

Synthesis, characterisation and evaluation of polyamide membrane

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In this paper, wholly aromatic polyamide has been synthesised from complex amine, 1,3-bis(3-amino benzamido)benzene or preformed amine (PFA), aromatic diamino carboxylic acid and aromatic dicarboxylic acid chloride. The synthesised polyamide, has functional amino and carboxyl groups. The polymer has been characterised by using IR and ¹H NMR. The membrane porosity has been determined by SEM. The evaluation of membrane has been done by using "Reverse Osmosis Test Cell" (Osmonics). The salt rejection (efficiency) and product water output rate (flux) have also been determined for different membranes with LiNO₃/LiCl combinations.

The development of polyamide membrane was taken up in order to overcome the inherent disadvantages in cellulose acetate^{1,2} membrane such as susceptibility to hydrolysis, higher acid dosing rate and shorter membrane life. The polyamide membranes are characterised by their high degree of salt rejection (efficiency) and flux, good mechanical strength, wide pH range and stability which makes this class of polyamide polymers superior³ and potentially useful for reverse osmosis. In this paper, wholly aromatic polyamide was synthesised from complex amine, 1,3-bis (3-amino benzamido) benzene or preformed amine (PFA), aromatic diamino carboxylic acid and aromatic dicarboxylic acid chloride. The results of SEM data, efficiency and flux rates are discussed.

Wholly aromatic polyamide was obtained by low temperature homogeneous polycondensation of preformed amine (PFA), aromatic diamino carboxylic acid and aromatic dicarboxylic acid chloride in polar solvent like *N,N*-dimethyl acetamide (DMAc). Aromatic polyamides having pendant carboxylic groups⁴ in the main repeating unit have higher water flux which exhibit good affinity with water. Asymmetric membranes prepared from these polymer samples were tested for their reverse osmosis performance. Although cellulose acetate membrane can desalinate brackish water¹, it has got the limitations of operating at narrow pH range and bacteriological deterioration. On the other hand, polyamide membranes can operate at wide pH range and have greater mechanical strength and chemical and bacteriological stabil-

ity³. The polyamide polymer synthesis^{5,6} involves stringent process conditions. An optimum molar ratio of reacting monomers was used in the reaction which was conducted between -30 to -25°C. This low temperature range was essential to suppress the attack of acid chloride on the solvent, DMAc⁷. Pore size can be increased by using additives such as LiCl and LiNO₃.

Experimental Procedure

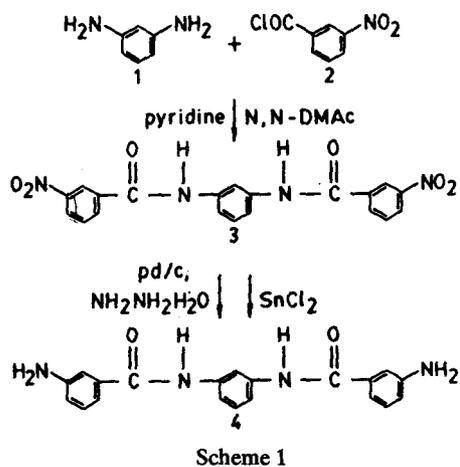
N,N-dimethyl acetamide (Spectrochem) was distilled twice over calcium hydride and stored over molecular sieves 4 Å. Pyridine was purified by distillation and stored over KOH pellets. 3,5-diamino benzoic acid (DABA, Aldrich) was recrystallised with isopropyl alcohol. All other chemicals (Aldrich) were used as such. IR spectra was recorded with Nicolet Fourier Transform Infrared Spectrophotometer. ¹H NMR spectra were recorded on a Joel FX-100 Spectrophotometer in DMSO-*d*₆ and melting points on a Dupont Differential Scanning Calorimeter (DSC). Photographs of 1000 magnification polyamide membranes were taken using Joel Scanning Electron Microscope (JSM 35). Membrane samples for SEM photographs were prepared by gold sputtering by using "Fine coat DC Ion-Sputter FC 1100". Membranes were tested by using "Osmonics Test Cell" using Braun + Leube Pump.

Synthesis of polyamide polymer

The synthesis of polyamide polymer was carried out in two steps.

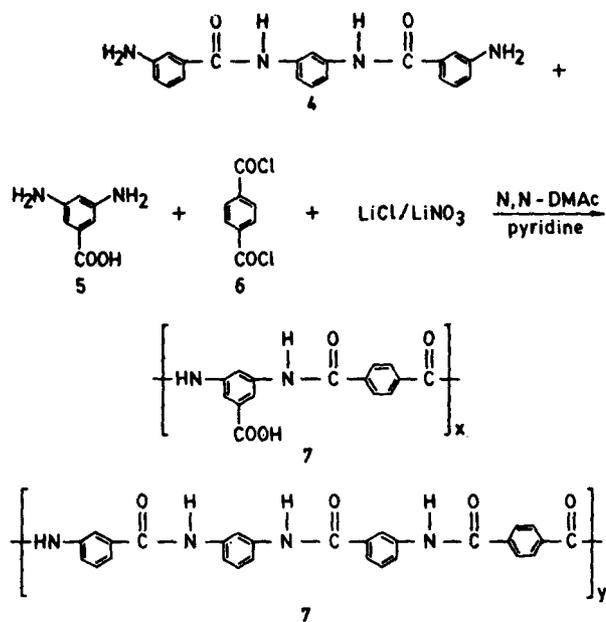
Synthesis of 1,3-bis(3-aminobenzamido) benzene (Preformed amine) - This is a crucial and im-

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portant intermediate in the synthesis of wholly aromatic polyamide polymer. It is a two-step reaction⁸. The nitro preformed amine (3) was synthesised by reacting metaphenylenediamine (1) (0.1 mol; 10.8 g) in 40 mL DMAc with 3-nitrobenzoyl chloride (2) (0.2 mol; 37.04 g) after the addition of (2) pyridine 16 mL was added. The nitro compound (3) was purified by dissolving in glacial acetic acid and yellow crystalline solid was obtained (m.p. 267°C (DSC)). The nitro compound (3) was reduced by Pd/C in hydrazine hydrate⁹ or by SnCl₂ to give 1,3-bis(3-amino benzamido) benzene (4) (Scheme 1). The PFA was purified by DMAc solvent (m.p. 214°C (DSC)). The detailed synthesis was already discussed elsewhere⁸.

Synthesis of wholly aromatic polyamide polymer—In a three-necked flask PFA (4) (0.0375 mol; 12.97 g), 3,5-diaminobenzoic acid (DABA) (5) (0.0125 mol; 1.90 g), lithium salts, viz., LiCl¹⁰/LiNO₃ were taken in DMAc. The flask was fitted with a guard tube, stirrer and an inlet tube for pure, dry nitrogen (Iolar grade) to maintain inert atmosphere. The flask with its contents was cooled to -30 to -25°C. DMAc (175 mL) acts as a proton acceptor and reacts with the liberated HCl. Terephthaloyl chloride (6) (0.050 mol; 10.2 g), (a slight excess of acid chloride) was taken in DMAc was added dropwise to the chilled amine with vigorous stirring followed by pyridine (8 mL) addition. The low temperature was maintained to take care of the exotherm generated during the reaction. The addition was completed in 30 min and the stirring was continued at low temperature for 3 h and at room temperature for 2 h. Brown, transparent, viscous polyamide polymer was obtained (Scheme 2)⁹ inherent viscosity H₂SO₄, 30°C) $\eta_{inh} = 0.5$ dL/g. The synthesised polyamide has functional amino and carboxyl groups. The



spectral data of synthesised polyamide polymer are given below:

IR: 1786-1726 (C=O); 3570-3125 cm⁻¹ (NH).
¹H NMR (100 MHz, DMSO *d*₆) δ 8.7 (d), (-NH, Ar-H) at C2 δ 8.3 (d) (2 Ar-H) at C4 and C6 δ 8.0 (m) (2H) δ 7.7 (d) (2H) (Aromatic protons in phthaloyl moiety). δ 7.3 (Q) at C2 δ 7.5 at C4 to C6 (metaphenylenediamine moiety) δ 10.8 and δ 11.4 (-COOH) δ 8.1 (S) (aromatic).

Results and Discussion

Casting of membrane—Membranes of good strength could be obtained directly from the polymer solution in DMAc (14% polymer and 10-40% by weight lithium salts). One of the important steps in membrane preparation is the partial evaporation of the solvent which controls the membrane structure and performance. The membranes were hand cast¹¹ in the form of flat sheet (25 cm × 20 cm) using Doctor's blade on a dry, clean glass plate. The film was drawn to the required thickness of 100-120 μ m. The plates were then subjected to thermal evaporation of the solvent in an air circulating oven at 110°C for 30 min. When the cast membrane was kept in oven, solvent evaporation is maximum during the first ten minutes resulting in skin formation and membrane anisotropy. Glass plate with membrane was removed from the oven and cooled to room temperature. The membrane was coagulated in DM water at temperature 3-5°C for one hour and the membrane was washed for 8-10 h with water to

Table 1 - Polyamide membrane performance at different additive concentrations (Temp. 25°C, pH 7)

Thickness μm	NaCl ppm	Additive feed %	Pressure kg/cm^2	Salt rejection %	Product water output (FLUX) GFD
LiCl					
100	10,000	10	50	88.0	7.5
115	10,000	20	50	88.8	8.3
100	10,000	30	50	90.5	9.0
110	10,000	40	50	92.3	10.0
LiNO ₃					
100	10,000	10	50	92.0	5.2
110	10,000	20	50	94.3	5.8
115	10,000	30	50	96.2	6.0
110	10,000	40	50	98.5	6.5
LiCl: LiNO ₃ (1:1)					
110	10,000	10	50	90.2	6.0
100	10,000	20	50	92.0	6.5
115	10,000	30	50	93.3	7.5
110	10,000	40	50	95.0	8.4

remove any unreacted solvent. The membrane matrix develops porosity during coagulation stage and depending on the residual solvent¹², the membrane morphology is decided. During the coagulation stage in ice-water mixture the membrane develops a more open, porous matrix. Thus, a judicious combination of residual solvent, presence of hydrophilic groups and an optimum concentration of LiCl and LiNO₃ result in more efficient polyamide membrane. To understand the morphology and pore structure, SEM studies were conducted on the membranes.

Testing of membrane—Tropan blue dye penetration test was carried out to prove the presence of pores in the dense layer which was absent on the skin side (active layer). The membranes were cut to a circular shape of 5 cm dia and were tested using "Osmonics Test Cell". The membrane was supported by a sintered porous stainless steel disc covered with filter paper and the salt water is pumped into the cell containing the membrane at a pressure greater than the osmotic pressure of the solution.

Polymer membranes were prepared with different additive concentrations and were tested at a pressure of 50 kg/cm² and salt-water concentration of 10,000 ppm. Salt rejection and product water output were determined for LiCl, LiNO₃ and their combinations. With LiCl additive, the results indicate that there was no significant increase of salt rejection (efficiency) with increase of additive concentration, whereas with LiNO₃,

the salt rejection was comparatively very high. It was also observed that the product water output was relatively high for LiCl based membranes compared to LiNO₃ based membranes. When used with optimum concentration of 1:1, with the mixture of LiCl and LiNO₃ for different concentrations ranging from 10 to 40% resulted in the increased efficiency and flux. Thus, it is observed (Table 1) that the performance of membrane can be increased by using 1:1 mixture of LiCl and LiNO₃ and 30-40% by weight of the polymer. In addition to LiCl and LiNO₃ additives, solvent evaporation and hydrophilic groups (-CO-NH-, -COOH) present in the polymer also play a vital role in increasing the efficiency and flux.

SEM studies—SEM studies revealed that the cast membranes have anisotropic structure with the active layer (skin layer) and the supporting layer (the surface in contact with the glass plate) assumes matrix structure during partial evaporation step.

Fig. 1 shows coarse, porous and cellular interiors in the polymer membrane where LiCl additive was used in the polymer. These membranes show relatively low salt rejection and high flux rates as reported by Sourirajan and Blais¹³. Fig. 2 shows packed columnar elements when LiNO₃ additive was used in the polymer. These membranes show relatively higher salt rejection with reduced flux rates. Fig. 3 shows the intermediate degree of porosity representing a broad spectrum of reverse

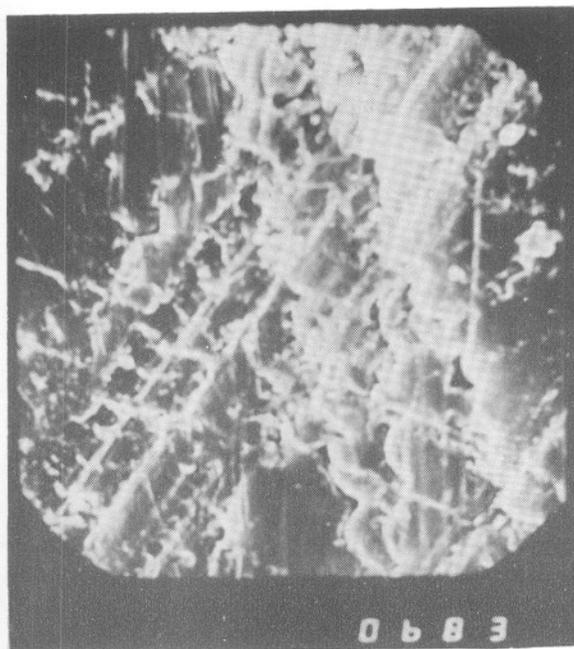


Fig. 1 - SEM showing coarse, porous and cellular interiors in the polymer membrane where LiCl additive was used (magnification 1000 \times).

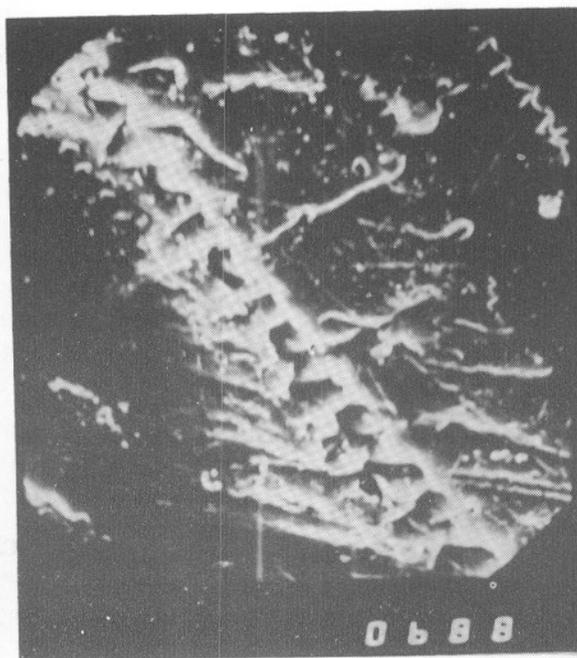


Fig. 3 - SEM showing the intermediate degree of porosity representing a broad spectrum of reverse osmosis when combination of additive system (LiCl + LiNO₃) was used (magnification 1000 \times)

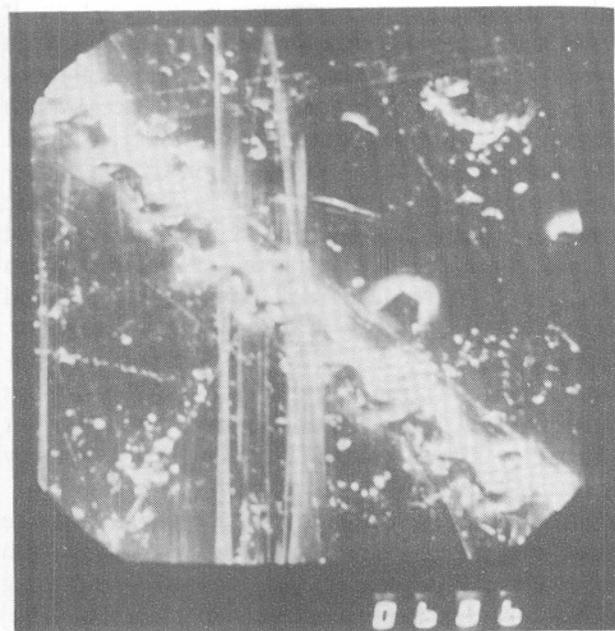


Fig. 2 - SEM showing packed columnar elements in the polymer membrane where LiNO₃ additive was used (magnification 1000 \times)

osmosis when combination of additive system (LiNO₃-LiCl) was used. The figure also shows strong interwoven ladder structure of the membrane with conspicuous pores. The micellar morphology^{13,14} was found in polyamide membrane.

Conclusions

Polyamide polymer was synthesised from PFA

and was characterised. Lithium salts, LiNO₃/LiCl were used either alone or in combination in the ratio of 1:1 and optimum concentration of additive (30-40%) fared well in exhibiting good flux rate and maximum salt rejection (efficiency).

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