltration Process Principles*, Ottawa Publication, Canada, 1985, p. 641.
16. R. W. Morrison, J. Preston, J. C. Randall, and W. B. Black, *J. Macromol. Sci. Chem.*, **A7**, 99 (1973).
17. J. C. Randel, R. W. Morrison, and J. Preston, *J. Macromol. Sci. Chem.*, **A7**, 119 (1973).
18. J. Preston, W. B. Black, and W. L. Hofferbert, Jr., *J. Macromol. Sci. Chem.*, **A7**, 45 (1973).
19. H. Herlinger, H. P. Hoerner, F. Druschke, W. Denneler, and F. Haiber, *J. Appl. Polym. Sci. Appl. Polym. Symp.*, **21**, 201 (1973).
20. H. Strathmann and A. S. Michaels, *Desalination*, **21**, 195 (1977).
21. E. W. Hughes and W. J. Moore, *J. Am. Chem. Soc.*, **71**, 2618 (1949).
22. H. Kakida, Y. Chatani, and H. Tadokora, *J. Polym. Sci. Polym. Phys. Ed.*, **14**, 427 (1976).
23. M. Panar, H. H. Hoehn, and R. R. Herbert, *Macromolecules*, **6**, 777 (1973).
24. R. C. Bindal, V. Ramachandran, B. M. Misra, and M. P. S. Ramani, *Sep. Sci. Tech.*, in press.

Received July 12, 1989

Accepted October 2, 1989