Studies on Polyurea Membrane

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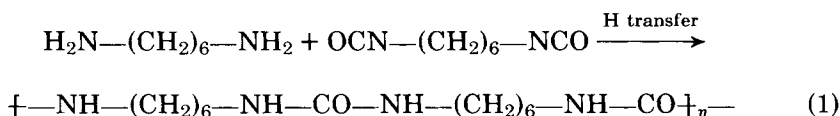
Synopsis

Synthesis of polyurea by interface polymerization of diisocyanate and diamine for preparation of polymer membrane for use in separation problems was investigated. A sulfuric-acid-based casting formulation was developed for the polymer prepared from 1,6-hexamethylene diamine and 1,6-hexamethylene diisocyanate. The resulting membrane is porous and highly permeable to water. However, salt rejection was found to be <20%, while high molecular weight solutes like milk, papain, and Na-alginate were found to be rejected 100%. The membrane is more like a sieve structure with the absence of an asymmetric layer. It is found to be resistant to many organic solvents, thus making it suitable for use in ultrafiltration applications.

INTRODUCTION

From the knowledge of the transport properties polyurea membrane has been reported as highly hydrophilic.[1] The basic linking unit in this polymer, —NH—CO—NH—, imparts both hydrophilic and stable properties to the parent polymer. The other nitrogen containing polymers like polyamides, polyhydrazides, and polybenzimidazoles have been studied extensively for use in desalination by reverse osmosis.[2-4] Studies on polyurea membranes for reverse osmosis/ultrafiltration have not been widely reported; however, its use as ultrathin films in composite membrane for water desalination and other applications is known.[5] Six polyureas have been synthesized in this laboratory by interface polymerization. Among them the polymer of 1,6-hexamethylene diamine and 1,6-hexamethylene diisocyanate has been investigated in detail and reported in this paper.

EXPERIMENTAL

Solvents and monomers were purified as described by Morgan.[6] Polymerization was carried out in a 500-mL round-bottomed flask attached with a thermometer, separating funnel, and a high speed stirrer. A known amount of diisocyanate solution in organic solvent was added slowly into an aqueous solution of diamine under rapid stirring. Precipitated polymer mass was diluted with methanol, filtered, washed with hot water followed by methanol and dried at 70°C under vacuum. In the case of poly(hexamethylene diamine–hexamethylene diisocyanate) reaction was carried out at +2°C and finally heated at 60°C for 3 h. The reaction route is shown as follows:

$$H_2N-(CH_2)_6-NH_2 + OCN-(CH_2)_6-NCO \xrightarrow{\text{H transfer}}$$

$$\{-NH-(CH_2)_6-NH-CO-NH-(CH_2)_6-NH-CO\}_n- \qquad (1)$$

Viscosity. Polymer viscosity was measured by an Ostwald Capillary Flow Viscometer at a constant temperature of $25 \pm 1°C$ and expressed as reduced viscosity η_{red} (0.5 g/100 mL of 98.08% H_2SO_4). The viscosity of the casting solution was measured by a Brookfield Synchrolectric Viscometer at $25 \pm 1°C$ and expressed in centripoises (cP).

Membrane Porosity. Membrane porosity was measured by the following relation:

$$\text{porosity } \% = \frac{W_1 - W_2}{W_1} \times 100$$

where W_1 and W_2 are the wet and the dry weight at 105°C of the membrane, respectively.

Reverse Osmosis Test. The reverse osmosis test was carried out by means of small membrane cell, supplied by Universal Water Corp., Del Mar, California. The rejection of salt was calculated by measuring the conductance of saline water, C_1, and permeate water, C_2, as given by the following relation:

$$R_{NaCl} (\%) = \frac{C_1 - C_2}{C_1} \times 100$$

The permeate flux was expressed in gallons per square foot of membrane area (17.5 cm^2) per day (GFD).

Ultrafiltration Test. An ultrafiltration test was carried out by using a cell supplied by the Amicon Corp., Lexington, Massachusetts, where the test solution was continuously stirred to minimize the formation of deposits on the membrane surface. A minimum 200 mL quantity of test solution was taken in the cell for the ultrafiltration test. The following solutes were studied for the concentration/separation purposes; the permeates were detected by different test methods as shown in Table I.
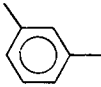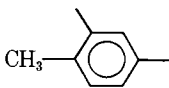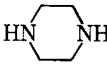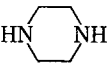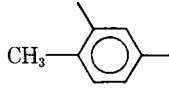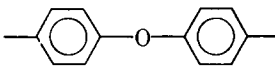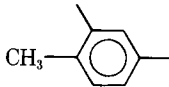
RESULTS AND DISCUSSION

Table II shows six polyureas synthesized from different monomers.

The polymers shown in Table II are all soluble in concentrated sulfuric acid and are found suitable for membrane preparation. Polymer no. 2, the polymerization product of hexamethylene diamine and hexamethylene diisocyanate, was investigated in detail. This polymer was reproduced several times before membrane study was carried out.

TABLE I
Molecular Weight and Detection Methods of Solute Systems

Solute	Average MW	Methods for its detection
Milk protein	15,000	N_2 estimation by Kjeldahl's method
Papain (10% solution)	20,000	Sugar refractometer
Na-alginate 0.1%, 0.25%, 0.50% solution	150,000	Acetone/alcohol precipitation
Hemoglobin 1.0% solution	68,000	Colorimetric analysis
Oil-emulsion (350 ppm oil content)	—	Chloroform–oil extraction

TABLE II
Polyureas from Different Diamines and Diisocyanates

	Diamine	Diisocyanate	Softening point (°C)	η_{red}
1.	(benzene ring structure)	$-(CH_2)_6-$	255–260	0.69
2.	$-(CH_2)_6-$	$-(CH_2)_6-$	270	1.35
3.	$-(CH_2)_6-$	CH_3-(benzene ring)$-$	225–230	0.47
4.	HN(ring)NH	$-(CH_2)_6-$	275	1.08
5.	HN(ring)NH	CH_3-(benzene ring)$-$	285	0.47
6.	$-$(benzene ring)$-O-$(benzene ring)$-$	CH_3-(benzene ring)$-$	290	—

Optimization of Membrane Casting Composition. Polyurea synthesized by interfacial polymerization is not soluble in organic solvents. It dissolves conveniently in concentrated sulfuric acid. Casting composition was optimized by varying the proportions of polymer ranging from 10% to 50% in sulfuric acid. Membrane strength increased with increase in polymer concentration, with simultaneous decrease in water permeability. A 50% polymer solution was difficult to handle. The membrane prepared out of this composition was rigid and less permeable to water. A 40% polymer solution was found suitable as it yielded a practically good membrane (21.2 kg/cm², strength at break). This membrane gave 250 GFD of pure water flux at 600 psi operating pressure. The various compositions studied gave no more than 20% of salt rejection for 5000 ppm NaCl solution.

Different additives like, poly(ethylene glycol), water, acetone, tetrahydrofuran, ethyl cellosolve and triethyl phosphate were added in different proportions ranging from 1.0% to 10.0% into the casting solution to examine their effect, on the membrane performance. Salt rejection could not be improved by any of these additives. Water permeability could be increased considerably after the addition of acetone, water, trimethyl phosphate, and tetrahydrofuran from 250 GFD initially to 300 GFD. Membrane porosity increases with the increase in water concentrations in the casting solutions (Fig. 1).

Optimization of Casting Conditions. Membrane was cast according to phase inversion method followed by solvent evaporation and gelling in nonsolvent medium. Membrane evaporation time ranging from 10 s to 60 s has no effect on the membrane performance because of the presence of nonvolatile sulfuric acid. During the course of a longer evaporation period, sulfuric acid absorbs moisture from the atmosphere and gells the membrane when it turns from transparent solution into a white, opaque, semigelled membrane. In Table III is shown the effect of different gelling bath compositions on the membrane performance.
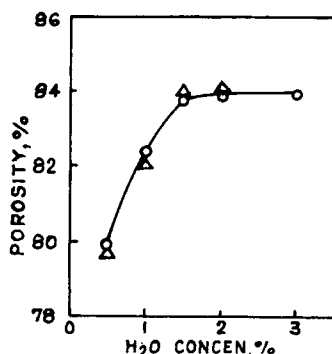
Fig. 1. Membrane porosity as a function of water concentration. Evaporation: (O) 10 SCE; (△) 60 SCE.

It was assumed from Table III that the diffusion rate of sulfuric acid in a sulfuric acid bath is less compared to the water and ice-water bath, thus resulting in a less porous membrane.

Membrane heat treatment after gelation has no effect on salt rejection. Product water flux increases after heat treatment, probably because of the shrinkage of the gel structure leaving bigger sized voids.

Optimized composition and casting conditions are shown in Table IV.

Testing of Polyurea Membrane for the Presence of Active Layer

Polyurea membrane is found very porous in nature giving rise to the doubt whether it is an asymmetric or uniformly porous gel. Membrane was tested in the reverse osmosis test cell, keeping the reverse side facing the feed solution; some peculiar behavior has been observed. Pressure was applied gradually and when it reached 65 psi, a jetlike flow of the permeate was observed, which was not seen below 65 psi pressure. This behavior can be explained on the basis of pore structure. The membrane has rather bigger-sized closed pores on the reverse side. During the pressurization there exists some level of pressure at which the pores start opening up, giving more passage for water to pass through. As the pressure was again slowly reduced, pores start closing, giving less passage to the water.

TABLE III
Effect of Gelling Bath Composition on the Membrane Performance

Gelling bath composition	Flux (GFD)	R_{NaCl} (%)	Remark
Water, 25°C	250–300	nil	Membrane separates out immediately from the glass plate
Ice water, 2°C	250–300	nil	Membrane separates out immediately from the glass plate
$1N$ H_2SO_4, 25°C	20	nil	Membrane separates out slowly
$2N$ H_2SO_4, 25°C	10	nil	Membrane sticks to the glass surface

TABLE IV
Optimized Casting Composition and Casting Conditions for Polyurea Membrane

Casting composition		
Polymer (wt %)	Concn H_2SO_4 (vol %)	Viscosity (cP)
40	100	13,600
Casting condition		
Evaporation time	10–60 s	
Gelling bath	2–25°C for 1 h	
Heat treatment	Nil	
Membrane thickness	150–200 μ	

Here an unusual polymer–solvent system has been used. A low boiling-point solvent and a high boiling additive generally forms a skin on the membrane–air interface. In this case there is no scope of evaporation of sulfuric acid from the membrane surface. As a result, no skin formation takes place on the upper surface. Absence of active layer is revealed by zero salt rejection even after giving heat treatment to the membrane at 90°C. Thus the membrane structure is
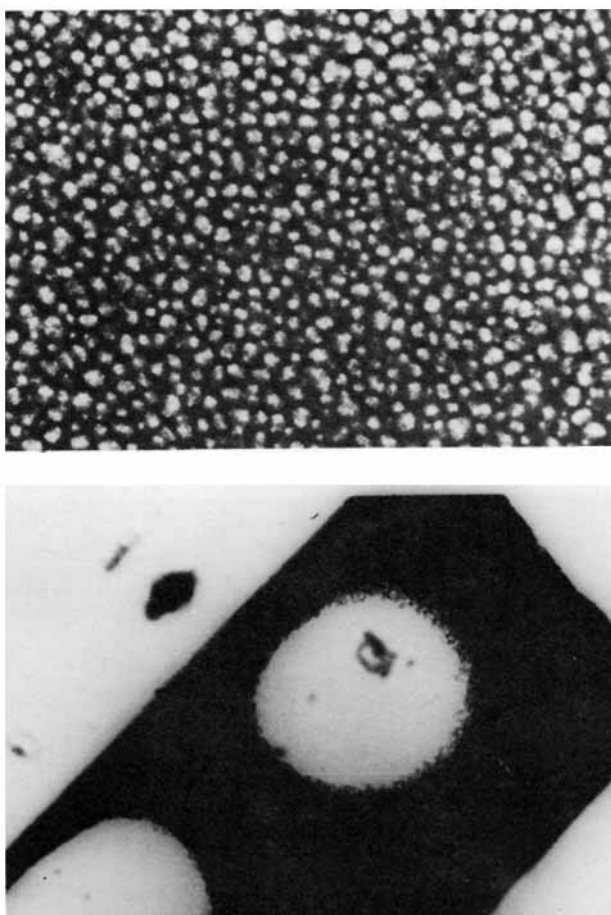

Fig. 2. Photomicrographs of the surface layer (top) and the cross section (bottom).

TABLE V
Solvent Resistance of Polyurea Membrane[a]

Solvent	Dissolve	Swelling	Unaffected
Acetone	−	−	+
Tetrahydrofuran	−	−	+
Dioxane	−	−	+
Dimethyl formamide	−	+	−
Dimethyl sulfoxide	−	+	−
Dimethyl acetacide	−	+	−
N-methyl-2-pyrollidone	−	+	−
0.1N NaOH	−	−	+ (5 months)
0.1N H₂S₄	−	−	+ (5 months)

[a] + = Yes; − = no.

uniformly porous, produced particularly during the gelation process because of the rapid exchange rate between sulfuric acid and water. These observations confirm that the polyurea membrane reported in this investigation is not an asymmetric type. An optical photomicrograph of the upper surface and cross section show evidence to the above observations (Fig. 2).

Solvent Resistance of Polyurea Membrane. A few membrane pieces of measured dimension were kept immersed in boiling organic solvents for 24 h. The results of which are shown in Table V. Membrane remained unaffected in common organic solvents and in dilute acid and alkali of 0.1 normality. It swells in amide type of solvents.

Ultrafiltration Separation/Concentration of Some Solutes. Being a porous structure, polyurea membrane was chosen to examine its utility in ultrafiltration applications. Whole milk, papain, and Na-alginate were found to be rejected 100% at 50 psi operating pressure, while hemoglobin could be rejected
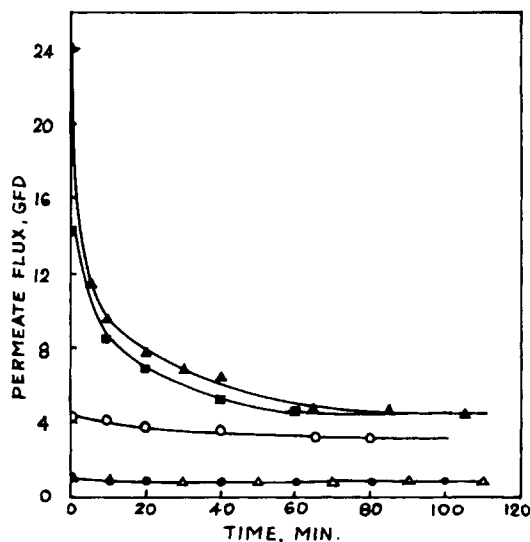

Fig. 3. Permeate flux as a function of time: (O) Na-alginate, 0.1%; (●) milk; (▲) hemoglobin; (■) oil emulsion; (△) papain, 10%.

80%. An oil emulsion containing 35,000 ppm of TDS and 350 ppm of oil (hydrocarbons) was tested; the permeate showed only traces of oil. No swelling or loosening of the structure occurred during this application. A plot of permeate flux as a function of time has been presented for five solutes (Fig. 3). A gradual flux decline has been observed in hemoglobin and in oil emulsion, while in Na-alginate, papain, and milk the flux decline rate is quite low.

CONCLUSIONS

Six types of polyureas have been synthesized by interface polymerization and characterized. Out of these, polyurea membrane of hexamethylene diamine and diisocyanate is found highly permeable to water and sodium chloride. The high permeability for water and low rejection of salt obtained are in agreement with the concept of a loose, open-structured gel membranes. Nevertheless, the results of this study indicate its utility in ultrafiltration application. Solvent-like sulfuric acid cannot form an asymmetric type membrane by phase inversion method. For this reason polymer soluble in organic solvents should be developed.

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