

# Novel wholly aromatic polyamide-hydrazides: 6. Dependence of membrane reverse osmosis performance on processing parameters and polymer structural variations

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Integrally skinned phase inversion membranes were successfully cast from dimethylacetamide solutions of a series of novel wholly aromatic polyamide-hydrazides for reverse osmosis performance. All the membranes were characterized for their salt rejection (percentage) and water permeability ( $\text{cm}^3 \text{cm}^{-2} \text{day}^{-1}$ ) of 0.5 N aqueous sodium chloride feed solution at 3924 kPa operating pressure. The effect of polymer structural variations together with several processing parameters to achieve the best combination of high selectivity and permeability were discussed. The polymers structural variations were obtained by varying their *para*- and *meta*-oriented phenylene rings content. The latter was changed from 0 to 50 mol%. The processing variables included temperature and period of the solvent evaporation of the cast membranes, coagulation temperature of the thermally treated membranes and annealing of the coagulated membranes, casting solution composition, membrane thickness and the operating pressure. During the thermal treatment step the asymmetric structure of the membranes with a thin dense skin surface layer supported on a more porous layer was established. The former layer seems to be responsible for the separation performance. The results revealed that the membrane performance depended strongly on the conditions of its processing as well as the structure of the polymer from which it is cast. Under identical preparation condition, substitution of *p*-phenylene rings for *m*-phenylene ones within the polymer series resulted in an increase in salt rejection capability of the membranes. This may be attributed to an increase in their chain symmetry associated with increased molecular packing and rigidity through enhanced intermolecular hydrogen bonding. This produces a barrier with much smaller pores that would efficiently prevent the solute particles from penetration. For a given membrane, the higher the temperature and the longer the period of the solvent evaporation would result in a membrane of lower solvent content and with a thicker skin layer and consequently led to higher salt rejection at lower water permeability. Further, annealing in deionized water at 100°C produced membranes with optimum salt rejection. Upon annealing, the membrane shrinks resulting in decreasing its pore size particularly in the skin layer. This membrane morphology change improved the salt rejection. Addition of lithium chloride to the casting solution produced a membrane with increased porosity and improved its water permeability. The effects of coagulation temperature and thickness of the membrane on the separation efficiency were also discussed. The optimum salt separation of the membranes was attained at nearly 4000 kPa operating pressure. Membranes showed rejection up to 99.5% at water permeability  $13 \text{cm}^3 \text{cm}^{-2} \text{day}^{-1}$ . © 1997 Elsevier Science Ltd.

(Keywords: polyamide-hydrazides; semipermeable membranes; reverse osmosis performance)

## INTRODUCTION

Reverse osmosis has attracted much attention as a water desalination process since 1950. Most of the candidate semipermeable reverse osmosis desalination membranes have been developed from organic polymer films. There are numerous successful membrane forming materials such as cellulose acetate<sup>1–5</sup>, nylon 4<sup>6</sup>, poly(hydroxyethyl methacrylate)<sup>7</sup>, poly(vinyl alcohol)<sup>8</sup>, ethylene-vinyl alcohol copolymer<sup>9</sup>, aromatic polyamide and polyamide-hydrazides<sup>10–15</sup>.

In general, semipermeable membrane characteristics are controlled by various preparation parameters: (1) the choice of casting solution solvents; (2) additive to the

casting solution<sup>13</sup>; (3) post-casting treatment such as solvent evaporation temperature and solvent evaporation period<sup>13–15</sup>; (4) coagulation medium and temperature<sup>10</sup>; and (5) post treatment operation such as annealing in deionized water<sup>10,13,15</sup> and exposure to concentrated mineral acids<sup>14</sup>.

In the earlier papers of this series<sup>16,17</sup>, several wholly aromatic polyamide-hydrazides were synthesized as highly viscous film forming solutions. They were structurally characterized by various proportions of *p*- to *m*-phenylene moieties contents. They are characterized by a number of properties that not only meet the desired requirements for polymer processing, but also demonstrate that these polymers are promising candidates for

several applications. They were highly soluble in various polar organic solvents, have high thermal and thermo-oxidative stability and have good mechanical and chemical resistance. They also exhibited high moisture sorption that would be useful for processing as synthetic fibres and membranes. These properties were found to be strongly affected by the polymers structural differences. The wholly *p*-oriented type of polymer, poly[4-(terephthaloylamino)salicylic acid hydrazide], or polymer I in this work, had been examined for use as membrane for reverse osmosis performance<sup>15</sup>. Its asymmetric membranes were characterized by their ability to reject sodium chloride from its aqueous solution. Its reverse osmosis performance was strongly influenced by the preparation conditions and the molecular weight.

In the present work, the above parameters will be studied along with the structural variations within a series of novel wholly aromatic polyamide-hydrazides to achieve the best combination of high salt rejection together with high water permeability.

## EXPERIMENTAL

### Polymer synthesis and characterization

The polymers evaluated in this study were prepared by a low temperature (at  $-5^{\circ}\text{C}$ ) solution (in anhydrous dimethylacetamide, DMAc) polycondensation reaction of *p*-aminosalicylic acid hydrazide (PASH) with an equimolar amount of either terephthaloyl chloride (TCI), isophthaloyl chloride (ICI) or mixtures of various molar ratios of TCI and ICI. The polycondensation was preceded through the addition of the solid acid chloride into the cooling DMAc solution of PASH. The resulting polycondensation reaction mixtures were precipitated into methanol, filtered and dried in vacuum at  $80^{\circ}\text{C}$ . This polymerization method was previously described in detail<sup>16,17</sup>. Five polymers containing various proportions of *p*- to *m*-oriented phenylene moieties were obtained. Their *p*-/*m*-ratio varied from 100/0 to 50/50 mol% as shown in Table 1. It can be noted that all the polymers have the same structural formula except in the way of linking the phenylene rings inside the polymer chains. The intrinsic viscosity values reflected the high molecular weights of these polymers (Table 1), although they are generally higher for polymers having high *p*-phenylene ring content. It would be expected that the molecular weights of these polymers are generally comparable since

the purity levels of the two acid chlorides used are similar. The higher intrinsic viscosity value of the wholly *p*-oriented type of polymer can be attributed to the higher rigidity and greater interchain H-bonding due to its higher chain symmetry and consequently its greater packing efficiency<sup>17,18</sup>.

Moisture regain of the polymer was performed in a chamber of 67% relative humidity at  $30^{\circ}\text{C}$ . A perfectly dry polymer sample of known weight was allowed to absorb moisture for about 24h until constant weight. Percentage moisture regain was calculated on the basis of weight difference.

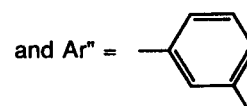
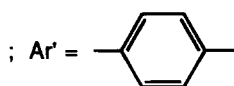
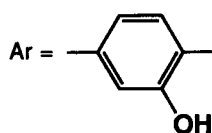
### Membrane preparation and characterization

The polymers were stirred in anhydrous DMAc at  $25^{\circ}\text{C}$  overnight to form 7wt% solutions. The membranes were prepared by casting these solutions on dry clean Pyrex glass plates to a uniform thickness of  $80\ \mu\text{m}$  with the aid of a specially designed glass rod. The plates were introduced into an air circulating electrically heated oven at a desired temperature for a selected time interval. This allows a partial evaporation of the solvent, particularly from the air facing surface of the casting solution, and correspondingly provides suitable pore size of the membrane. The plates were then immersed into deionized water overnight at  $25^{\circ}\text{C}$  to complete exchange of the residual solvent with water. The membrane thicknesses ranged from 4 to  $8\ \mu\text{m}$ . The appearance of the membranes depended on the temperature and duration of exposure in the oven evaporative step. The membranes thermally treated at high temperature and over a long period appeared completely transparent for their little or no residual solvent content. Those treated at low temperature or over a short period showed opacity because of their high residual solvent content and consequently large pores that filled with  $\text{H}_2\text{O}$  at the time of coagulation. The solvent free membranes were examined directly or after annealing in deionized water at pre-selected temperatures for various time intervals.

All the membranes were characterized for their salt rejection and water permeability. Reverse Osmosis High-Pressure Testing Equipment (Bioengineering Co. Ltd., Japan, Type RO-3) was used to measure the transport properties of the evaluated membranes. The reverse osmosis cell is diagrammatically shown in Figure 1. It consisted of two detachable parts and is made of stainless steel to avoid corrosion occurrence. The two parts were

Table 1 Some characteristics of wholly aromatic polyamide-hydrazides

Polymer	<i>p</i> -/ <i>m</i> -Phenylene units in polymer (%)	Repeat unit	$[\eta]^a$ dl g <sup>-1</sup>	MR <sup>b</sup> (%)
I	100/0	$\text{--HN--Ar--CONHNH--CO--Ar'--CO--}_n$	5.10	18.7
II	90/10	$\text{--HN--Ar--CONHNH--CO--(Ar')}_{0.8}\text{CO--HN--Ar--CONHNH--CO--(Ar'')}_{0.2}\text{CO--}_n$	3.93	19.2
III	75/25	$\text{--HN--Ar--CONHNH--CO--(Ar')}_{0.5}\text{CO--HN--Ar--CONHNH--CO--(Ar'')}_{0.5}\text{CO--}_n$	2.86	20.6
IV	60/40	$\text{--HN--Ar--CONHNH--CO--(Ar')}_{0.2}\text{CO--HN--Ar--CONHNH--CO--(Ar'')}_{0.8}\text{CO--}_n$	1.74	21.3
V	50/50	$\text{--HN--Ar--CONHNH--CO--Ar''--CO--}_n$	1.20	22.1



<sup>a</sup> Determined in DMAc at  $30^{\circ}\text{C}$ , polymer concentration was  $0.5\ \text{g dl}^{-1}$

<sup>b</sup> Moisture regain was determined at  $30^{\circ}\text{C}$  and relative humidity 67% and based on the dry polymer weight

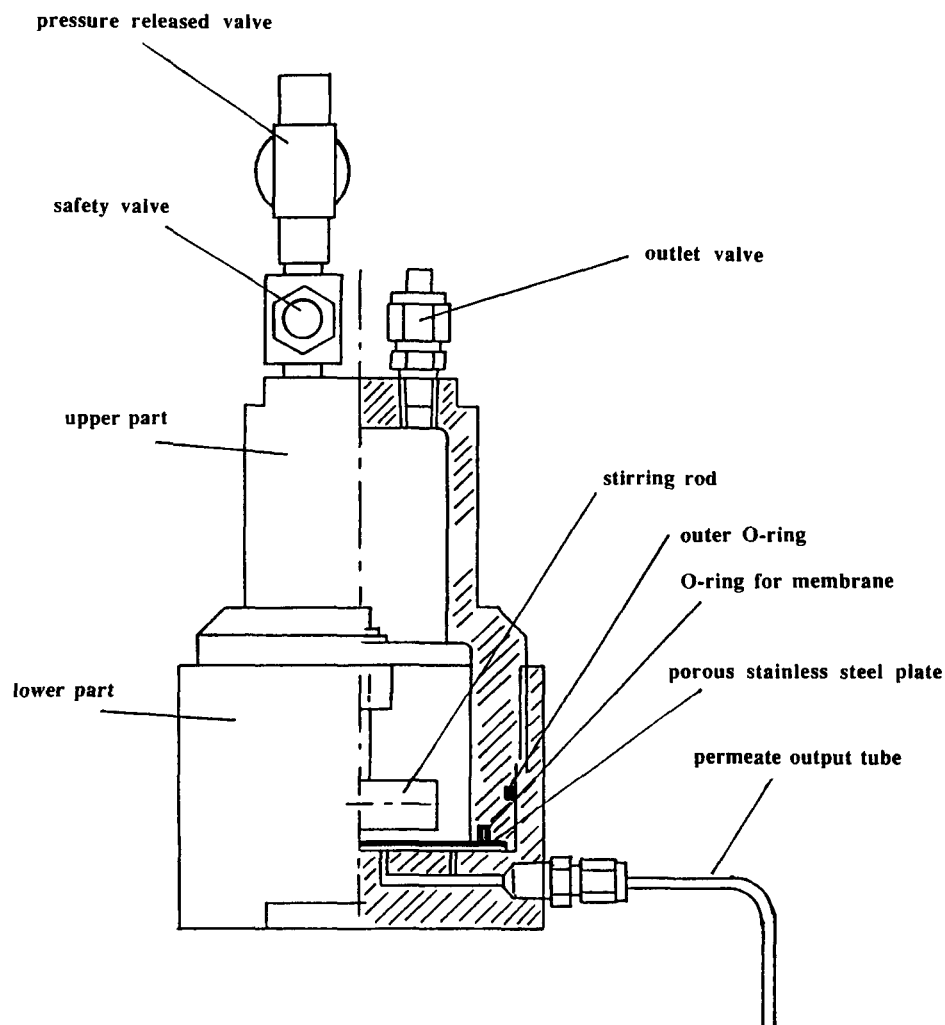


Figure 1 Reverse osmosis cell (RO cell)

tightly fixed in proper alignment with a rubber O-ring. Membranes (of an effective area of  $36.3\text{ cm}^2$ ) to be examined were supported by a porous plate and fixed in the upper part. A magnetic, Teflon-coated stirrer rod was placed over the membrane to prevent concentration polarization that may occur as a result of the lower ability of the salt to penetrate through the membrane. The stirrer rod was driven by a magnetic stirrer motor underneath the reverse osmosis cell. The reverse osmosis cell was filled with the feed solution ( $0.5\text{ N}$  aqueous sodium chloride solution) from its outlet valve opening in the upper part. Then the pressure was applied by connecting the outlet valve with a nitrogen cylinder through a high pressure stainless steel pipe. The applied pressure was controlled by the use of a pressure gauge that recorded pressures between 0 and  $9810\text{ kPa}$ . The applied pressure was  $3924\text{ kPa}$  in all the reverse osmosis tests. The skin surface, which was exposed to the air during thermal treatment, of the membrane faced the feed solution. Permeated water, which collected from the lower part of the reverse osmosis cell, was measured and expressed in  $\text{cm}^3\text{ cm}^{-2}\text{ day}^{-1}$ . The salt rejection was determined from the difference between the concentration of sodium chloride in the feed and in the permeated water by means of a standardized digital conductivity meter and expressed as percentage salt rejection. Reverse osmosis tests were allowed to run at least for 7 h during

which a steady state of measured properties was achieved.

## RESULTS AND DISCUSSION

### General characteristics

The investigated polymers have shown good solubility in various polar organic solvents such as DMAc, dimethyl sulfoxide, N-methyl pyrrolidone and hexamethyl phosphoramide. They also showed good mechanical characteristics and high chemical resistance towards various chemical reagents such as DMAc, boiled water and  $1\text{ N}$  NaOH and HCl solutions<sup>16,17</sup>.

All the evaluated polymers exhibited strong hydrophilicity. This can be evidenced by their high moisture regain values that lie between 19 and 22%, as illustrated in Table 1. The hydrophilicity of these polymers can be related to their polar structures that possess an amide (NHCO), a hydroxyl ( $-\text{OH}$ ) and a hydrazide (CONHNHCO) group per repeating unit. These polar groups absorb much water and exhibit hydrophilicity of these polymers. The enhancements of the moisture regain of these polymers relative to that of the polyamides<sup>19</sup> (5%) is attributable to the presence of the above-mentioned three functional groups against only one amide group in the polyamide repeating unit. Further, the hydrophilicity

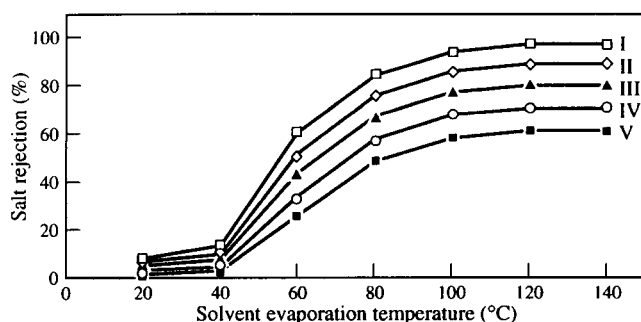
is increased with increasing the *m*-oriented phenylene rings content in the investigated polymer. This may be attributed to the wholly *p*-oriented type of polymer I which is more strongly hydrogen bonded (N–H···O–) than those containing *m*-phenylene rings as a result of its greater chain symmetry and shorter interchain distance. The separation between the macromolecular segments of the *m*-phenylene containing polymers would be further expected, particularly in the presence of water, and consequently the inter- or intrahydrogen bonds would be partially sterically prevented. Thus they are free to interact with water<sup>1,20</sup>. The high hydrophilicity advantage of these polymers allows their prepared membranes to be stored in a dry condition without any change in their transport properties. All the above-mentioned characteristics are of prime requirements for membrane processing and as a guide to selecting these polymers as membrane-forming materials for reverse osmosis applications.

A preliminary examination of reverse osmosis performance of these polymer membranes, cast at 20°C for 1 h and coagulated in deionized water at 25°C, exhibited poor selectivity (2–8% salt rejection) at high water permeability (700–1025 cm<sup>3</sup> cm<sup>-2</sup> day<sup>-1</sup>). This reflects the porous structure of these membranes that could be attributed to their high residual solvent content. In general, the porosity of the membrane is controlled by several processing parameters, in particular thermal treatment operations. Thus, the latter may offer a good route towards meeting the requirements for separation of salt.

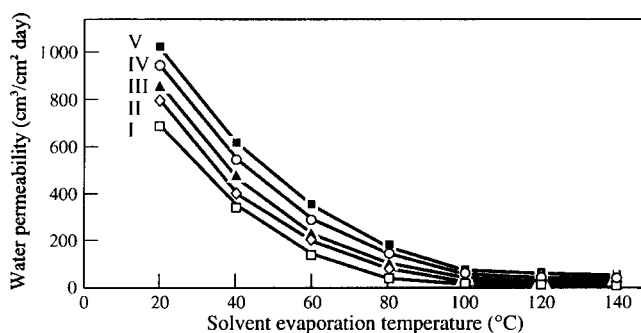
T.g.a. studies revealed that these polymers are thermally stable and no weight loss was observed until about 300, 287, 270, 260 and 255°C for polymers I, II, III, IV and V, respectively, at which the chemical transformation of the polymers into the corresponding polyamide 1, 3, 4 oxadiazoles<sup>16,17,21</sup> occur. The relatively high boiling point of the solvent, DMAc (163°C), permits us to examine long range thermal treatment and select the solvent evaporation temperature between 20 and 140°C.

#### Factors affecting membrane performance

**Solvent evaporation temperature.** The effects of solvent evaporation temperature on salt rejection efficiency and water permeability of various membranes are shown in Figures 2 and 3, respectively. The membranes were formed from different polymer samples (I, II, . . . , and V), thermally treated at temperatures between 20 and 140°C for a fixed period of 1 h and coagulated in deionized water at 25°C. The results represented the average of three comparable experiments for each membrane and the result of each experiment was given after attaining the equilibrium of the measured properties. Regardless of the polymer structure, all the membranes showed the same behaviour. As seen in Figure 2, the salt rejection efficiency of these membranes increased by increasing the solvent evaporation temperature and ranged from 8–98%, 6.5–90%, 5–81%, 3–72% and 2–62% for polymers I, II, III, IV and V membranes, respectively, when the temperature rose from 20 to 120°C. In addition, it is worth mentioning that the optimum salt rejection of the membranes was achieved when the solvent evaporation temperature was 120°C and the increase of temperature did not show further improvement of the membrane selectivity. In contrast to the salt rejection power, the water permeability (Figure 3) of these membranes reduced by increasing the solvent evaporation temperature.



**Figure 2** Effect of solvent evaporation temperature on salt rejection efficiency of various membranes. The membranes were prepared from different polymers, thermally treated at temperatures between 20 and 140°C for a fixed time of 1 h and coagulated in deionized water at 25°C



**Figure 3** Effect of solvent evaporation temperature on water permeability of various membranes. The membranes were prepared from different polymers, thermally treated at temperatures between 20 and 140°C for a fixed time of 1 h and coagulated in deionized water at 25°C

All the membranes have been prepared by a classical phase inversion process that involves the conversion of the polymer solutions into two phase systems, a microporous phase fixed on a macroporous phase. This is achieved by various thermal treatment conditions which are significantly affected by membrane morphology and consequently its reverse osmosis performance. Clearly, during the solvent evaporation, the polymer concentration on the surface which faces the air side increases due to loss of the solvent. It will cause a low porosity of this membrane surface resulting in high salt rejection at low permeability. The other surface of the cast polymer solution (in contact with the glass plate) possesses more solvent content due to the difference in diffusion rate of the solvent from this surface and produces a more porous side on coagulation. At higher evaporation temperature, the solvent evaporation rate rapidly rises to such a level that solvent loss on the surface of the cast film cannot be compensated by solvent diffusion from the interior of the film surface. The polymer soon separates from the casting solution and forms a skin layer on a membrane surface. As a result, an asymmetric flat sheet membrane is obtained which consists of a thin dense skin surface layer supported on a porous layer.

The increase of the solvent evaporation temperature for a fixed period leads to the formation of much smaller pores, especially in the dense skin layer of the asymmetric membrane, which improve its salt rejection efficiency. As the boiling point of DMAc is high, a low evaporation temperature results in a membrane of high solvent content and the possibility of existence of large pores on the membrane becomes high after immersion in the

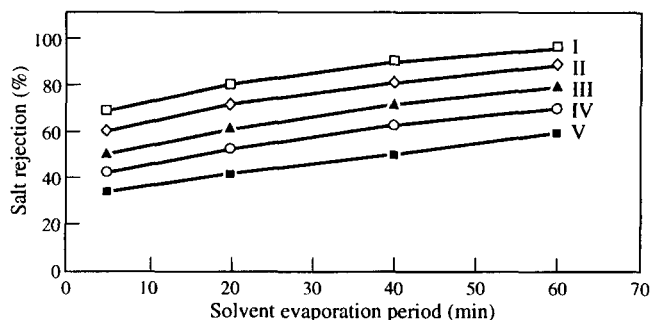
coagulation bath. This leads to low salt rejection at high permeability.

Concerning the polymer structure (at a particular temperature and given period), the salt rejection power of the investigated membranes increases with increasing the *p*-oriented phenylene rings content of the polymer. For example, the salt rejection efficiency (Figure 2) is improved from 62% to 98% when the *p*-oriented phenylene rings content increased from 50% (polymer V membrane) to 100% (polymer I membrane). While the salt rejection power of the polymer II, III, and IV membranes lies between these two extreme values. In contrast to the salt rejection, the permeability of these membranes (Figure 3) increased by increasing the *m*-oriented phenylene ring content of the polymer.

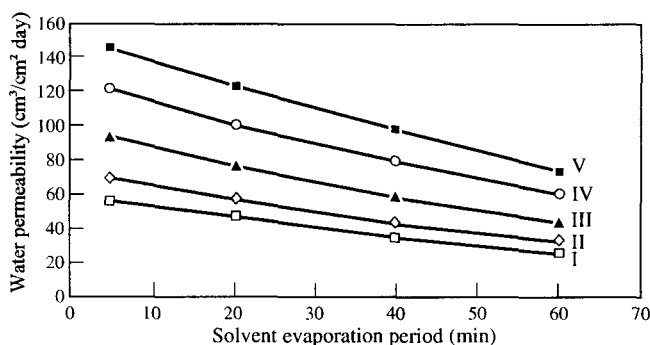
From these results, the polymer structure clearly and significantly influenced the membrane characteristics. The increases in the *p*-oriented phenylene moieties content of the prepared polymers (from V to I) results in an increase in their chain symmetry associates with increased molecular packing and rigidity through enhanced intermolecular hydrogen bonding<sup>12,16,17,21</sup>. The observation reported earlier by Hughes *et al.*<sup>22</sup>, Herlinger *et al.*<sup>23</sup> and Northolt *et al.*<sup>24</sup> would seem to support the above expectation. They estimated the HN...O distance for interchain hydrogen bonds for wholly aromatic polyamides. This is in the range of 2.9–3.1 Å for all polymers containing *p*-phenylene whereas it is about 3.5 Å for polymers containing *m*-phenylene. The hydrogen bonds are not formed if the interchain distance is greater than 3.3 Å<sup>22</sup>. Thus the probability of hydrogen bond formation is decreased by increasing the *m*-phenylene rings content in the prepared polymer.

Under identical preparation condition, it would be expected that the chains of the more rigid polymer I are efficiently packed to each other and aligned in a more regular supermolecular manner. They are held together by a more intensive network of shorter and stronger intermolecular hydrogen-bonding than those of the less rigid polymer V. As a result the polymer I membrane produces a barrier with much smaller pores that would efficiently prevent the solute particles from penetration and lead to an improvement in its salt rejection. On the other hand, the polymer V membrane produces a barrier with no, or longer and weaker, interchain hydrogen bonds that would be easier for both salt and water molecules to penetrate and improve the water permeability at reduced salt separation. Further, the long interchain distance of *m*-phenylene containing polymer led the oxygen atoms of the hydroxyl, amide and hydrazide groups to interact considerably with water and consequently become sites of water sorption (bound water). According to the theory of water transport<sup>25,26</sup>, the bound water content is responsible for selective permeation of water through the membrane. Bound water has the ability to form hydrogen bonds to free water molecules. Therefore, water can be forced through the membrane selectively. Increasing water sorption, by increasing *m*-phenylene ring content, permits increased membrane permeability.

**Solvent evaporation period.** Correlations between the solvent evaporation period and salt rejection efficiency as well as water permeability of several membranes are presented in Figures 4 and 5, respectively. The membranes were formed from different polymer samples, thermally



**Figure 4** Effect of solvent evaporation period on salt rejection efficiency of various membranes. The membranes were prepared from different polymers, thermally treated at fixed temperature at 100°C for different intervals between 5 and 60 min. All the membranes were coagulated in deionized water at 25°C



**Figure 5** Effect of solvent evaporation period on water permeability of various membranes. The membranes were prepared from different polymers, thermally treated at fixed temperature at 100°C for different intervals between 5 and 60 min. All the membranes were coagulated in deionized water at 25°C

treated at 100°C for various time intervals, which ranged between 5 and 60 min, and coagulated in deionized water overnight at 25°C.

The results revealed that all the membranes showed a similar trend which is summarized by an increase in salt rejection power and a reduction in water permeability as the solvent evaporation period increases. In the case of polymer I membranes, the salt rejection efficiency is increased from 68.5 to 94.5% and the permeability reduced from 57.3 to 27 cm<sup>3</sup> cm<sup>-2</sup> day<sup>-1</sup> as the solvent evaporation period rises from 5 to 60 min. This behaviour is in good agreement with the Dvornic test results<sup>14</sup>. Under similar preparative and testing conditions, he reported that the asymmetric membranes prepared from poly[4-(terephthaloilamino)benzoic acid hydrazide] showed 94.3% salt rejection at 18 cm<sup>3</sup> cm<sup>-2</sup> day<sup>-1</sup> water permeability in the case of a 60 min evaporation period. The salt rejection power and water permeability of polymer V changed from 34 to 59% and 146 to 75.2 cm<sup>3</sup> cm<sup>-2</sup> day<sup>-1</sup>, respectively, at the above-mentioned period range.

Again, the salt rejection power of these membranes is increased by increasing the *p*-oriented phenylene ring content of the polymer. The membranes formed from polymer I exhibited the highest salt rejection and lowest permeability while those prepared from polymer V showed the lowest salt rejection and highest permeability. The membranes cast from the other three polymers (II, III, IV) exhibited separation capabilities in between these two extreme values. At a particular solvent evaporation

temperature for a selected time interval, the percentage salt rejection was arranged in the order I > II > III > IV > V. This is attributed to the reasons described in the previous factor.

From the above result, it could be concluded that the longer the evaporation period at fixed temperature would result in a membrane of lower residual solvent content and with thicker skin layer. This leads to a more dense structure and consequently improves the salt separation of the membrane at lower permeability.

**Coagulation temperature.** The effects of coagulation temperature on the salt rejection and water permeability of various membranes are summarized in Table 2. The membranes were cast from the same polymer sample I, thermally treated at 100°C for 5 min and coagulated in deionized water at different temperatures of 0, 25, and 50°C. The results reveal that their salt rejection is not

significantly changed. This may be attributed to the similarity of the active (dense) layer of these membranes that is formed during the evaporative step and preserved on coagulation. On the other hand, their water permeability is appreciably increased with decreasing the coagulation temperature. This may be explained according to the observations made by McKinney and Rhodes<sup>10</sup>. They suggested that the anisotropy structure of the membrane was preserved by coagulation at 25°C. The membrane coagulated in an ice-water bath, at 0°C, showed a highly open matrix with very big pores. On the other hand, a very dense, collapsed structure was established when the membrane coagulated at 50°C. From these, it is clear that coagulation temperature controls the structure (porosity) of the membrane in particular, its supported layer and consequently its water permeability<sup>10</sup>.

**Annealing.** Results of the annealing of various membranes in deionized water at different temperatures of 70 and 100°C for several time intervals of 0, 5, 10, and 15 min are illustrated in Tables 3 and 4. The membranes were cast from polymer samples I, III and V under identical preparative conditions except solvent evaporation temperature. In Table 3, the cast membranes were thermally treated at 120°C while those of Table 4 at 60°C.

In general, the reverse osmosis performance of these membranes is clearly affected by annealing at either 100°C or 70°C with an increase in salt rejection and simultaneous reduction in water permeability. Upon

**Table 2** Reverse osmosis performance of polymer I membranes. They were thermally treated at 100°C for 5 min and coagulated in deionized water

Coagulation temperature (°C)	Salt rejection (%)	Water permeability (cm <sup>3</sup> cm <sup>-2</sup> day <sup>-1</sup> )
0	67.3	84.5
25	68.5	57.3
50	68.9	31.3

**Table 3** Effect of annealing in deionized water on polyamide-hydrazides membranes performance. All membranes were thermally treated at 120°C for 1 h and coagulated in deionized water at 25°C

Annealing temperature (°C)	Annealing time (min)	Polymer I membranes		Polymer III membranes		Polymer V membranes	
		Salt rejection (%)	Water permeability (cm <sup>3</sup> cm <sup>-2</sup> day <sup>-1</sup> )	Salt rejection (%)	Water permeability (cm <sup>3</sup> cm <sup>-2</sup> day <sup>-1</sup> )	Salt rejection (%)	Water permeability (cm <sup>3</sup> cm <sup>-2</sup> day <sup>-1</sup> )
70	0	98.0	16.6	81.0	40.0	62.0	65.0
	5	98.3	15.8	84.1	38.0	63.2	61.0
	10	98.5	14.5	85.1	35.0	64.9	58.0
	15	98.4	14.8	85.1	34.0	65.0	59.0
100	0	98.0	16.6	81.0	40.0	62.0	65.0
	5	99.3	14.5	89.1	36.0	69.5	51.0
	10	99.5	13.0	91.5	30.0	70.7	53.0
	15	99.5	12.8	91.4	31.0	71.0	52.0

**Table 4** Effect of annealing in deionized water on polyamide-hydrazides membranes performance. All membranes were thermally treated at 60°C for 1 h and coagulated in deionized water at 25°C

Annealing temperature (°C)	Annealing time (min)	Polymer I membranes		Polymer III membranes		Polymer V membranes	
		Salt rejection (%)	Water permeability (cm <sup>3</sup> cm <sup>-2</sup> day <sup>-1</sup> )	Salt rejection (%)	Water permeability (cm <sup>3</sup> cm <sup>-2</sup> day <sup>-1</sup> )	Salt rejection (%)	Water permeability (cm <sup>3</sup> cm <sup>-2</sup> day <sup>-1</sup> )
70	0	61.0	140.0	44.0	235.0	26.0	350.0
	5	64.1	136.0	46.9	223.0	28.4	342.0
	10	64.6	130.0	47.5	215.0	29.1	339.0
	15	64.7	131.0	48.0	214.0	29.1	341.0
100	0	61.0	140.0	44.0	235.0	26.0	350.0
	5	67.5	132.0	49.9	225.0	30.1	342.0
	10	70.7	120.0	52.8	220.0	32.7	335.0
	15	70.5	120.0	52.9	219.0	32.5	334.0

annealing at 100°C for 15 min, the salt rejection of the polymer I membrane reaches 99.5% at permeability  $12.8 \text{ cm}^3 \text{ cm}^{-2} \text{ day}^{-1}$  (as seen in Table 3). These data and others previously reported<sup>15</sup> can be confirmed by similar results made by Dvornic<sup>14</sup>. Under equivalent preparative and testing conditions, he reported a salt rejection 91.2% at permeability  $11.76 \text{ cm}^3 \text{ cm}^{-2} \text{ day}^{-1}$ . From the results of Table 3, it can be noted that the salt rejection of the membranes annealed at 100°C was improved from 1.5% to 14% relative to that of the corresponding unannealed ones. On the other hand, the same membranes annealed at 70°C showed an improvement as much as 0.5% to 5%. This reflects that the salt rejection improvement of the membranes annealed at 100°C is nearly three orders of magnitude that of those annealed at 70°C. Moreover, this improvement did not require much time and the maximum salt rejection was attained after 10 min of exposure to annealing. The membranes cast at 60°C (Table 4) showed similar behaviour when annealed at 100°C and their selectivity improved by about three fold for those annealed at 70°C.

During annealing, the membrane shrinks resulting in a decrease in its pore size, particularly in the skin layer. This was supported by electron microscopic studies reported earlier by McKinney and Rhodes<sup>10</sup> who suggested that on annealing a consolidation of the skin layer occurred with little effect on the membrane interior matrix. This leads to change in membrane morphology and consequently improves the salt rejection with a reduction of its water permeability. The higher the annealing temperature the greater the decrease in pore size. This is the reason for a significant increase in salt rejection when annealing at 100°C.

Comparing the data of Tables 3 and 4, it can be seen that the membranes cast at 60°C exhibited a higher improvement in salt rejection than that of those cast at 120°C on annealing either at 70°C or 100°C. This may be attributed to the fact that the pores of membranes cast at 60°C are relatively big. They should therefore be significantly decreased during membrane shrinking on annealing. The action of the latter is apparently efficient and results in a remarkable improvement in salt rejection. The pores of the membranes cast at 120°C are originally sufficiently small to reject sodium chloride molecules. Thus annealing seems to have a limited effect on their pore size leading to little improvement in their salt rejection capabilities.

**Casting solution composition.** The casting solution composition is considered one of the most important parameters influencing membrane performance. Lithium chloride was used as an additive to develop the reverse osmosis performance of the membrane<sup>13</sup>. Table 5 summarizes the effect of the amount of lithium chloride added to the casting solution on polymers I and V membrane performance. The membranes were prepared under identical preparative conditions (they were thermally treated at 100°C for 1 h, coagulated in deionized water at 25°C) except for the amount of lithium chloride added.

When the salt/polymer weight ratio in the casting solution increases from 0.1 to 0.5 the permeability of the water increases by about one order of magnitude. However, the salt rejection remained almost unchanged. The maximum permeability occurred at salt/polymer weight ratio of 30 to 40% in casting solution. Further, polymers

**Table 5** Effect of LiCl/polymer ratio in casting solution on the salt rejection and water permeability. Polymer concentration was maintained at 7 wt% while changing the LiCl/polymer ratio. All the membranes were thermally treated at 100°C for 60 min and coagulated in deionized water at 25°C

Membrane type	LiCl/polymer (weight ratio)	Salt rejection (%)	Water permeability ( $\text{cm}^3 \text{ cm}^{-2} \text{ day}^{-1}$ )
I	0	94.5	27.0
	0.1	94.9	35.0
	0.2	94.7	42.0
	0.3	93.9	54.0
	0.4	94.4	55.0
	0.5	93.9	53.0
V	0	59.0	75.2
	0.1	58.7	92.0
	0.2	59.2	120.0
	0.3	59.9	140.0
	0.4	58.5	147.0
	0.5	58.4	147.0

**Table 6** Effect of membranes thickness on their reverse osmosis performance. All membranes were thermally treated at 100°C for 40 min and coagulated in deionized water at 25°C

Membrane thickness ( $\mu\text{m}$ )	Polymer I membranes		Polymer V membranes	
	Salt rejection (%)	Water permeability ( $\text{cm}^3 \text{ cm}^{-2} \text{ day}^{-1}$ )	Salt rejection (%)	Water permeability ( $\text{cm}^3 \text{ cm}^{-2} \text{ day}^{-1}$ )
5	89.0	36.2	50.0	99.1
8	88.8	30.3	49.7	80.2
13	89.1	22.8	49.9	63.4
21	88.7	6.9	50.2	22.1

II, III and IV membranes showed a similar trend when they were subjected to the same examination.

When the casting layer of the polymer solution is thermally treated, the solvent evaporates and the lithium chloride is concentrated particularly on the air facing surface of the casting solution. On coagulation, the lithium chloride leaves the casting membrane resulting in an increase of its porosity. As the lithium chloride concentration increases, the number of the pores on the membrane increases. This is the reason for significant increase in water permeability.

Since the crystal radius<sup>27</sup> of the lithium crystal (0.60 Å) is smaller than that of the sodium crystal (0.95 Å), the size of the pores resulting from the lithium chloride leaching becomes sufficiently small and efficiently prevents sodium chloride molecules from penetration. This leads to no change in salt rejection efficiency.

**Membrane thickness.** Table 6 summarizes the effect of thickness of the membranes on their reverse osmosis performance. They were prepared from polymer samples I and V, thermally treated at 100°C for 40 min and coagulated in deionized water at 25°C. It can be seen from these data that the water permeability is inversely proportional to the membrane thickness. The salt rejection is not substantially influenced.

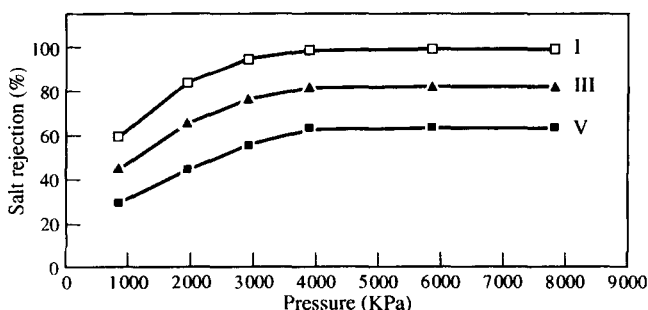
Since all the cast membranes were exposed to identical solvent evaporation conditions, they possess a similar active (dense) layer that is actually responsible for the selectivity of the finished membrane. Thus all the membranes exhibit comparable salt rejection percentage. The water permeability decrease produced by increasing the

thickness of the membrane suggests a blocking effect to hinder the movement of water molecules through the membrane.

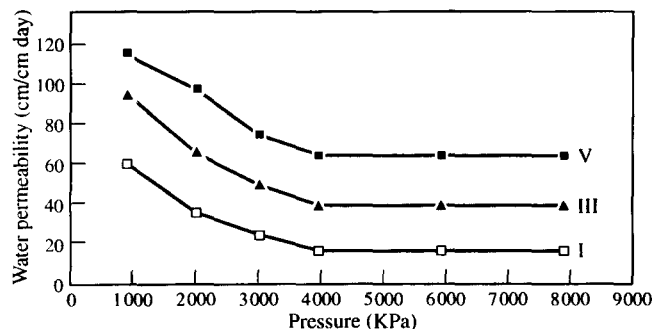
However, similar trends were also found in all other membranes prepared from other polymer samples, so that it seems possible to conclude that such behaviour appears to represent a general feature for all membranes of the polyamide-hydrazide membrane family.

**Applied pressure.** When the pressure is applied the structure of the membrane is compressed and the distance between the polymer chains becomes very short leading to the formation of strong hydrogen bonding between them. As the pressure increases, more cross linking would occur, resulting in a membrane with a more impenetrable barrier to sodium chloride. On the other hand, densification of the membrane structure by compaction under pressure reduced its water permeability.

The effects of the operating pressure on salt rejection efficiency and water permeability of polymers I, III and V membranes are illustrated in Figures 6 and 7, respectively. The membranes were thermally treated at 120°C for 1 h and coagulated in deionized waters at 25°C. The operating pressures were selected between 981 and 7848 kPa. It is clear from Figures 6 and 7 that all the membranes showed similar behaviour. As would be expected, the salt rejection efficiency is increased with increasing the applied pressure and at the same time, the water permeability is decreased. The maximum selectivity was attained at nearly 4000 kPa and the increase in the operating pressure did not result in further improvement in salt rejection capabilities.



**Figure 6** Effect of the operating pressure on salt rejection of polymers I, III and V membranes. All the membranes were thermally treated at 120°C for 1 h and coagulated in deionized water at 25°C



**Figure 7** Effect of the operating pressure on water permeability of polymers I, III and V membranes. All the membranes were thermally treated at 120°C for 1 h and coagulated in deionized water at 25°C

## CONCLUSIONS

The above results and discussion lead to the following general conclusions:

(1) Several semipermeable asymmetric membranes have been prepared from a series of novel wholly aromatic polyamide-hydrazides for reverse osmosis performance.

(2) Membrane performance was found to be strongly affected by the polymer structural variations and several processing parameters. As a result, it is quite possible to prepare membranes (from the same polymer sample) with considerably different properties by varying the processing parameters. Also, membranes with comparable characteristics could be obtained from different polymer samples by adjusting these parameters.

(3) High salt rejection capability could be achieved after the thermal treatment of the membranes at relatively high temperatures between 100 and 120°C for long time intervals from 40 to 60 min during which the asymmetric structure was established. This structure appeared as a thin dense skin layer supported on a spongy porous material. The former layer is responsible for the salt rejection efficiency.

(4) Coagulation of the membranes in deionized water at 25°C preserved their asymmetric structure.

(5) Annealing in deionized water, particularly at 100°C, comprised a way for preparation of potentially useful membranes for single-stage separation process that requires high separation.

(6) Lithium chloride as an additive to the casting solution offered an additional route towards meeting the requirement for improving water permeability of the membrane.

(7) Thickness of the membrane is an important variable for water permeability control.

(8) The membrane selectivity clearly depended on the operating pressure, reaching its maximum when the applied pressure was about 4000 kPa.

(9) Finally, the polymers with high *p*-phenylene rings content, I, II and III have all the reverse osmosis membrane-forming properties. They showed salt rejection above 80% at permeability within the level required. However, those possessing a high content of *m*-phenylene rings would be expected to exhibit some potential for ultrafiltration or other similar process.

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