Synthesis, characterization and reverse osmosis performance of poly(amide–sulfonamide)s

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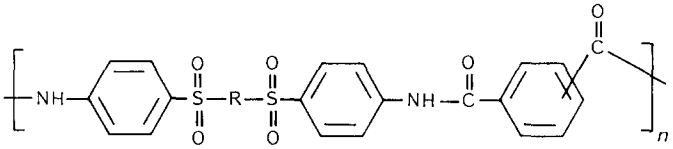
Poly(amide–sulfonamide)s **1–4** were synthesized by low-temperature solution polycondensation of diamino monomers **5** and **6** with isophthaloyl chloride/terephthaloyl chloride in *N,N*-dimethylacetamide (DMAc). The polymers were adequately characterized for their properties. Membranes were fabricated from PASA **2** under different casting conditions by varying the casting solution composition, evaporation temperature and evaporation time. The reverse osmosis (RO) tests for these membranes were performed with 1000 ppm aqueous sodium chloride feeds at 20 to 40 kg cm^{-2} operating pressure. Membranes showed salt rejections of up to 97.9% at a flux of over 11.9 cm per day. The RO performances of the membranes remained unchanged after treatment with dilute acid, alkali and oxidizing agent.

(Keywords: poly(amide–sulfonamide)s; membrane materials; synthesis; thermal and chemical stability; reverse osmosis)

INTRODUCTION

Considerable interest has been generated in recent years in the synthesis of new polymeric membrane materials for separation processes[1,2]. In particular, the demand to develop durable membrane materials which are applicable to complex industrial wastewater treatment and/or recycling of industrial raw materials is enormous[3]. The viability of using the reverse osmosis (RO) technique in industrial and environmental applications in fact hinges on the development of low-cost and high-performance membrane materials. Membrane materials that have desirable properties such as high water permeability, high salt rejection and resistance to chemical and biological attack are most appealing. For instance, polyamides, polybenzhydrazides, polyurea and polybenzimidazole membranes have been studied extensively[4–6]. Recently, poly(amide–hydrazide)s and polysulfonamides have been developed for RO applications[7,8]. The former materials are merited to have excellent water permeability, whereas the latter are claimed to be highly resistant to chemical attack. Since polyamides and polysulfonamides have been proven to be promising polymeric membrane materials for RO applications, we believe that poly(amide–sulfonamide)s (PASAs), which contain both amide and sulfonamide linkages in their polymer backbones, would be viable materials in separation processes. In this report, we describe the synthesis, characterization and RO studies of PASAs **1–4**.



PASAs 1–4

Polymer	R	Phthaloyl chloride
1		Terephthaloyl
2		Isophthaloyl
3	$HNCH_2CH_2NH$	Terephthaloyl
4	$HNCH_2CH_2NH$	Isophthaloyl

EXPERIMENTAL

Materials

Acetanilide (Fluka), calcium chloride (Fluka), calcium hydride (Fluka), calcium oxide (Fluka), chloroform (Ajax), chlorosulfonic acid (Fluka), concentrated hydrochloric acid (China National Chemicals), 1,2-diaminoethane (Fluka), lithium nitrate (Fluka), piperazine (Merck) and phthaloyl chlorides (Fluka) were of analytical grade and were used as received. *N*-Methyl-2-pyrrolidone (NMP) (Aldrich) and *N,N*-dimethylacetamide (DMAc) (Fluka) were dried with calcium chloride and then distilled over calcium hydride and stored over molecular sieves before use.

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Apparatus

I.r. spectra were recorded on a Hitachi 270-30 infra-red spectrophotometer. ^{1}H n.m.r. spectra were measured in d_6-DMSO with a Bruka WM 250 superconducing n.m.r. spectrometer. Thermal characterizations of the polymers were carried out on a Perkin–Elmer DSC-1B and a Shimadzu thermal analyser DT-40. The inherent viscosities were measured at a concentration of 0.5 g dl^{-1} in DMAc at 25°C in a capillary viscometer (Schott Gerate).

Methods

Polymer synthesis. The diamino monomers **5** and **6** were synthesized as described elsewhere[9]. The polymers were synthesized by low-temperature polycondensation. Optimum polymerization conditions emerged by systematically varying the mole ratio of diamino monomer to phthaloyl chloride. A typical preparation of a PASA is as follows. To a DMAc solution of the crude monomer cooled in an ice–salt bath was added, with stirring, 0.9 to 1.0 equivalent of solid phthaloyl chloride (*p*- or *m*-isomer) in one portion. The mixture was stirred until all the chloride dissolved while the bath temperature was controlled at −17°C. Then enough calcium oxide was added for the neutralization of the acid evolved. The pH of the final solution was adjusted to between 6 and 7. The solution was further stirred at room temperature for 2 h. The polymer was formed by diluting the mixture with 10 ml of DMAc and then pouring this mixture into 500 ml of water. The viscosities of the polymers obtained from different mole ratios of the two reactants were compared.

Polymer characterization

Spectroscopic studies. Each of the new polymers was adequately characterized by i.r. and ^{1}H n.m.r. spectroscopic methods.

Solubilities. The solubilities of the polymers (0.1 g) were determined at room temperature (20°C) in different solvents (5 ml). The solutions were shaken vigorously if the polymers failed to dissolve, and the mixtures were warmed in a hot-water bath for complete dissolution.

Viscosities. The inherent viscosities (ν_{inh}) of 0.5 g dl^{-1} solutions of the polymers in DMAc were measured using a capillary viscometer.

Thermal characterization. About 2 mg of each PASA in the form of an amorphous powder were subjected to differential scanning calorimetry (d.s.c.) measurements at a heating rate of 10°C min^{-1}. The thermal stabilities of the polymers were determined by thermogravimetric analysis (t.g.a.). Experiments were carried out on samples about 10 mg at a heating rate of 10°C min^{-1} to 500°C.

Asymmetric membrane casting

Flat sheet asymmetric RO membranes were prepared by the following solution casting technique. The casting solution was prepared with a composition of 19.5% (by weight) of polymer, 77.0% of DMAc and 3.5% of lithium nitrate. The resultant mixture was left undisturbed for several days until complete dissolution of the polymer was achieved. The polymer solution was transferred into a clean glass centrifuge and centrifuged to settle any traces of dirt and particles. Then, the dust-free polymer solution was immersed in an ultrasonic water bath for 2 to 4 h for degassing. In this way a clear, dust-free, homogeneous polymer casting solution was prepared.

The casting solution was poured into a clean, dry, glass plate (25 × 20 cm) and spread with the aid of a specially made glass tube to form a uniform thin film. The thickness of the cast solution was controlled by two rings of copper wire of 0.3 mm in diameter fixed at the two ends of the glass tube. The glass plate was put onto a preheated hotplate maintained at a temperature of 70°C. To minimize temperature differences over the surface of the hotplate an aluminium plate was placed between the glass plate and the hotplate. The evaporation period was varied between 15 and 40 min. Then, the glass plate was cooled and immersed in a water bath for 5 h at room temperature. This operation removed the residual salt and solvent from the membrane. All the membranes were stored in deionized water until testing at ambient temperature. Any imperfections (i.e. small holes and non-uniformities) in the membranes were spotted by means of a light box.

Membrane RO performance evaluation

RO testing unit. The RO testing unit fabricated in-house is shown in *Figure 1*. It consists of a 230 l capacity feed reservoir (FR) connected to the two-stage centrifugal pumps (Tonkaflo) (DP), each with a flow capacity of 12 l min^{-1} and a discharge pressure of 27.5 kg cm^{-2}, and a plate-type RO unit. The feed pressure and the outlet pressure were controlled by two valves NV_1 and NV_2 respectively. Two separate pressure gauges G_1 and G_2, with measuring ranges from 0 to 40 kg cm^{-2}, were used for measuring the inlet and outlet pressures, respectively, of the RO units. A circular membrane (M) of diameter 60 mm was placed in the test cell with the skin facing the incoming feed. The membrane was supported on porous polypropylene (PP) and nylon fabric (NF). Rubber O-rings were used to seal the membranes and ensure leak-free operations. In all RO test experiments the effective membrane area was kept at 12.56 cm^2.

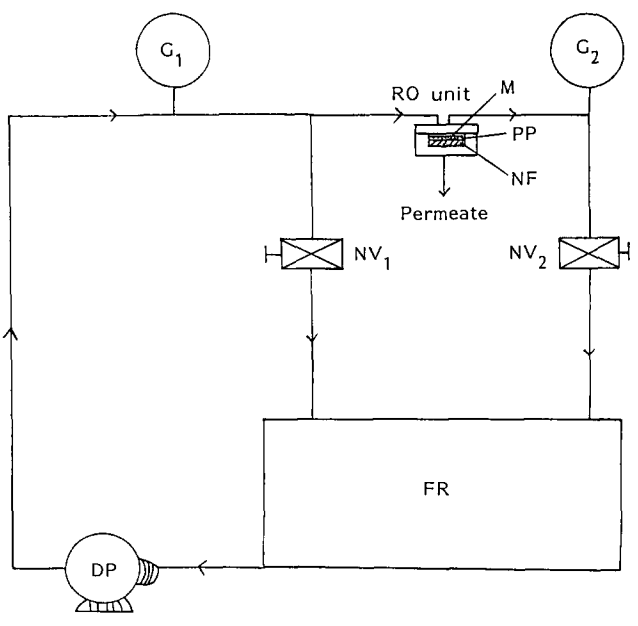


Figure 1 Reverse osmosis testing unit

RO tests. Most of the water permeability and salt rejection tests were performed for a 1000 ppm aqueous sodium chloride feed solution at room temperature. The tests for feed solution were performed over 4 h with an interval of 30 min. The operating pressure was kept constant at 20 kg cm^{-2} for most of the tests. The permeate volumes were measured in ml. The concentrations of ions in the feed and in the permeate were determined by a standardized digital conductivity meter. Permeate fluxes were recorded in metres per day and salt rejections were recorded as per cent salt rejection.

RESULTS AND DISCUSSION

Polymer preparation

Effect of the purity of the monomers. The crude diamino monomers **5** and **6** were prepared via a three-step reaction sequence. Attempts to purify them by recrystallization were unsuccessful. The stoichiometric balance and the purity of the two monomers in the polycondensation reaction are the two most crucial factors affecting the molecular weight (*MW*) of the polymer formed. Owing to the great tendency towards hydrolysis of phthaloyl chloride and the uncertainty in the purities of the synthesized diamino monomers, absolute control of the stoichiometric balance of the two monomers cannot be achieved in a simple manner. To minimize the hydrolysis of acid chloride, a solid sample of the acid chloride was added to the DMAc solution of the diamino compound in the polycondensation reaction. By systematically varying the mole ratio of the two monomers, the optimum conditions for obtaining the highest *MW* emerged. The relative *MW* of the polymer formed was conveniently monitored by the viscosity measurement. *Figure 2* shows the relationship between the viscosity of the polymer and the mole ratio of the two monomers. Depending on the purity of the crude diamino monomer, the maximum viscosity corresponding to the highest *MW* of the polymer occurs at a different mole ratio of the two monomers. For a purer diamino compound, not only is the maximum of the curve more clearly defined, but also the mole ratio of the two monomers is closer to 1:1. After some experimentation, polymers with film-forming properties (i.e. $\nu_{inh} > 0.6$) could be obtained. At the optimum mole ratio of the two monomers, PASA **3** derived from terephthaloyl chloride exhibits a higher inherent viscosity than PASA **2** derived from isophthaloyl chloride. However, both polymers appear to be tough enough for RO application.

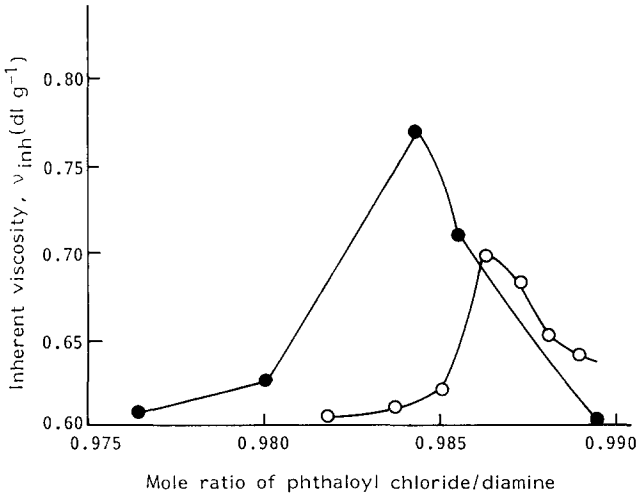


Figure 2 Effect of mole ratio of monomers on inherent viscosity: (○) PASA **2**; (●) PASA **3**

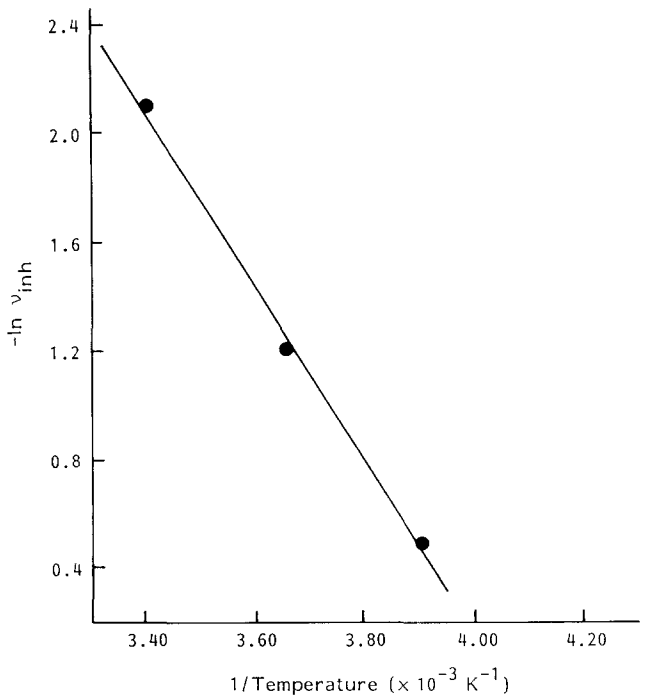
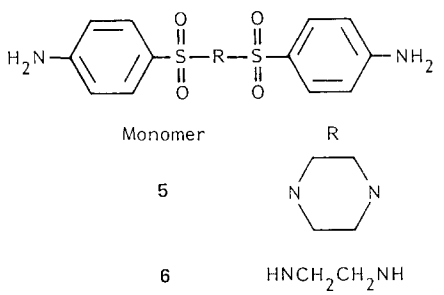


Figure 3 Arrhenius plot between temperature and the inherent viscosity of the polymer. The ratio of the monomers was kept constant in the polymerization reaction



Effect of temperature. The initial temperature of polycondensation greatly influenced the *MW* of the resulting polymer. An Arrhenius plot in *Figure 3* shows the effect of reaction temperature on the degree of polymerization of PASA **3**. The optimum temperature for preparing a high *MW* polymer appears to be the ice–salt bath temperature (−17°C), whereas polymerization at a higher temperature only yields polymers of limited *MW*. The lower initial temperature apparently suppresses some side reactions normally induced by the initial heat released by the exothermic polymerization. However, the lowest temperature possible for the polymerization is restricted by the melting point of the solvent (i.e. −20°C). A similar effect was observed for the preparation of PASA **2**.

Effect of solvent. A prerequisite for high polymer formation is that the solvent should dissolve the polymer sufficiently to permit complete polymerization. In this regard, polymerization in both NMP and DMAc,

two highly polar aprotic solvents, proceeded in a homogeneous state throughout the reaction to afford relatively high *MW* PASAs.

Polymer characterization

I.r. and ^1H n.m.r. The structures of the polymers were adequately characterized by i.r. and ^1H n.m.r. spectroscopic methods. Spectroscopic data are consistent with the assigned structures[9].

Solubility. With the exception of PASA **1**, all the PASAs were highly soluble in polar solvents such as DMAc, DMF, dimethyl sulfoxide (DMSO) and NMP. On the other hand, the presence of polar amide and sulfonamide groups in the backbone of the polymer renders the polymers insoluble in acetone, diethyl ether, chloroform, *m*-cresol, ethanol and tetrahydrofuran.

Thermal characterization. From the d.s.c. studies, the PASAs were found to exhibit fairly high T_g values in the range 239 to 271°C. Their thermal stabilities were evaluated by t.g.a. Typical t.g.a. curves are shown in *Figure 4*. A close examination of the curves reveals that the PASAs are thermally stable and do not decompose on heating below 330°C. Their thermal stabilities compare favourably with those of structurally similar polymers.

Membrane evaluation

Because of its low solubility in DMAc, PASA **1** cannot be used for fabricating membranes. The presence of acidic sulfonamide hydrogens renders PASAs **3** and **4** soluble in concentrated sodium hydroxide solution. It is anticipated that membranes made from these materials will dissolve in contact with strongly alkaline solutions. Thus their scope of application is restricted. After these considerations, PASA **2** emerged as the best candidate for a detailed RO evaluation study.

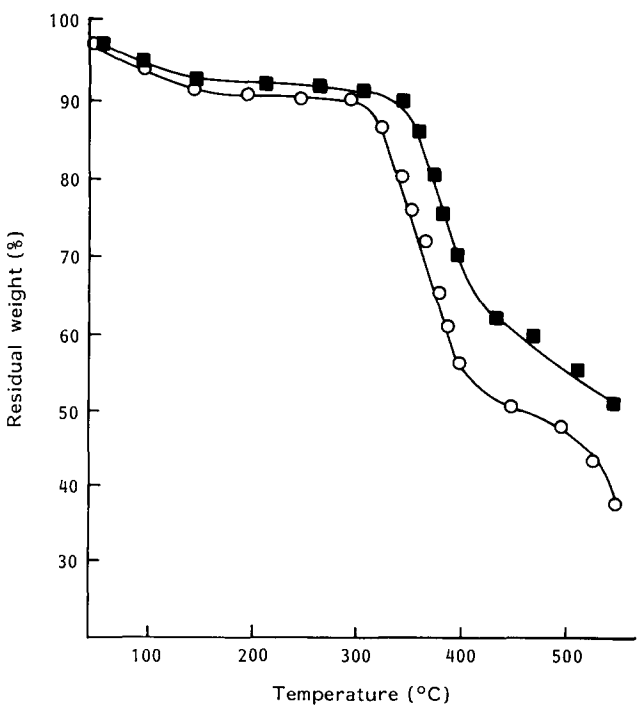


Figure 4 T.g.a. curves of PASAs (heating rate 10°C min^{-1}): (○) PASA **2**; (■) PASA **3**

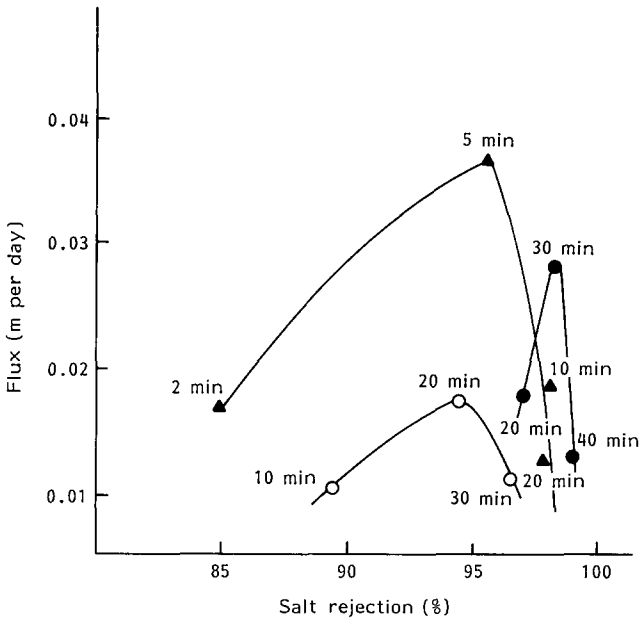


Figure 5 Effect of evaporation time and evaporation temperature on membrane characteristics: (●) 45°C; (○) 55°C; (▲) 65°C. Operating pressure 20 kg cm^{-2}; feed solution 1000 ppm aqueous sodium chloride

Effect of evaporation temperature and evaporation time. The effects of evaporation time and evaporation temperature on the RO performance of PASA **2** are shown in *Figure 5*. For different evaporation temperatures and times, excellent salt rejections (>85%) were observed for all cases of study. Variation in evaporation temperature substantially altered the flux rate of the membrane. For instance, at the evaporation temperature of 65°C, an increase in evaporation time from 2 min to 20 min at 20 kg cm^{-2} operating pressure resulted in an increase in salt rejection from 85.1 to 97.6% while the flux reached a maximum of 0.037 m per day, corresponding to an evaporation time of 5 min. This particular combination of evaporation temperature and time (i.e. 65°C and 5 min) represents the optimum conditions for the fabrication of membranes with high flux and excellent salt rejection. For lower evaporation temperatures, longer evaporation times were required to produce membranes with reasonable flux rates.

Effect of pressure. The PASA membranes are strong enough to sustain up to 40 kg cm^{-2} pressure. As shown in *Figure 6*, a three-fold increase in flux rate was achieved by doubling the pressure from 20 kg cm^{-2} to 40 kg cm^{-2}. Such a flux rate is favourably comparable with the commonly used cellulose acetate membrane. It is gratifying to see that the salt rejection of the membrane remained outstanding (>96.5%) over a wide range of applied pressure.

Effect of casting solution composition. The flux rate and salt rejection of the PASA **2** membrane are highly dependent on the composition of the casting solution. The effect of lithium nitrate concentration in the casting solution on the performance of the membrane is shown in *Table 1*. With an increase in lithium nitrate concentration from 3.5 to 5.5%, a drastic increase in the flux and a marginal decrease in salt rejection was observed. By using lithium chloride as the pore-forming agent (casting solution V), the membrane performance in

Table 1 Effect of casting solution composition on PASA **2** membrane[a]

Casting solution	Polymer (%)	Pore-forming agent[b] (%)	DMAc (%)	Evaporation time (min)	Flux (m per day)	Salt rejection (%)
I	19.5	3.5	77.0	5	0.0745	96.9
II	19.7	4.6	75.7	5	0.1097	95.2
III	19.3	5.0	75.7	5	0.1221	93.3
IV	19.2	5.5	75.3	5	0.1879	94.7
IV	19.2	5.5	75.3	3	0.3170	86.9
V	17.0	3.0	80.0	5	0.1050	85.3

[a] Operating pressure of 30 kg cm^{-2}
[b] Solutions I to IV, $LiNO_3$; solution V, LiCl

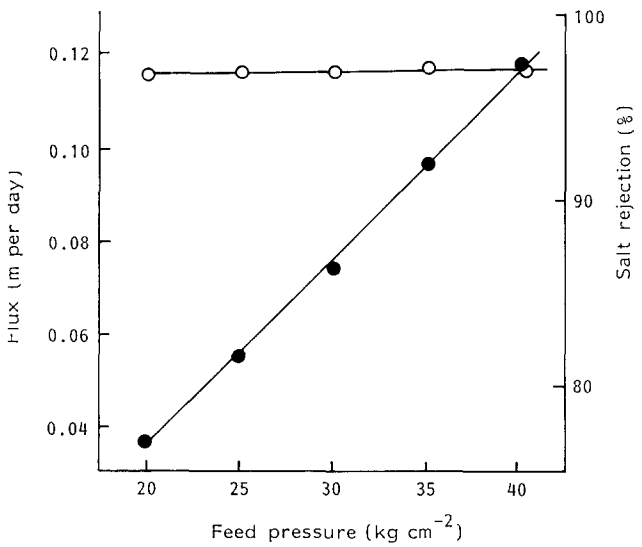


Figure 6 Effect of pressure on membrane performance: (○) salt rejection; (●) flux rate

Table 2 Effect of chemical treatment on RO performance[a]

Immersion solution[b]	Flux (m per day)	Salt rejection (%)
0.1 M HCl	0.0294	97.9
0.1 M NaOH	0.0370	96.6
0.005% chromic acid	0.0298	87.5
0.002% chromic acid	0.0358	95.6

[a] Operating pressure of 30 kg cm^{-2}
[b] Immersion time of 3 weeks

terms of the flux and salt rejection appeared to be less satisfactory.

Membrane resistance to chemical treatment. In order to define the chemical inertness of the membrane towards strong acid, alkali and oxidizing agents, the PASA membranes were subjected to chemical treatments prior to the RO studies. The fresh membranes were immersed in 0.1 M hydrochloric acid, 0.1 M sodium hydroxide, and 0.005% and 0.002% chromic acids for a period of 3 weeks. Subsequent RO tests on these membranes revealed that the membrane performance remained unchanged after treatment with dilute hydrochloric acid, sodium hydroxide and chromic acid (*Table 2*). However, the membranes deteriorated appreciably after immersion in a relatively high concentration of chromic acid.

CONCLUSIONS

Poly(amide–sulfonamide)s of film-forming viscosities were synthesized for RO membrane preparation. By systematically varying the mole ratio of the two monomers, the optimum conditions for obtaining the polymer of highest molecular weight emerged. All polymers investigated in this study were found to exhibit good thermal and chemical stabilities. The RO membrane performance was found to be dependent on casting solution composition, evaporation time and evaporation temperature. This chemically inert membrane material has the potential to be used in RO separation processes.

ACKNOWLEDGEMENTS

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