Investigation of the specific role of chemical structure on the material and permeation properties of ultrathin aromatic polyamides

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Introduction of crosslinking into a polyamide structure results in significant improvement in the permeation performance of the corresponding thin film composite (TFC) membranes. In order to identify the source of this improvement, a series of measurements were conducted to ascertain the mechanical, structural, and chemical properties of two polyamides — polymetaphenylene trimesamide (a network polyamide), and polymetaphenylene isophthalamide (a linear polyamide). Permeation measurements revealed that the network polyamide evidences higher water flux as well as salt rejection compared to the linear polyamide. The higher water flux was attributed mainly to the higher hydrophilicity (arising from the hydrolysis of unreacted carboxylic acid groups in the structure) of the network polyamide. Hydrophilicity was found to overwhelm other factors such as the film thickness and chain mobility. On the other hand, the high rejection was found to be due to a combination of high hydrophilicity, greater negative charge, and greater rupture strength of the network polyamide.

1. Introduction

In addition to desalination, reverse osmosis (RO) membranes are now increasingly being used for a variety of other separation operations in the chemical, environmental, and food industry.[1–3] The ability of the RO membranes to affect the separation of components from the feed stream — permselectivity — is mainly attributed to the "active layer." In thin-film-composite (TFC) membranes, the active layer is a thin film (usually a polymeric dense film), which is mounted on a support layer. The support layer has high porosity, and provides mechanical rigidity to the active layer to withstand the high pressures usually encountered in separation operations. The requirement of high fluxes for economic viability predicates a thin active layer. At the same time, the active layer should be defect-free, to obtain the necessary permselectivity. Polyamide active layers synthesized by the interfacial polymerization (IP) of aqueous diamines and organic multifunctional acid chlorides meet this dual requirement. Consequently, IP-TFC membranes are the most widely used for RO and environmental separations.[4,5]

Permeation of the solvent and solute components through the active layer occurs *via* the solution diffusion mechanism.[6] This mechanism postulates that the solvent and solute molecules are sorbed into the polymer and diffuse through the polymeric structure, to be desorbed on the other side. Permselectivity thus depends upon the comparative solvent and solute fluxes through the active layer. These fluxes would greatly depend upon polymer–solvent/polymer–solute interactions[7] and polymer chain mobility.[8] Indeed, prior research has shown that a certain degree of crosslinking is necessary to obtain an active layer with high permselectivity.[9] However, crosslinking is one of several factors affecting membrane performance. The other factors could include film hydrophilicity, solvent and solute diffusivities, solvent and solute solubilities, *etc.* In IP, crosslinking is usually achieved by using a trifunctional reactant, *e.g.* trimesoyl chloride (TMC) so that crosslinking as well as linear chain formation occur simultaneously.[10,11] This complicates the situation since the

other factors mentioned above themselves change with crosslinking. In addition, the macroscopic mechanical properties of the active layer too could contribute to the final membrane performance.[12]
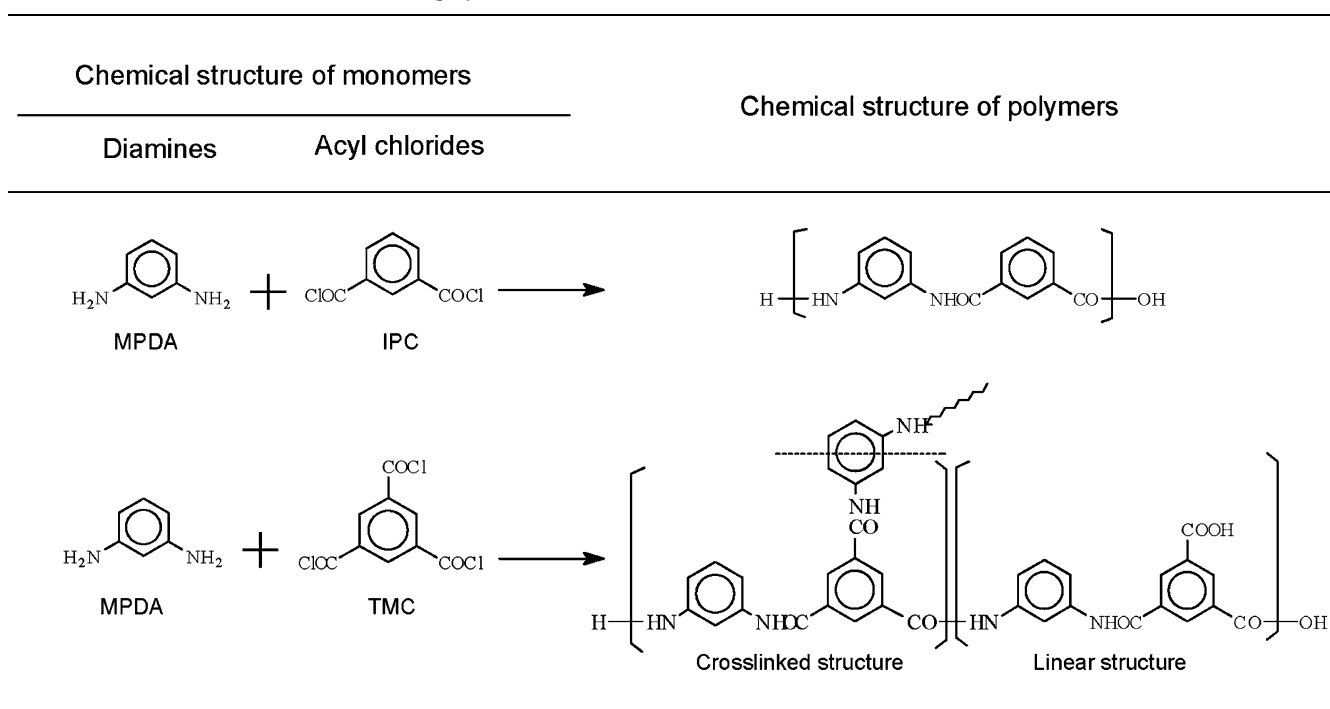
Numerous researchers have studied the IP technique for active layer formation.[13–15] However, we believe that a systematic investigation to ascertain the mechanisms whereby crosslinking (specifically, crosslinking induced by an addition reaction in IP) influences membrane performance would still be greatly valuable. The resulting insights would provide a better understanding of the solvent–solute–polymer interactions, and could potentially help in devising new IP reactant systems. In this research, we have focused on addressing the effects of the polymer structure by measuring and comparing the mechanical, structural, and chemical properties of a linear and a network polyamide.

2. Experimental

2.1 Materials

The linear polyamide, polymetaphenylene isophthalamide (MPIA), was made using the reactants *m*-phenylenediamine (MPDA) in the aqueous phase and isophthaloyl chloride (IPC) in the organic phase (*n*-hexane). For the network polyamide (polymetaphenylene trimesamide — MPTA), the reactants were MPDA and TMC. The reaction schemes are shown in Table 1. It may be noted that the differences between the two polyamides arise solely due to crosslinking occurring because of the trifunctional nature of TMC.

IPC (Aldrich, 98%) and TMC (Aldrich, 98%) were distilled under vacuum at 170 and 160 °C respectively. The purified forms were stored in a vacuum desiccator containing calcium chloride to prevent hydrolysis of the acyl chloride groups. MPDA (Aldrich, 99%) too was distilled under vacuum at 170 °C and the purified form was filled in a dark bottle with N$_2$ gas and stored in a refrigerator. The solvent for acyl chlorides, *n*-hexane, was dried by shaking with magnesium sulfate and then distilling. Before using the purified *n*-hexane

DOI: 10.1039/b109790c

Table 1 Chemical structures of monomer and polyamide

Chemical structure of monomers

| Diamines | Acyl chlorides |

Chemical structure of polymers

Crosslinked structure   Linear structure

within 1–2 days, it was stored in a tightly closed bottle with Molecular Sieve A® to prevent dissolution of water. For the preparation of the diamine solution, RO purified and deionized water was used.

2.2 Thin film synthesis and characterization details

In order to elucidate the effect of the material properties on the permeation performance, different kinds of measurements were performed to characterize the thin films. The chemical properties were inferred from contact angle, salt–water solubility, and membrane permeation measurements, while the mechanical properties were inferred from thickness and rupture strength measurements. Now, the measurement conditions are dictated by the measurement technique, and hence would be different from the high-pressure conditions the membrane experiences in actual filtration operation. However, it must be noted that the chemical properties, *viz.*, hydrophilicity and salt–water solubilities, as well as the rupture strength are independent of pressure.

The thin films were synthesized using the unstirred non-dispersion method of IP.[16] In IP, the reactants are present in two mutually immiscible phases — an amine aqueous phase and an acyl chloride organic phase. When these are brought into contact, the reactants diffuse and react at the interface *via* a polycondensation reaction to produce the polymeric thin film. For synthesis, 0.5 weight per volume (w/v) % aqueous MPDA solution and 0.1 w/v% acyl chloride solution in *n*-hexane were used. The synthesis was performed at 20 °C with a constant contact time of 2 min. For water–salt solubility measurements the thin film synthesis was conducted in a wide reservoir vessel. For thickness and contact angle measurements, the thin films were prepared on a glass plate under otherwise identical reaction conditions. After IP, the thin films were washed with acidic water, methanol, and fresh water to remove the unreacted monomer remnants and occluded salt. The pure solid polymer masses thus obtained were dried under vacuum at room temperature and then used with no additional post-treatment.

To measure the active layer film thickness, the treated films were semi-dried in air at room temperature, placed on a glass plate and scratched using a sharp knife. The scratched valley depths were measured using a Tencor P-10 surface profilometer. The profiler tip applied a 3.0 mg force, and a scan speed of 0.1 mm s^{-1} was used for the measurements. Because the IP film possessed an irregular surface, the thickness variation was found to be high, on the order of 30 nm. To minimize error, nine repeats were performed.

Contact angle measurements using an image analyzer system (PAS PX-380) were conducted to assess the hydrophilicity of the active layers. Sets of liquid droplets were placed on the active layer films and a video camera recorded their shape. To minimize error, six repeats were performed. The surface tension of dispersion and the polar force for polymers can be obtained from the following equation,[17]

$$\cos \theta = \frac{4\left(\frac{\gamma_s^d \gamma_L^d}{\gamma_s^d + \gamma_L^d}\right)}{\gamma_L} + \frac{4\left(\frac{\gamma_s^p \gamma_L^p}{\gamma_s^p + \gamma_L^p}\right)}{\gamma_L} - 1 \qquad (1)$$

where, θ is the contact angle of the liquid, and γ_L, γ^d_L, and γ^p_L are the total surface tension, the dispersion force, and the polar force of surface tension for a standard liquid, respectively. γ^d_S and γ^p_S are respectively the dispersion force and the polar force of surface tension for the polymer. Using the contact angle values with the reference liquids as shown in Table 2 and the surface components of the reference liquids, the components of surface tension for the thin film polymer could be determined.

The dissolved water concentration in the thin films (C_w) was determined gravimetrically. Purified samples were saturated with a 2000 ppm NaCl aqueous solution and then vacuum-dried completely. The dried and weight-measured samples were

Table 2 Dispersion and polar force components of surface tension (dyne cm^{-1}) of reference liquids (20 °C)

Reference liquids	γ^d_L	γ^p_L	γ_L
Water	29.1	43.7	72.8
Glycerol	37.4	26.0	63.4
Formamide	35.1	23.1	58.2

Superscript d and p refer to the dispersion and polar components, respectively

put in a chamber, which was saturated with moisture at 25 °C. After one day, the samples were again weighed and the water solubility coefficient (C_w) was calculated using eqn. (2)

$$C_w = \frac{|M'' - M'|/18}{V_p} \qquad (2)$$

where $|M'' - M'|$ is the mass of absorbed water and V_P is the polymer volume. To minimize experimental error, nine replicates were used.

The immersion method[18] was chosen to measure salt solubility. Dried and weighed samples were immersed in a large volume (100 mL) of 2000 ppm NaCl solution for salt saturation and then placed in a large volume (100 mL) of deionized water for 3 days to achieve an equilibrium state. The salt concentration was then measured using a standardized digital conductivity meter (YSI model 32) at 25 °C. Salt solubility is usually defined in terms of the "partition coefficient" K_s, given by eqn. (3)

$$K_s = \left(\frac{M_{PS}}{V_p}\right) \Big/ \left(\frac{M_S}{V_S}\right) \qquad (3)$$

where V_S is the solution volume, and M_{PS} and M_S are the salt mass in the polymer and solution, respectively. To minimize experimental error, nine replicates were used.

Permeation measurements were performed on entire TFC membranes. The TFC membranes were prepared via a two-step process: first, an asymmetric porous polysulfone support membrane was fabricated,[9] and then the thin film active layers were prepared by in-situ IP[12] on the support layer under otherwise identical reaction conditions described above. The permeation performance was measured using continuous high-pressure RO testing equipment (Akico Co., BSO-100K-3). A diaphragm pump was used for recycling the aqueous NaCl solution (2000 ppm) and the system was maintained at 3.03 MPa pressure and 25 ± 1 °C temperature. The feed flow rate was fixed at 10 L h^{-1}. The salt rejection R describes the fraction of the depletion of salt in the permeate compared to the feed and is given by eqn. (4)

$$R(\%) = \left(1 - \frac{C_s''}{C_s'}\right) \times 100 \qquad (4)$$

where, C_s' and C_s'' are the salt concentrations in the feed and permeate streams respectively. The permeate and feed salt concentrations were measured using a standardized digital conductivity meter (YSI Co. model 32). To minimize experimental error, 3 replicates were performed.

Measuring the mechanical properties of the active layer films in their as-formed state is quite challenging, since the films are ultrathin, and obtaining the macroscopic sizes necessary for analysis using conventional instruments such as an instron is very difficult. To this end a promising technique, "pendant drop mechanical analysis (PDMA)," for directly measuring the mechanical properties of unsupported IP films was reported by Greenberg and coworkers.[19] PDMA was applied to measure the non-normalized structural parameter, the rupture strength (S_R) of unsupported thin films. PDMA first requires the formation of an IP film over the surface of a drop of diamine monomer solution by immersing the drop into a solution containing the acyl chloride monomer. This film-covered drop is then pressurized in a controlled fashion and the resulting pressure-deformation behavior is monitored. The rupture strength (S_R) of the thin films was obtained from the pressure and the drop-radius at the instant of IP film rupture. An earlier paper discusses the details of the measurement protocol.[12]

3. Results and discussion

The permeation measurements showed a statistically significant difference in the permeation performance of the linear and
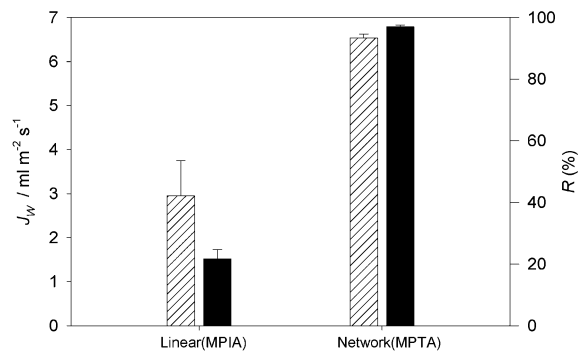
Fig. 1 Effect of polymer structures on the permeation performance. Note that the performance of membrane made by the reaction of MPDA (0.5 w/v%) with acyl chlorides (0.1 w/v%) were obtained by 3.03 MPa, 2000 ppm NaCl solution at 25 °C (hashed column: J_w, filled column: R).

Table 3 Measured values of the rupture strength (S_R) and thickness (t) of MPIA and MPTA

|	Linear (MPIA)	Network (MPTA)
Rupture strength/Pa m	0.87 ± 0.42	5.74 ± 0.40
Thickness/nm	83.1 ± 18	152.9 ± 12

network polyamides (Fig. 1). The linear polyamide possessed not only low salt rejection, but also low water flux, compared to the network polyamide. The exact contribution of the mechanical, structural, and chemical properties and the source of this difference in the permeation values is discussed in the following sections.

3.1 Factors affecting water flux

Table 3 reports the measured values of the rupture strength (S_R) and thickness (t) for the two polyamides.

S_R is a lumped parameter, which is influenced by the rupture stress (a material characteristic), and the active layer film thickness (a structural characteristic). S_R provides an estimate of the RO conditions that will result in the rupture (failure), and hence defect formation in the active layer of a TFC membrane. The appearance of defects in a membrane leads to a change in the mode of solute and solvent transport because the defects allow the bulk flow of brine solution. When the defects are minute in the form of microscopic pinholes, the bulk flow is sufficiently small compared to the solvent transport via solution-diffusion, so that water flux stays relatively constant. However, the bulk flow still causes a dilution of the permeate, thereby resulting in decreased salt rejection. In fact, previous studies by Roh[12] and Applegate[20] have concluded that while the bulk flow of brine affects R by as much as 40%, its influence on J_w is negligibly small. In such a case, a modification to the solution-diffusion mechanism,[6] called the "solution-diffusion imperfection"[21] model can accurately predict solvent and solute transfer. Based on the insights provided from this model and from S_R measurements, Roh and coworkers[12] determined the limiting values of S_R for similar thin films. An $S_R < 5$ Pa m greatly reduces R without affecting J_w. Furthermore, an $S_R < 3$ Pa m leads to greatly reduced R as well as an increased J_w.

As evidenced from Table 3, the linear polyamide, MPIA, has a low S_R (<3 Pa m) while the network polyamide, MPTA, has high S_R (>5 Pa m). This implies that for MPTA, the permeation characteristics are determined by its inherent material properties including hydrophilicity, molecular chain mobility, chemical structure, etc. On the other hand, for MPIA, the permeation characteristics are also influenced by the partial rupturing of the active layer. However, in light of the previous
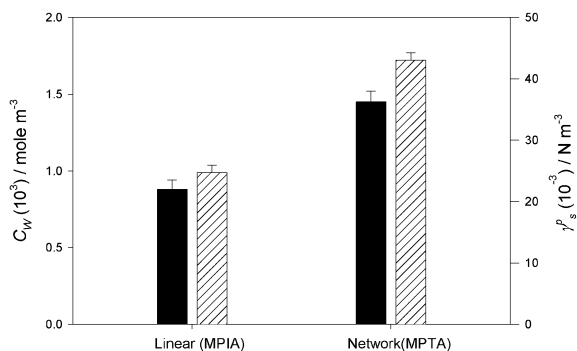
Fig. 2 Dependence of the water permeation coefficient and the salt permeation coefficient on the acyl chloride monomers (hashed column: C_w, filled column: γ^p_s).

studies mentioned,[12,20] the low J_w values of the linear polyamides are surprising, and suggest that J_w is influenced more prominently by some other factors.

Now, water and salt permeation are generally inversely proportional to the film thickness (t).[6] However, the linear polyamide film was found to be thinner than its network counterpart (Table 3), thereby indicating that J_w is still influenced by some other factors to the extent that the thickness contribution is nullified. Permeation could also be influenced by polymer chain mobility. In the absence of any limiting crosslinking, the mobility of the molecular chains in the linear polymer is higher.[8] Since higher chain mobility usually translates to higher permeation values, this would imply that the linear polyamide should possess higher water flux compared to the network polyamide. However the observed behavior is exactly opposite, thereby strongly suggesting that the permeation properties are affected more by the chemical properties of the two polymers.

The chemical properties — the polar force of surface tension (γ^p_s) and the concentration of dissolved water in the membrane (C_w) — are shown in Fig. 2. In the two polyamides under investigation, the main components affecting the polar force are an amide bond, an amine and a carboxylic acid end-group, and a free carboxylic acid group in the network structure as seen in Table 1. Now, the unreacted acyl chloride groups in TMC can easily be converted to the corresponding carboxylic acids through hydration. The amine and carboxylic acid groups are more hydrophilic than the amide bonds in the polyamide. For the formation of the linear polyamide, the amine and the acyl-chloride groups of the respective aqueous and organic phase reactants mutually react to form amide bonds. Since in a polymer, the end-groups are much fewer, the linear polyamide should have far less free amine and carboxylic acid end groups compared to the amide bonds. As these are high hydrophilic components, the linear polyamide should possess lower hydrophilicity. In contrast, the network polyamide formed by the reaction between MPDA and TMC has far more unreacted acyl-chloride groups, which subsequently are converted to free carboxylic acid groups, and hence contribute to the hydrophilicity of the network polyamide. As expected, the network polyamide evidences higher γ^p_s and C_w values, as shown in Fig. 2. We feel that it is the high degree of hydrophilicity of the network polyamide that contributes to its high water flux.

3.2 Factors affecting salt rejection

As described earlier, if the active layers possess adequate rupture strength for withstanding the high pressures typically encountered in RO, the rejection R is governed only by the inherent material properties of the active layer. Otherwise, R is additionally affected by the bulk flow of brine caused by the rupture of the active layer.

Here, we shall first discuss the effect of the inherent

properties of the polymer. Now, the thickness affects the salt as well as water permeation in qualitatively similar fashion and hence should not significantly affect salt rejection. For an active layer possessing adequate rupture strength, as seen from eqn. (4), salt rejection depends upon the ratio of the water and salt fluxes. High salt rejection implies that the water flux is relatively high compared to the salt flux.

To study how the material properties affected R, the absorption of salt (K_s) and water (C_w) were measured, and the salt ($K_s D_s$) and water permeation coefficient ($C_w D_w$) were estimated. Now, the diffusion of water (D_w) and salt (D_s) molecules depends upon the polymer chain mobility. Previous research[8] utilizing cross polarization/magic angle spinning ^{13}C solid nuclear magnetic resonance (NMR) indicates that the linear polyamide does evidence smaller spin lattice relaxation times ($T_{1\rho}$). $T_{1\rho}$ is considered to be a useful parameter to assess molecule chain motion, and indicates that the linear polyamide would possess higher chain mobility. Correspondingly, D_w and D_s would be higher for the linear polyamide. However, D_w and D_s would decrease by the same extent for the network polyamide. On the other hand, the absorption of water (C_w) and salt (K_s) are greatly influenced by polymer hydrophilicity and negative charge. A hydrophilic polymer will absorb more water (high C_w). Likewise, a high negative charge would result in low interaction between salt and polymer[7] and hence in low sorption of the salt. Since the linear polyamide (MPIA) possesses low hydrophilicity and low negative charge (free carboxylic acid), it should evidence lower C_w and higher K_s than the network polyamide (MPTA). The higher rejection evidenced by the network polyamide is thus seen to be mainly because of its chemical properties.

So far, only the effect of the intrinsic polymer material properties has been considered. As seen earlier, for a polymer with inadequate rupture strength (S_R), the defects generated by subjecting the membrane to the high separation pressures result in a bulk flow of brine solution. The mechanical strength measurements (Table 3) revealed that S_R for the linear polyamide is much lower than the critical value of 3 Pa m. Hence it is prone to defect formation and hence to the bulk flow of brine. The lower salt rejection of the linear polyamide can hence be explained in terms of a synergistic effect of the chemical properties and the mechanical properties of the polymer.

4. Conclusions

The network polyamide was found to possess superior rupture strength, compared to the linear polyamide. Because of this superior rupture strength, the active layer formed from the network polyamide can well withstand the high separation pressures. In contrast, due to its weaker rupture strength, the linear polyamide active layer probably ruptures in the large pore region of the underlying support layers. Thus, while solution-diffusion is the mode of separation for the network polyamide, separation by the linear polyamide can best be described by the solution-diffusion-imperfection mechanism, which incorporates a term for the bulk flow of brine solution through the defects. This results in much reduced rejection values for the linear polyamide.

Permeation experiments conducted on the two polyamides revealed that the linear polyamide evidences inferior rejection as well as flux values. Though the solution-diffusion-imperfection mechanism can explain the inferior rejection performance, it is not sufficient to explain the smaller flux values. The measurements conducted on the two polymers suggest that the hydrophilicity of the polymer is the main cause for the difference in water flux — the linear polyamide has less hydrophilicity, and hence, less water flux, compared to the network polyamide. In addition, the measurements suggested

that the film thickness, density, and free-volume have a comparatively insignificant effect on the water flux.

In addition to the smaller rupture strength, the inferior rejection values of the linear polyamide could also be attributed to the differences in the salt and water partition coefficients. Since the linear polyamide has less negative charge due to the presence of fewer free carboxylic acid groups, it would lead to a higher dissolved salt concentration, and hence to lower rejection.

Crosslinking thus affects the membrane performance in several ways, some direct and some indirect. The direct effect is reflected through the development of defects (and hence lower rejection) for the linear polyamide. On the other hand, the increased hydrophilicity and higher negative charge of the network polyamide due to the presence of the carboxylic acid groups are indirect effects, which however, greatly impact water flux as well as rejection.

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