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Aromatic Polyamide Hydrazide Membranes for Reverse Osmosis Separations

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Abstract

Wholly aromatic polyamide hydrazide (PAH) polymers were synthesized by low temperature polycondensation from freshly prepared *m*-amino benzhydrazide, *p*-amino benzhydrazide, isophthaloyl chloride, and terephthaloyl chlorides in dimethyl acetamide solvent. A series of film-forming polymers prepared by altering the molar ratios of the reacting monomers was characterized in terms of % moisture regain, η_{inh}, and x-rays. Asymmetric membranes prepared from selected polymer samples were tested in reverse osmosis test cells, and the pure water permeability and the membrane constant were determined. An optimum meta:para molar ratio of the reacting monomers has been identified for the best performance under reverse osmosis which gave solute separation close to 98% for a feed concentration in the range of seawater. The PAH membranes appear to be potential barrier candidates for treatment of effluents containing ammonium, nitrates, etc. and radioisotopes. Separation data for a few other solute systems were also evaluated and compared with those obtained from cellulose acetate membranes.

INTRODUCTION

The prime requirement of polymers suitable as barrier materials (*1*) for use in reverse osmosis (RO) separations are optimum polarity, high molecular weight, and mechanical strength. The family of nitrogen-containing aromatic polymers combine many of these useful properties and have made available membranes for a broad spectrum of RO separations. The aromatic polyamide class of polymers (*2*, *3*) is reported to be superior to conventional cellulose acetate membranes with respect to high pressure and high temperature service conditions, apart from their inherent chemical and bacterial stability. Development of asymmetric cellulose acetate membranes suitable for radioactive separations (*4–6*) and effluent treatment (*7*)

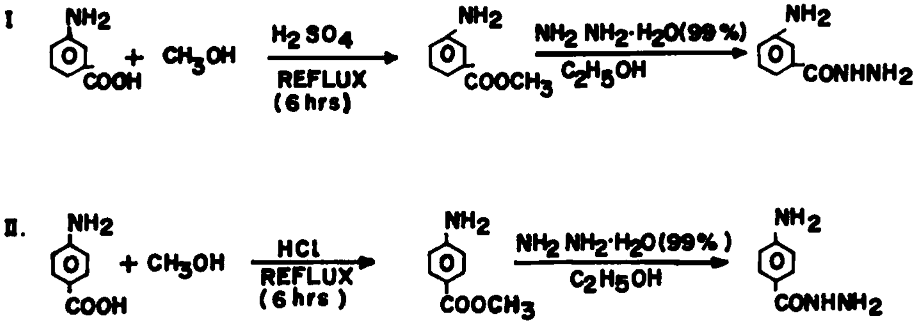

FIG. 1. Synthesis of (I) mABH and (II) pABH.

was reported earlier from this laboratory. The synthesis of high molecular weight aromatic polyamide membranes (*8*) was taken up subsequently, and the RO performance of membranes derived from simple poly(*m*-phenylene isophthalamide) polymer has been reported (*9*). Polyamide hydrazide polymers which contain a higher percentage of polar group in the polymer backbone are another promising candidates for RO separations. Some studies recently reported (*10–15*) on the synthesis, characterization, and membrane transport properties of polyamide hydrazide polymers. The effect of varying the molar ratios of the meta- and para-substituted reacting monomers on RO performance under the higher feed concentrations encountered in seawater desalination are reported in this paper.

EXPERIMENTAL

Monomers

The *p*-amino benzhydrazide (PABH) and *m*-amino benzhydrazide (MABH) were freshly synthesized from *m*/*p*-amino benzoic acid (obtained from Ferac, Berlin, West Germany) as per reaction scheme given in Fig. 1. MABH was purified by recrystallization in chloroform (melting point 91–92°C). PABH was purified by recrystallization from a 1 : 1 demineralized water and ethanol mixture (melting point 222–224°C). The elemental analyses of MABH and PABH are shown in Table 1. Isophthaloyl (IPC) and terephthaloyl chloride (TPC) (reported purity 98%), Fluka A.G., were similarly obained, distilled under vacuum, and recrystallized from dry hexane (melting points 44 and 83°C, respectively). Dimethyl acetamide (DMAc) was fractionally distilled under reduced pressure (boiling point 56–58°C at 11 mmHg pressure) and stored over Molecular Sieve 4A. Polymers of desirable properties and degrees of polymerization (DP $\approx$ 100) require conversions of over 99%. To achieve such high conversions in

TABLE 1
Elemental Analysis of MABH and PABH Monomers

	Elemental composition (%)			
	C	H	N	O
MABH:				
Observed	55.60	5.86	28.17	10.37
PABH:				
Observed	55.86	5.75	28.39	10.00
Calculated	55.62	6.00	27.80	10.58

practice, one has to use a very accurate equimolar ratio of monomers which is only possible when the monomers are of very high purity. Thus, special care was taken in the purification of MABH (which is photo sensitive) and IPC and TPC (which are moisture sensitive) by doubly and freshly purifying them before use.

Polymer Synthesis

Aromatic polyamide hydrazide polymer was synthesized by a low temperature polycondensation reaction by adding equimolar amounts of solid IPC and TPC to a cooled solution (−10°C) of MABH and PABH in DMAc solvent, which also acts as an acid acceptor. The polymerization was carried out under nitrogen for 2 h at −10°C by using an ice–salt mixture and then at ambient temperature for 6 h in a three-neck reaction vessel fitted with a mechanical stirrer. The polymer solution was filtered and precipitated in deionized water. It was washed several times with water, followed by washing with acetone. It was dried at 100°C under vacuum. Since this polymerization reaction is exothermic, the decrease in reaction temperature will give a higher equilibrium degree of polymerization DP_e as evident from

$$\frac{\partial \ln DP_e}{\partial (1/T)} = \frac{-\Delta H}{2R}$$

However, lowering the temperature can cause a considerable decrease in the rate of reaction. Based on these considerations, the reaction was first carried out at −10°C and afterward at room temperature because the higher concentration of monomers at the beginning compensates for the low reaction rate at low temperature. Subsquently with time, the number of reactive groups and the diffusion of the resulting bulky polymer molecules decreases, which necessitates a higher reaction temperature.

The % moisture regain values were evaluated gravimetrically by equilibrating oven dry polymer samples at 25°C and 65% RH. The solution viscosity was evaluated by using an Ubbelohde viscometer with 0.5% polymer solution in DMAc. The results are expressed as η_{inh}. Powder x-ray diffractographs of the polymer samples were recorded between 2θ values of 10 and 56° by using a Siemen x-ray diffractometer.

Asymmetric membranes from the polymer samples were prepared by dissolving 14.3% polymer with 4.76% lithium nitrate as additive in DMAc. Membranes were made by wiping the solution over a glass plate to uniform thickness and subjecting them to thermal evaporation of the solvent in an air circulating oven at 90°C for 25 min. After oven drying the nascent film was coagulated in demineralized water maintained at 25°C. The membrane samples were subjected to a dye test.

The membrane performance was evaluated in terms of water permeability (cm/d) and % solute separation for a 4.5% sodium chloride feed solution at 60 kg/cm^2 pressure.

RESULTS AND DISCUSSION

Polymer Characterization

Percent Moisture Regain

The % moisture regain data obtained for polymer Samples I to XI synthesized by systematically varying the meta/para composition of the reacting monomers are shown in Table 2. The results indicate that moisture regain is between 11.9 and 13.6% for polymer Samples I to VII whereas there is a gradual decrease in these values for VII to XI. Water molecules are adsorbed to the polymer by forming hydrogen bonds with its amide linkages. If there is one water molecule per amide in the polymer chain, the calculated moisture uptake is 11.8%. The slightly higher values observed for Samples I to VII may be attributed to second-order hydrogen bonding between water–water molecules at the same sites. It also appears that with increasing para monomers there is increasing intermolecular hydrogen bonding between the polymer chains, which is reflected by an increase in mechanical strength, improved film-forming properties, and a decrease in solubilities. Moisture regain data show that for up to 60% para monomers (i.e., up to Sample VII) the extent of intermolecular hydrogen bonding does not sterically prevent the water molecules from forming hydrogen bonds with the available amidic linkages in the polymer network.

TABLE 2
Moisture Regain of Various Aromatic Polyamide Hydrazide Polymers

Sample	Polymer	Monomer ratio (mol%)				Moisture regain (%)
		MABH	PABH	IPC	TPC	
1	I	100	—	100	—	11.92
2	II	90	10	90	10	11.98
3	III	80	20	80	20	12.39
4	IV	70	30	70	30	13.00
5	V	60	40	60	40	15.59
6	VI	50	50	50	50	12.80
7	VII	40	60	40	60	12.37
8	VIII	30	70	30	70	10.51
9	IX	20	80	20	80	7.14
10	X	10	90	10	90	2.51
11	XI	—	100	—	100	2.55

The lower values for Samples VII to XI indiate that beyond 60% para-monomer the extent of intermolecular hydrogen in the polymer chain is very high, which lowers the moisture regain. Strong intermolecular hydrogen bonding in these samples is also indicated by their low solubility in DMAc. Note that the reaction rate of the hydrazide group with acid chloride is seven times faster than that of the amide group (*16*). Consequently, the polymer chain is predominantly made up of a tail-to-tail combination, resulting in two hydrazide groups being brought closer to each other.

Solution Viscosity

The η_{inh}s of Polymers III, IV, V, and VI are shown in Table 3. The results indicate that the values increase as the para-substituted monomer

TABLE 3
Membrane Characterization Data for Selected Polyamide Hydrazides

Sample	Polymer	η_{inh} (dL/g)	PWP (cm/d)	Membrane constant (A) (g·mol/cm^2·s·atm) ($A \times 10^7$)
1	III	0.41	89.94	9.76
2	IV	0.59	85.60	9.16
3	V	0.74	79.707	8.57
4	VI	0.86	51.66	5.53

content in the polymers increases. The higher η_{inh} values obtained for increasing para-substituted polymers could be due to an increased degree of polymerization and higher chain rigidity.

X-Ray Diffraction Data

At the molecular level, it is expected that an increase in chain rigidity is associated with polymers of a higher para content which develop denser packing of the macromolecular segments. This dense packing of polymer segments is expected to be held together by short-range intermolecular hydrogen bonds. X-ray diffractographs of polymer Samples III, IV, and VI are shown in Fig. 2. It can be seen that the x-ray diffractograph of polymer Sample VI shows sharper peaks than do those of Samples VII and IV. Increasing the para content in polymers results in sharper diffraction patterns, indicating more ordered structures.

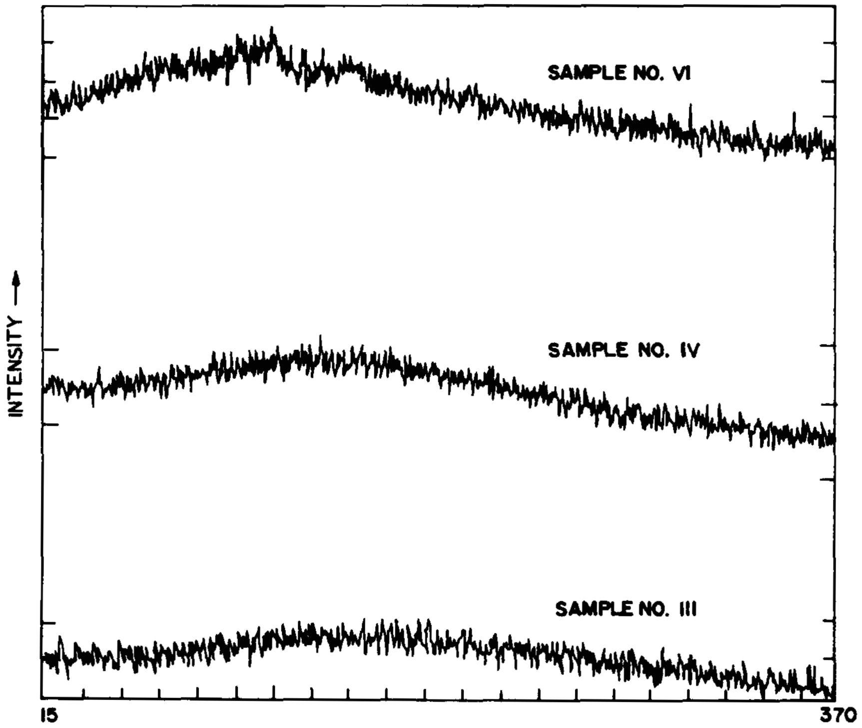

FIG. 2. X-ray diffraction pattern of PAH polymers.

Membrane Characterization

The pure water permeability (PWP) and membrane constant (A) values for the membrane samples are shown in Table 3. The membrane constant (A) is evaluated from measured PWP values by

$$A = \frac{(\mathrm{PWP}) \times \rho \times 10^{-3}}{M_B \times 3.6 \times P \times 24}$$

where M_B = molecular weight of water
PWP = pure water permeability in cm/d
ρ = density of water in g/cm^3
P = operating pressure in atmosphere
A = Membrane constant in g·mol·cm^{-2}·s^{-1}·atm^{-1}

The pure water permeability is significantly affected by the molar ratios of the reacting monomers. It can be seen that the water permeation rates decline steadily as the ratio of the para-substituted monomers increases. It is well known that the hydrogen bonding ability of polymers directly affects the RO performance by altering the structure of water (*17*). If the hydrogen bonds are sterically prevented from forming intermolecularly, they become free to interact with water and modify its structure near the membrane barrier. The increase in para-substituted monomer appears to facilitate para–para linkages in the chain, and this could lead to some sort of structure ordering due to interchain polar interactions. The presence of sequential ordering in these types of polymers is also reflected in the DTA spectra reported (*8*) earlier from this laboratory.

RO Performance

The RO performance for a feed concentration of 4.5% sodium chloride solution at 60 kg/cm^2 operating pressure is given in Table 4. Note that the observed RO performance of the membranes greatly depends on the basic physicochemical properties of the polymer and on the membrane's morphological characteristics. The permeability of water and solute through the membranes is determined by the structure of the skin surface, which is formed during thermal evaporation of the solvent. The casting solution structure is an important criterion for comparing a series of polymers when the other membrane casting conditions are kept identical. The number and size of the supermolecular aggregates in the casting solution particularly determine the final skin structure (*18*). Polymers with a higher solubility in an aprotic solvent will have a larger number of smaller polymer aggregates in solution compared to polymers with a smaller solubility. The RO

TABLE 4
RO Performance of Polyamide Hydrazides

Sample	Polymer	Water flux (cm/day)	Solute separation (%)	Solvent flux^a (N_B) ($\times 10^5$)	Solute flux^a (N_A) ($\times 10^8$)	N_B/N_A ($\times 10^3$)
1	III	52.41	96.34	3.37	1.69	1.99
2	IV	49.89	96.10	3.21	1.71	1.87
3	IV(a)	38.19	97.16	2.46	0.954	2.57
4	V	36.42	97.93	2.31	0.663	3.53
5	VI	26.58	96.85	1.71	0.737	2.32

^{a}Expressed in $g \cdot mol \cdot cm^{-2} \cdot s^{-1}$.

separation data were explained (*19*) based on the polar, nonpolar, and solubility parameters of the polymers derived from liquid chromatography experiments. For example, the polar parameters are higher for polyamide hydrazide than for polyamide, and the opposite is true with respect to nonpolar parameters. Variation in the meta/para ratios for the polyamide hydrazide polymer gives rise to differences in the polar character.

It appears that from 100% meta- to 100% para-polymer the ratio of the polar to nonpolar parameter increase slightly, which explains the increasing solute separation and reduced permeate flux shown by our data. Consequently, polymer samples containing more meta linkages may have a favorable morphology combined with more free polar groups, which accounts for the enhanced water permeation and moderate separation. The increase in para content in polymers from Samples III to VI lowers the water permeation rate with a corresponding improvement in solute separation. This could be due to the reduced polar character of higher para-containing polymers. The slight decrease in solute separation observed in Sample VI could be due to the unfavorable morphological structure expected from increased para–para linkages.

Semipermeability

The solvent water flux (N_B) and solute flux (N_A) through the membrane samples under RO conditions were computed and are shown in Table 4. The ratio of solvent to solute fluxes (N_b/N_A) can be considered as an empirical parameter for comparing the semipermeability of a series of polymer candidates. The ratio of water and solute permeabilities for various polymers are compared and reported elsewhere (*2*). It can be seen from

Table 4 that N_B/N_A increases and reaches a maximum for Polymer V, which indicates an optimum molar ratio for productive RO membranes.

Separation of Other Solutes

The % solute separation of various inorganic and organic solutes for cellulose acetate and polyamide hydrazide (IV) membranes are shown in Table 5. It can be seen that while a typical cellulose acetate membrane exhibits lower separation for most of the solutes, polyamide hydrazide membranes appear to offer higher levels of separation for all the solutes. In particular, ammonium nitrate, which is poorly separated by cellulose acetate membranes, is well rejected by polyamide hydrazide membranes. Borate, however, is poorly rejected by both membranes. The separation of various organic and inorganic solutes is governed by the steric, polar, and nonpolar interaction of the polymer material with the solutes. The enhanced polar and nonpolar parameters for polyamide hydrazide (*19*) compared to those of cellulose acetate could be responsible for the higher permeate flux and increased solute separation of polyamide hydrazide. It appears that the nature and extent of interaction between the barrier material and the solutes are noticeably different for cellulose acetate and polyamide hydrazide.

CONCLUSIONS

A series of film-forming, wholly aromatic polyamide hydrazide polymers was synthesized by varying the molar ratios of the *m*/*p*-amino benzhydrazides, isophthaloyl chloride, and terephthaloyl chloride. The reverse osmosis performances of these polymeric membranes were evaluated and compared with those obtained from cellulose acetate membranes. Mem-

TABLE 5
Separation of Some Inorganic and Organic Salts[a]

		Solute separation (%)	
Sample	Solute	Cellulose acetate	Polyamide hydrazide
1	Sodium chloride	89.9	95.4
2	Ammonium chloride	87.8	96.8
3	Ammonium nitrate	79.3	96.2
4	Sodium acetate	89.7	96.4
5	Sodium oxalate	97.3	97.6
6	Sodium tetraborate	83.2	90.4

[a] Feed concentration of solutes: 1000 ppm. Pressure: 40 kg/cm^2.

branes with a 60/40 molar ratio of meta-/para-substituted monomers appear to give optimum performance with feed concentrations in the range encountered in seawater desalination, and solute separations close to 98% could be achieved. Whereas this may not be sufficient to obtain potable water from seawater, it may meet situations where higher product salinity with a lower recovery can be practised. However, further work is necessary to obtain a satisfactory seawater RO membrane. Another potential area for the application of these membranes is in low level radioactive waste treatment. Even with the solute rejections achieved in the above experiments, these membranes have the potential to give higher decontamination factors (DF) than cellulose acetate membranes and even in other methods of decontamination, except for evaporation (which in any case is energy intensive). These membranes also appear to be potential candidates for the treatment of effluents containing amonium and nitrates. Further work with modified polymers appears to give promise of better solute rejection and hence suitability for seawater desalination.

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