Development of Poly(*meta*-Phenylene Terephthalamide) as a Membrane Material for the Reverse Osmosis Process

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Synopsis

The low temperature, homogeneous, solution polycondensation method is optimized to synthesize poly(*meta*-phenylene terephthalamide). The product is characterized and is also evaluated as a membrane material by studying its dense membrane. The fabrication technique of the osmotic flat membrane of poly(*meta*-phenylene terephthalamide) is studied and its high-pressure performance is tested. The optimized flat membrane is characterized.

INTRODUCTION

Commercial applications of cellulosic membranes underlined their shortcomings. The development of the reverse osmosis (RO) technology has made "aromatic polyamides" imminently suitable for a broad spectrum of the RO application. Dupont's NOMEX poly(*meta*-phenylene isophthalamide) is in captive, limited scale production and is available solely in the form of hollow fine fiber RO module. Hence the study was undertaken to develop poly(*meta*-phenylene terephthalamide) as a membrane material.

EXPERIMENTAL

Synthesis of Poly(*m*-Phenylene Terephthalamide)

Stoichiometric amounts of the laboratory purified monomers, *m*-phenylene diamine and terephthaloyl chloride, are used. The solvent, dimethyl acetamide (DMA, BDH grade), amount used is such that the final viscous dope is 10–12% polymer solution.

The experimental parameters studied are: reaction temperature −10–+5°C; period of addition of terephthaloyl chloride 2–20 min; condensation period 5–120 min; with or without neutralization of the liberated HCl with either lithium hydroxide or carbonate or calcium carbonate during the polycondensation reaction.

The product is obtained by precipitation in water, is thoroughly washed with water, is dried at 110°C, and is characterized (Table I). The yield is 90–95% of the theoretical expectation.

Poly(*m*-Phenylene Terephthalamide) Dense Membrane

The viscous unneutralized reaction dope is used for the preparation of the dense membrane of poly(*m*-phenylene terephthalamide). The technique

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TABLE I
Characteristics of Laboratory Synthesized Poly(*m*-Phenylene Terephthalamide)

Characteristic	Value
Elemental analysis (%)	C, H, N = 66.8, 4.0, 11.5 respectively
Molecular weight	50,000–60,000
Inherent viscosity (H_2SO_4, 30°C) (dL/g)	0.9–1.2
Softening point	Does not soften up to minimum 300°C

is the same as used by McKinnen[1] and Frommer et al.[2] Prolonged vacuum drying is necessary to remove the last traces of the solvent and HCl. This dense membrane characteristics along with those of the secondary cellulose acetate (CA) are mentioned in Table II.

Poly(*m*-Phenylene Terephthalamide) Optimized, Practical, Osmotic Membrane

The components (wt %) of the membrane casting solution are: polymer 12, lithium chloride 50 of the polymer, and the rest DMA as the solvent. The casting solution viscosity is about 45,000 CP. As the solvent possesses high boiling temperature, prolonged drying time and higher temperature than those required for the CA membrane are necessary.

The optimized membrane fabrication parameters are: as-cast thickness 0.6 mm, evaporation period 20 min, and evaporation temperature 120°C. Circular membrane samples (effective area 18.92 cm^2) were tested on a laboratory type RO cell, using 5000 ppm NaCl aqueous feed solution, 40 kg/cm^2 operating pressure, and each time the operation period being 6 h. The optimized flat osmotic membrane produced 800–900 L/m^2 day (i.e., about 16–18 gal/ft^2 day) product flux and 90–85% salt rejection, respectively. Table III contains the characteristics of the optimized flat osmotic membrane of poly(*m*-phenylene terephthalamide) and also those of the CA osmotic membrane.

RESULTS AND DISCUSSION

The more convenient and widely applicable low temperature, homogeneous, solution polycondensation in an amide solvent has been adopted for the synthesis of poly(*m*-phenylene terephthalamide). This method is optimized to obtain suitable grade (Table I) of this polymer. The elemental analysis of this polymer fairly coincides with the theoretical values; its softening point is consistent with the literature observations.

It is axiomatic that what is sought for RO is a material with high perme-

TABLE II
Characteristics of Poly(*m*-Phenylene Terephthalamide) (I) and CA(II) Dense Membranes

Characteristic	Value
Specific water content of (I) (g/cm^3)	38.4×10^{-2}
Specific water content of (II) (g/cm^3)	11.1×10^{-2}
Salt (NaCl) absorption[a] by (I) (g/cm^3)	3.4×10^{-3}
Salt (NaCl) absorption[a] by (II) (g/cm^3)	3.8×10^{-3}

[a] 3.5% (wt/vol) NaCl aqueous solution used.

TABLE III
Characteristics of Osmotic Poly(*m*-Phenylene terephthalamide) and CA Membranes

Characteristic	Value	
	Poly(*m*-phenylene terephthalamide)	CA
Specific water content (g/cm³)	0.75	0.70
Salt absorption[a] (g/cm³)	1.44×10^{-2}	0.82×10^{-2}
Water flux (by direct osmosis) (g/cm² s)	1.15×10^{-4}	1.28×10^{-4}
Solute flux (by direct osmosis[a]) (g/cm² s)	0.74×10^{-7}	1.1×10^{-7}

[a] 3.5% (wt/vol) NaCl aqueous solution used.

ability to water and low permeability to salt. According to Table II, the values of the specific water content and salt absorption of poly(*m*-phenylene terephthalamide) dense membrane are, respectively, higher and lower than those of CA dense membrane. This indicates that the former is at least as good a membrane material as the latter.

An unusual aspect of some of the aromatic polyamide solutions is the necessary presence of dissolved inorganic salts (lithium chloride in the present case). The solvents are frequently incapable of dissolving or retaining in solution such polymers without the addition of as much as 100% of the polymer weight in lithium or calcium salts, which are believed to cause a reduction in intermolecular interaction and thus enhance the solubility of the macromolecular substance in the solvent.

Poly(*m*-phenylene terephthalamide) osmotic membrane fabrication parameters are optimized. The membrane characteristics can be controlled by adjusting the evaporation rate and the drying time, which affect the residual solvent in the membrane precursor at the time of coagulation. The polymer/additive/solvent system of the casting solution is also an important factor to prepare good membranes. The performance of the optimized poly(*m*-phenylene terephthalamide) membrane is favorably comparable with that of the conventional secondary cellulose acetate membrane, when applied for brackish water desalination under identical operational conditions. This observation is supported by the comparison of the characteristics (Table III) of these two types of osmotic membranes.

CONCLUSIONS

On a laboratory scale the synthesis of poly(*m*-phenylene terephthalamide) is optimized, and the product is characterized. The dense membrane characteristics of this polymer indicate it to be at least as good a membrane material as secondary cellulose acetate, which observation is supported by the high-pressure performance and the characteristics of the osmotic membrane of this polymer.

References

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