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High Solute Rejecting Membranes for Reverse Osmosis: Polyetheramide Hydrazide

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Abstract

Synthesis of benzhydrazide polymers and determination of reverse osmosis properties of their membranes were reported earlier. Although high solute rejections could be achieved, their performance was not adequate for seawater desalination or for high radioactive decontamination factors (DF). In the process of investigation of polymers with improved performance, the same hydrazide polymers modified by incorporation of additional monomers with ether linkages were synthesized by low temperature polycondensation of freshly prepared *m*-amino benzhydrazide, *p*-amino benzhydrazide, and 4,4′-diamino diphenyl ether, with isophthaloyl chloride and terephthaloyl chloride in dimethyl acetamide solvent. A series of film-forming polymers prepared by altering the molar ratios of the reacting monomers were characterized in terms of percent moisture regain, inherent viscosity, solubility parameters, and interfacial sorption characteristics. Asymmetric membranes prepared from these polymer samples were characterized in terms of the pure water permeability constant and the solute transport parameter, and were tested for their reverse osmosis performance. An optimum mole ratio of reacting monomers has been identified for the synthesis of polymer and the resulting membrane offered the best performance for reverse osmosis (salt rejection as high as 99.4% for 3.5% sodium chloride solution). The incorporation of aromatic ether linkages in the polyamide benzhydrazide polymeric chains appears to alter the polar and nonpolar character of the bulk polymer, and also the membrane solution interface characteristics, resulting in enhanced solute separation. These membranes appear to be potential candidates for single-stage seawater desalination and also for a variety of industrial effluent treatment applications for significantly high DF radioactive effluent treatment.

INTRODUCTION

The synthesis and reverse osmosis (RO) performance of a series of polyamide hydrazide polymers having varying isomeric compositions of amino benzhydrazides and acid chlorides were recently reported from our laboratory (*1, 2*). The membranes gave solute rejections up to 97.9% and water flow of the order of 0.36–0.50 m/d. Although the solute separations obtained were quite high compared to cellulose acetate (CA) membranes, they were not adequate either for seawater desalination or for high decontamination factors (DF) radioactive waste treatment. The presence of polar groups like sulfone, amide, ether, isocyanate, and imide groups in close proximity to aliphatic and aromatic hydrocarbons is known to alter the polar and nonpolar character and also the interfacial water structure, resulting in improved separation characteristics under RO conditions. In order to further improve performance, it was decided to modify the polymers by introducing ether linkages into the polymer backbone containing aromatic amide and hydrazide functional groups. Accordingly, a series of polyether amide hydrazides with varying proportions of ether linkages in the polymer backbone has been synthesized. Their RO performance has been evaluated and is reported herein.

EXPERIMENTAL

Monomers

p-Amino benzhydrazide (PABH) and *m*-amino benzhydrazide (MABH) were freshly synthesized (*1*) from *m*/*p*-amino benzoic acid (obtained from Fluka A.G.) and were twice recrystallized. Isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC) (obtained from Fluka A.G.) were similarly purified before use. The details of synthesis and purification of PABH, MABH, IPC, TPC, and dimethyl acetamide (DMAC) were reported earlier (*2*). 4,4′-Diamino diphenyl ether (DADPE, obtained from Fluka A.G.) was twice recrystallized from ethanol (melting point 190–192°C).

Polymer Synthesis

Polyether amide hydrazide polymer was synthesized by a low temperature polycondensation reaction by adding stoichiometric amounts of solid IPC and TPC to a precooled solution (−10°C) of MABH, PABH, and DADPE. Polymers suitable for making membranes were obtained by careful attention to the purity, stoichiometric equivalence, stirring, temperature, and time. The details of polymer synthesis are the same as in Ref. *2*.

Polymer Characterization

The percent moisture regain values were evaluated gravimetrically by equilibrating dry polymer samples at 25°C and at 80% RH. The solution viscosity was evaluated with an Ubbelohde viscometer by using a 0.5% polymer solution in DMAC. The results are expressed as η_{inh}.

Synthesis and Characterization of Membranes

Dopes from the polymer samples were prepared by dissolving 14.3% polymer in DMAC by using 4.7% lithium nitrate. Membranes were made by wiping the solution over a clean glass plate to a 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 cooled to room temperature and coagulated in demineralized water at 25°C. The membrane performance was evaluated in an RO test set up (*3*) by using 3.5% sodium chloride feed solutions at specified operating pressures. The feed and permeate samples were analyzed by conductivity measurements.

RESULTS AND DISCUSSIONS

Polymer Characterization

Moisture Regain

Five different polymer samples (designated E1, E2, E3, E4, and E5) were synthesized by varying the mole percentages of MABH and DADPE as per the details of their mole compositions as given in Table 1. The percent moisture regain data obtained for the five polymer samples are given in Table 2. The results indicate that the moisture regain values decrease from 9.71 to 7.87% for polymer samples E1 to E5. The moisture regain values for polyamide benzhydrazide polymer without an ether group in the polymer chain are also given in the table for the sake of comparison.

TABLE 1
Monomer Composition

		Molar composition (%)				
Sample No.	Polymer No.	MABH	DADPE	PABH	IPC	TPC
1	E1	63	7	30	70	30
2	E2	60	10	30	70	30
3	E3	55	15	30	70	30
4	E4	50	20	30	70	30
5	E5	45	25	30	70	30
6	PBH	70	—	30	70	30

TABLE 2
η_{inh}, Moisture Uptake Data

Sample No.	Polymer No.	Moisture uptake (%)	η_{inh} (dL/g)
1	E1	9.71	0.61
2	E2	9.65	0.63
3	E3	8.02	0.70
4	E4	7.88	0.72
5	E5	7.87	0.71
6	PBH	13.00	0.59

The moisture regain values are found to be highest for polybenzhydrazide polymer. The incorporation of ether linkages in the chain replaces a fraction of amide and hydrazide groups with amide and ether groups in addition to increasing the net *para*-substituted monomeric units in the polymer backbone. Possible structures of these two polymers are presented in Fig. 1. The replacement of a hydrazide group with an amide and ether group is expected to alter the polar character of the polymer, and incorporation of an additional aromatic hydrocarbon group is expected to alter the nonpolar character of the polymer. The moisture regain values decrease with increasing ether and amide linkages. The lower moisture regain values could also arise because increasing the net *para*-substituted monomeric units with increasing ether content facilitated enhancement of intermolecular hydrogen bonding between adjacent chains.

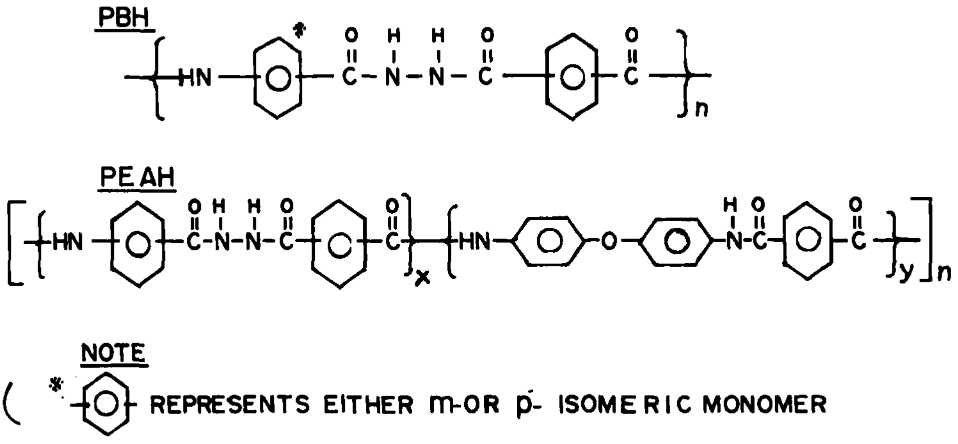

FIG. 1. Possible structures of PBH and PEAH polymers.

Solution Viscosity

The η_{inh}s of the various polymer samples are given in Table 2. The results indicate that the solution viscosity values increase as the DADPE monomeric units in the polymer increase. The higher η_{inh} values obtained for increasing *para*-substituted polymers could be due to increased degrees of polymerization and higher chain rigidity.

Solubility Parameters

Among the quantitative parameters characterizing the physicochemical nature of polymer materials, the solubility parameter (δsp) is useful for representing the bulk property of the polymer (*4*). δsp is considered (*5, 6*) to consist of three components representing individual contributions from dispersion forces (δd), dipole–dipole forces (δp), and hydrogen bonding forces (δh), so that

$$(\delta sp)^2 = \delta d^2 + \delta p^2 + \delta h^2 \tag{1}$$

The quantity δsp and its components can be calculated (*4*) for each structural unit comprising a given polymer by applying the additivity principle with quantities assigned for the structural group by using a set of relations reported in the literature (*4*). The numerical quantities involved for the various parameters of different structural groups are also listed in the literature (*4*). By using these data, the polar (δh), nonpolar (δd), and overall solubility parameters for polymer samples under study in this paper were calculated, and they are shown in Table 3. The corresponding values for nonether-containing polyamide benzhydrazide and cellulose acetate (acetyl content 39.8%) polymers are also given for the sake of comparison. The δsp values for ether-containing polymer samples were found to be

TABLE 3
Computed Solubility Parameters for Polymer Samples

Sample No.	Polymer No.	Solubility parameter, δsp	Polar component, δh	Nonpolar component, δd
1	E1	15.97	9.337	9.24
2	E2	15.93	9.287	9.237
3	E3	15.76	9.204	9.234
4	E4	15.70	9.123	9.23
5	E5	15.63	9.042	9.226
6	PBH	16.1	9.25	9.44
7	Cellulose acetate	12.7	6.33	7.60

lower than those for nonether-containing PBH polymer samples. Increasing the DADPE monomeric units in the polymer chains progressively decreases the overall solubility values, as can be seen for the corresponding values for polymers E1 to E5. It can also be seen that the incorporation of ether linkages in the polymer chain decreases the polar component and lowers the nonpolar component of the solubility parameter as compared to nonether-containing polymer samples. Comparison of these parameters with cellulose acetate polymer indicates that the aromatic polyamide polymers as RO membrane materials are distinctly different in their polar and nonpolar character compared to cellulose acetate materials.

Interfacial Sorption Characteristics

The interfacial sorption characteristics of the polymer membrane materials are represented (*4*) by data on K'_{NaCl} (equilibrium distribution coefficient for the solute between bulk solution and at the interface) and V_s/m (specific volume of interfacial water in m^3/g). These are two important factors involved in RO transport. On the basis of the preferential sorption and capillary flow mechanism of reverse osmosis (*4*), a higher value of V_s/m together with a lower value of K'_{NaCl} are desirable properties for polymer membrane materials in order to achieve high solute separations in reverse osmosis. It is well recognized (*7*) that liquid chromatography (LC) experiments simulate the equilibrium conditions prevailing at membrane–solution interfaces in RO/UF experiments, and hence LC data offer an effective means of characterizing the sorption behavior of membranes at interfaces.

The V_s/m data for various cellulosic and noncellulosic polymer membrane materials have been reported by Sourirajan (*4*). By assuming the additivity principle, the contribution of various structural units to interfacial water sorption has been evaluated by linear regression analysis (*4*). By using these data, V_s/m values have been calculated for various ether-containing polyamide hydrazide polymers, and they are shown in Table 4. The V_s/m values decrease for ether-containing polyamide hydrazides. Increas-

TABLE 4
Computed Interfacial Water and Solute Sorption Data for Polymer Samples

Sample No.	Polymer No.	$(V_s/m) \times 10^6$ (m^3/g)	K'_{NaCl}
1	E1	0.444	0.534
2	E2	0.441	0.525
3	E3	0.437	0.511
4	E4	0.432	0.496
5	E5	0.427	0.482
6	PBH	0.451	0.555

ing ether substitution progressively lowers interfacial water sorption values. It has been reported (*4*) that the number of interfacial water molecules for various structural groups associated with the aromatic polyamide type of polymer is less than 3. The number of water molecules associated with the ether group is estimated to be 1.43 per unit component and 2.11 per amide group.

The data on K'_{NaCl} are of particular interest in the choice of membrane materials for desalination applications. Data on K'_{NaCl} for a number of polymer candidates, as obtained from LC experiments, have been similarly analyzed, and structural group contributions for K'_{NaCl} have been reported in the literature (*4*). By using these data, K'_{NaCl} values have been calculated for polyether amide hydrazide polymers and are shown in Table 4. It can be seen that K'_{NaCl} values are lower for ether-containing polyamide hydrazide polymers, indicating the possibility of achieving higher solute separation under RO test conditions.

Membrane Characterization

Pure Water Permeability and Solute Transport Parameter

The pure water permeability (*PWP*) constant (*A*) and the solute transport parameter ($D_{AM}/K\delta$) for the membrane samples are shown in Table 5. The membrane constant (*A*) is evaluated from the measured *PWP* values for a specified pressure. The solute transport parameter ($D_{AM}/K\delta$) was computed by using experimentally measured values of the product rate (*PR*) and the solute separation factor (*f*) under RO test conditions through the use of Sourirajan's transport equation (*4*) as given below:

$$A = PWP/M_B \cdot S \cdot 3600 \cdot P \qquad (2)$$

$$N_B = A[P - \pi(X_{A2}) + \pi(X_{A3})] \qquad (3)$$

TABLE 5
Membrane Characterization Data

Sample No.	Polymer No.	$A \times 10^8$ (mol $H_2O/m^2 \cdot S \cdot kPa$)	$(D_{AM}/K\delta) \times 10^8$ (m/s)
1	E1	8.82	10.15
2	E2	8.361	12.29
3	E3	5.322	2.565
4	E4	3.322	2.401
5	E5	2.988	3.15
6	PBH	9.338	13.42

$$N_A = \left[\frac{D_{AM}}{K\delta}\right](C_2X_2 - C_3X_3) \tag{4}$$

$$(PR) = N_B \cdot M_B \cdot S \cdot 3600\left\{1 + \frac{m_1(1 - f)M_A}{1000}\right\} \tag{5}$$

$$X_{A3} = \frac{N_A}{N_A + N_B} \tag{6}$$

PWP is found to be affected by the molar ratios of the reacting monomers. The values decline steadily as the ether-containing *para*-substituted monomeric unit content increases. This corresponds well with the computed interfacial water sorption (V_s/m) data which also decrease with increasing *para*-substituted ether groups in the structure. The moisture uptake data measured for these polymer samples show a similar trend. The lowering of interfacial water sorption values with corresponding declining water permeability for polymer samples E1 to E5 compared to the PBH polymer sample could be due to ether and amide groups replacing some of the amide and hydrazide groups and also due to increasing *para*-substitution in the polymer chain. The membrane constant (A) values also decrease for polymer samples E1 to E5, and the PBH polymer has a relatively higher A value. The solute transport parameter values are higher for PBH polymer samples and are lower for ether-containing PBH polymer samples. Membrane samples E3 and E4, containing 15 and 20 mol% DADPE, respectively, have the lowest $D_{AM}/K\delta$ values and as such appear to have the optimum mole composition for higher solute separation under RO conditions.

RO Performance

The RO performances for sodium chloride feed solutions for various membrane samples are given in Table 6. The water permeation rates decline for membrane samples E1 to E5. The solute separation factor (f) is higher for ether-containing polyamide hydrazide polymer membranes compared to PBH polymer. Membrane samples E3 and E4 appear to give the highest solute separation factors. Whereas they both appear suitable for seawater desalination and for low level radioactive waste decontamination, E3 gives a significantly higher water flux than E4. The enhanced solute separation observed in the case of ether-containing polyamide hydrazide polymers is also reflected in the K'_{NaCl} values calculated based on reported LC experimental data. The incorporation of ether/amide groups in the polymeric chain as replacements for a part of the amide/hydrazide groups reduces not only the number of water molecules associated with these functional

TABLE 6
RO Performance Data[a]

Sample No.	Polymer No.	Water permeation rate (m/d)	Solute separation
1	E1	0.462	0.9844
2	E2	0.412	0.98
3	E3	0.393	0.9935
4	E4	0.242	0.99
5	E5	0.227	0.986
6	PBH	0.499	0.961

[a] Feed = 0.5988 *M* sodium chloride.
Operating pressure = 6864 kPa.
Membrane area = 1.625×10^{-3} m^2.

groups, but also the equilibrium water sorption values at the membrane–solution interface, resulting in improved RO performance. There appears to be an optimum mole composition with respect to DADPE for obtaining the best solute separation.

CONCLUSIONS

A series of film-forming wholly aromatic polyether amide hydrazide polymers was synthesized by varying the mole ratios of *m*/*p*-amino benzhydrazides, 4,4′-diaminodiphenyl ether, and iso/terephthaloyl chlorides. The polymer samples were characterized in terms of moisture regain, η_{inh}, solubility parameters, and interfacial sorption. The reverse osmosis performances of these polymer membranes were evaluated and compared with those obtained for polybenzhydrazide polymers synthesized without ether linkages. Membranes with polymers formed by a combination of 50 to 55% mole ratios of *meta*-amino benzhydrazides, 30% mole ratio of *para*-amino benzhydrazides, and 20 to 15% mole ratios of 4,4′-diamino diphenyl ether, with a 70/30 mole ratio of iso- and terephthaloyl chlorides, appear to give optimum performance with a feed concentration in the range encountered in seawater desalination. Solute separations up to 99.4% with respect to sodium chloride in test cell conditions could be achieved. The membrane samples prepared with the above optimized monomer composition appear to be suitable for single-stage seawater desalination. The high solute separation achievable for polyether amide hydrazide membranes makes them suitable for a variety of industrial applications including separation and concentration of radioisotopes from effluents. They provide very high decontamination factors and volume reductions.

NOMENCLATURE

K'_{NaCl}	interfacial distribution coefficient for sodium chloride
V_s/m	specific volume of water (m^3/g)
A	pure water permeability constant, $kg \cdot mol \cdot H_2O/m^2 \cdot s \cdot kPa$
PWP	pure water permeation rate through the given area of membrane surface (kg/h)
S	effective membrane area (m^2)
M_A, M_B	molecular weight of solute, water
P	operating pressure (kPa)
D_{AM}	diffusivity of solute in membrane phase (m^2/s)
$(D_{AM}/K\delta)$	solute transport parameter (m/s)
N_B	solvent water flux through membrane ($g\text{-}mol/m^2 \cdot s$)
C	molar density of solution ($g\text{-}mol/m^3$)
X_A	mole fraction of solute
m_1	solute molality
(PR)	product permeation rate (kg/h)
f	solute separation factor

Subscripts

1	bulk solution
2	concentrated boundary layer solution
3	permeated product solution

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