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The selective layer of pressure-induced water desalination membranes is an ultrathin and highly crosslinked aromatic polyamide (PA) film that separates salt from water based on differences in permeability, which is a product of diffusivity and solubility. Characterizing the transport properties of the selective layer is necessary in understanding its permselective performance. However, measuring transport of ultrathin films in general is nontrivial. Here, Poroelastic Relaxation Indentation (PRI) is employed as a simple deswelling technique for measuring the transport properties of these ultrathin selective layers.

Generally, quantifying the transport properties of thick membranes is relatively straightforward *via* well-established gravimetric, spectroscopic and optical measurement techniques. However, the selective layer of current state-of-the-art water desalination membranes is designed to be quite thin with thicknesses ranging from ~20 nm to 200 nm. Because the diffusion coefficient (D_i) for a permeating species through the thickness (h) of the selective layer scales with the diffusion time (t_i) as $D_i \sim h^2/t_i$, measuring transport of these materials is challenging due to the fast diffusion time across the thickness of the layer. Additionally, other materials properties of the crosslinked polymer relevant to transport cannot be easily quantified without resorting to multiple measurement techniques.

Previously, PRI was demonstrated as an indentation-based technique for measuring the transport properties of thin swollen polymer gel layers (Fig. 1).¹⁻³ Briefly, PRI is a load relaxation test that measures the transport properties of a polymer gel layer by correlating the time-scale of the load relaxation process to the time required for solvent transport away from the gel region under mechanical deformation. By relating the contact area (πa^2) to the poroelastic relaxation time (τ_P), the diffusion coefficient of a particular solvent through the

Deswelling of ultrathin molecular layer-by-layer polyamide water desalination membranes

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polymer gel layer can be extracted based on the theory of poroelasticity,

$$D_{\rm i} \approx a^2 / \tau_{\rm p,i}.$$
 (1)

According to eqn (1), the poroelastic relaxation time scales with the contact area, thus implying that the time-scale of the PRI measurement can be adjusted experimentally. This control of the poroelastic relaxation time with contact area has been demonstrated previously.²⁻⁴

While Chan and coworkers suggested that PRI is applicable to ultrathin films because it is measuring lateral as opposed to through-thickness transport for these highly geometricallyconfined layers,^{1,2} the measurement has not been experimentally demonstrated for the ultrathin selective membrane layers used in water desalination. In this work, the PRI technique is adapted to measure the transport properties of four ultrathin crosslinked PA films that are synthesized *via* molecular layer-bylayer (mLbL). Specifically, the water diffusion coefficient, the volume fraction of water lost due to deswelling, as well as the intrinsic permeability of these ultrathin crosslinked PA films are characterized using this one single testing approach.

Ultrathin films of four PA networks are synthesized on silicon substrates *via* mLbL.^{5,6} The mLbL is a solution based



Fig. 1 Schematic of the Poroelastic Relaxation Indentation (PRI) testing approach used to measure the transport properties of ultrathin polyamide (PA) films.

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polymerization approach that builds the PA film one monomer layer at a time via alternating deposition and reaction of the triacid chloride and diamine monomers. The four networks investigated consist of the same triacid chloride (trimesoyl chloride, TMC) but different diamines. Details of the mLbL procedure used to synthesize these networks are reported recently.6 The networks are poly(diethylenediamine trisamide) (P(DDTA)), poly(*m*-phenlyene trisamide) (P(mPDTA)), poly-(o-phenlyene trisamide) (P(oPDTA)), and poly(p-phenlyene trisamide) (P(pPDTA)), with dry thicknesses, 23.2 ± 0.8 nm, $20.7 \pm$ 0.3 nm, 30.9 \pm 0.4 nm and 24.1 \pm 3.9 nm, respectively, as measured by specular X-ray reflectivity. Since previous study on the water vapour swelling of these PA networks show that they swell in water, therefore, each sample was briefly annealed at 210 °C for 5 min prior to PRI testing to prevent film delamination during swelling in water during PRI testing.

The transport properties of the PA films are then measured using PRI. Fig. 1 illustrates the PRI testing approach of a swollen PA film indented with a glass probe using a custombuilt contact mechanical testing instrument.² In this study, the PA film is suspended inside a deionized water reservoir by securing the substrate surface to the load cell/nanopositioner assembly. The PA film is then allowed to swell in water for at least 1 h to reach swelling equilibrium. Compared with previous PRI studies that measures deformation and then correlate it to contact area using Hertzian contact mechanics,^{1,2,7,8} the PA film was mounted upside down to allow for direct imaging of the contact area, which circumvents the challenge in quantifying the exact deformation of an ultrathin film using the current contact mechanical testing instrument.

Following equilibration, the PRI test begins by approaching the PA film into contact with the hemispherical glass probe (R = 8.6 mm) at a constant displacement rate $(10 \ \mu m \ s^{-1})$ until a predefined initial compressive load (P_o) is reached. Upon deformation, a contact area develops at the film–probe interface that increases with the initial compressive load. During the entire test, the load (P) and contact area are measured as a function of testing time (t). The test is completed when the load relaxes to a long-time steady-state value (P_f) . Each sample was indented several times at three different initial compressive loads in order to establish different contact areas. Thus the test can span from 100 s to 10 min.

Representative PRI results for P(DDTA) at three initial compressive loads are shown in Fig. 2. Fig. 2a shows the change in load and contact radius (*a*) with testing time and Fig. 2b are optical micrographs of the contact area at the P(DDTA)–probe interface at three initial compressive loads. PRI is a load relaxation test characterized by a constant deformation. Therefore, the load relaxes to a lower value with testing time whereas the contact area is constant with testing time irrespective of the initial load applied because the deformation is constant for a given test. Eventually, a long-time steady-state load is reached, but the time required to reach steady state increases with the contact area, and is observed for all the PA films investigated.

For polymer gels, this relaxation is associated with timedependent processes including viscoelastic and poroelastic processes. One or both of these relaxations can occur depending



Fig. 2 Representative PRI results of P(DDTA) at three initial compressive loads (P_o). (a) Plots of load (P), open symbols, and contact radius (a), filled symbols, as a function of testing time (t). (b) Optical micrographs of the contact area (πa^2) as indicated by the grey area within the blue circle. The rings are Newton's interference rings caused by the light reflections between the probe and P(DDTA) film.

on the size of the contact area because each characteristic relaxation process is defined by different sets of materials properties.^{2,3,7,9} Viscoelastic relaxation is determined by the ratio of the polymer viscosity and modulus of the gel. Since these two materials properties are independent of the size of the contact for our PRI tests, this implies that the viscoelastic relaxation time is independent of the contact area. However, poroelastic relaxation is associated with solvent migration due to an applied deformation. Hence, the volume ($\sim a^3$) of the deformed gel defines the amount of solvent that will migrate. The larger the deformed volume, the longer the solvent permeation time, which means that the poroelastic relaxation time depends on the contact area.

In order to identify these relaxation times, the Maxwell–Weichert relaxation model is used to fit the load relaxation curves. This model has been previously applied to describe the concurrent viscoelastic and poroelastic relaxations of polymer gels and the expressions are,⁷

$$P(t) = P_{\rm V}(t) + P_{\rm P}(t),$$
 (2)

$$P_{\rm V}(t) = (P_{\rm o} - P_{\rm i})\exp(-t/\tau_{\rm V}), \qquad (3)$$

$$P_{\rm P}(t) = P_{\rm f} + (P_{\rm i} - P_{\rm f})\exp(-3.63t/\tau_{\rm P}), \qquad (4)$$

where P_i , τ_V and τ_P are the intermediate load, viscoelastic and poroelastic relaxation time, respectively. Eqn (3) describes the viscoelastic relaxation process as a simple Maxwell element characterized by a single viscoelastic time. Eqn (4) describes the poroelastic relaxation process of an ultrathin film in the limit of high geometric confinement, *i.e.* when the ratio of contact radius *versus* film thickness, a/h > 1.5.²

The relaxation times for all the PA films were extrapolated by fitting eqn (2) to the load relaxation curves (Fig. 2a). Table 1 is a summary of the relaxation times for all the materials. With the exception of P(oPDTA) that only display viscoelastic relaxation, P(DDTA), P(pPDTA) and P(mPDTA) all display viscoelastic and poroelastic relaxations.

To compare the relaxation times with contact area, Fig. 3 is a plot of the relaxation time *versus* contact radius for the four PAs. In general, the viscoelastic relaxation times span from ≈ 2 s to ≈ 30 s and are independent of the contact radius. However, the poroelastic relaxation times span from ≈ 150 s to ≈ 400 s and increase with the contact radius, which is consistent with previous PRI studies.^{1,2,7,8} The water diffusion coefficient of the PAs that display poroelasticity can be determined by fitting eqn (1) to Fig. 3. The figure shows that the water diffusion coefficient of all three PAs is indistinguishable from each other, which is estimated to be $D_{\rm w} \approx 3.76 \times 10^{-12}$ m² s⁻¹. This value is in good agreement with the reported water diffusion coefficient ($\approx 2.2 \times 10^{-12}$ m² s⁻¹ to 3.3×10^{-12} m² s⁻¹) for a bulk sample of cross-linked aromatic PA measured using infrared spectroscopy.¹⁰

A subtle but important point about measuring the diffusion coefficient using PRI compared to other commonly used measurement techniques is that PRI is measuring the lateral diffusion of ultrathin films as opposed to through thickness diffusion.² Therefore, direct comparison of the diffusion coefficients between PRI and other techniques would require isotropic transport properties of the polyamide layer. There is indirect evidence suggesting that these polyamide networks have isotropic transport properties. X-ray reflectivity results on the P(mPDTA) show that there is little to no change in the electron density for films ranging from ≈ 20 nm to 90 nm in thickness.6 Since the electron density obtained from X-ray reflectivity is reporting a volume-averaged density of the material, any change in this value would indicate changes in the polymer density. Therefore, the results suggest little or no chain orientation for the mLbL polyamide films used in this study.

The difficulty in obtaining poroelastic relaxation times for the P(oPDTA) system is due to the limitation of the PRI

Table 1 Contact radius (*a*), and extrapolated values of viscoelastic relaxation time (τ_V), poroelastic relaxation time (τ_P) of the PAs.

Sample	<i>a</i> (µm)	$\tau_{V}\left(s\right)$	$\tau_{\mathrm{P}}\left(s\right)$
P(DDTA)	20.1	5.4	_
	28.0, 27.1, 24.6	6.6, 7.9, 9.0	196, 186, 159
	35.7, 36.3, 37.1	3.8, 9.2, 6.5	376, 329, 364
P(pPDTA)	26.3	2.1	
	31.4, 31.4, 29.9	16.0, 7.9, 7.0	250, 241, 249
	35.6, 34.5, 34.7	17.5, 8.7, 9.8	303, 313, 298
P(mPDTA)	27.2	1.9	_
	31.3, 31.1, 32.7	5.5, 10.8, 9.5	_
	34.3, 33.8, 34.1	25.6, 13.6, 8.9	335, 323, 357
P(oPDTA)	25.2	3.4	
	32.2, 32.9, 32.8	11.3, 21.6, 6.1	_
	35.4, 35.7, 36.4	11.0, 10.6, 13.8	_



Fig. 3 Relaxation time *versus* contact radius of the four PAs. The relaxations times were extracted from fitting eqn (2) to the load relaxation curves. The dashed curve is a fit to the poroelastic relaxation times using eqn (1).

instrument in measuring the low degree of deswelling for this PA. In PRI, the degree of deswelling is quantified by the drained Poisson's ratio, which is calculated by comparing the initial and final compressive load,

$$v_{\rm D} = 1 - \frac{P_{\rm o}}{2P_{\rm f}} \,.$$
 (5)

Using eqn (5), $v_{\rm D} = 0.4976$, 0.4977, 0.4980 for P(DDTA), P(*p*PDTA) and P(*m*PDTA), respectively. These ratios approach the incompressibility limit of 0.5, suggesting that the amount of water migration for these materials is quite small. This result is not surprising given their low initial water content. Specifically, the amount of water migration, quantified as volume fraction of water loss $\Delta \phi_{\rm w}$, can be estimated with this relationship,

$$\Delta \phi_{\rm w} = \frac{(P_{\rm o} - P_{\rm f})}{P_{\rm o}} = 1 - \frac{1}{2(1 - \nu_{\rm D})} \,. \tag{6}$$

Based on eqn (6), $\Delta \phi_w \approx 0.48\%$, 0.46%, 0.39% for P(DDTA), P(*p*PDTA) and P(*m*PDTA), respectively, which indicates that the amount of water migration is quite low but still measureable by PRI. The P(*o*PDTA) is expected to have an even lower volume fraction of water loss because it has the lowest initial water content of the four PAs, which helps to explain the difficulty in measuring the poroelastic relaxation.

Besides quantifying the water diffusion coefficient, the parameters obtained from PRI can be used to determine the intrinsic permeability (*k*) of the PA network, which has been shown to be an estimate of the characteristic mesh size ($\xi \approx k^{0.5}$) of a polymer gel.^{2,8,11}

The intrinsic permeability is defined by Darcy's law.¹² Darcy's law relates the water permeation rate (dV/dt) per unit area $(A = \pi a^2)$ to the intrinsic permeability, the water viscosity (η_w) , the pore pressure defined as the pressure drop along the length of the pore $(\Delta p/z)$, plus a constant (*C*),

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{k}{\eta_{\mathrm{w}}} \frac{A\Delta p}{z} + C \;. \tag{7}$$

Specifically, the intrinsic permeability is determined by taking the derivative of eqn (7) with respect to the pore pressure,

$$k = \left(\frac{\eta_{\rm w}}{A}\right) \frac{\mathrm{d}(\mathrm{d}V/\mathrm{d}t)}{\mathrm{d}(\Delta p/z)} \,. \tag{8}$$

Based on eqn (8), the intrinsic permeability can be determined by the ratio of dV/dt versus $\Delta p/z$.¹²

Since PRI is essentially a gravimetric measurement technique, the parameters obtained from PRI can be substituted into eqn (8). The water permeation rate is estimated as the change in water mass of the PA over a characteristic time. As discussed previously, the change in water mass is quantified based on the initial and long-time loads while the characteristic time is the poroelastic relaxation time. Therefore, the volumetric permeation rate is defined as,

$$\frac{\mathrm{d}V}{\mathrm{d}t} \approx -\frac{P_{\mathrm{o}} - P_{\mathrm{f}}}{\rho_{\mathrm{w}}g\tau_{\mathrm{p}}},\tag{9}$$

where ρ_w is the density of water and *g* is gravitation constant. The pore pressure is related to the initial compressive load normalized by the contact area as well as the swollen thickness of the PA layer (*h*) measured previously,¹³

$$\frac{\Delta p}{z} \approx -\frac{\sigma_z}{z} = \frac{P_{\rm o}/A}{h} \,, \tag{10}$$

where Δp is estimated to be $-\sigma_z$. Incorporating eqn (9) and (10) into eqn (8) yields the relationship between intrinsic permeability and parameters measured by PRI,

$$k \approx \frac{\eta_{\rm w}}{A} \frac{{\rm d}V/{\rm d}t}{P_{\rm o}/Ah} \,. \tag{11}$$

The water permeation rates and pore pressures calculated from PRI for P(DDTA), P(*p*PDTA) and P(*m*PDTA) are summarized in Table 2. Based on these values, the average intrinsic permeability for each PA network is then determined using eqn (11) with a water viscosity of 8.9×10^{-4} Pa s.¹⁴

As Table 2 shows, the intrinsic permeability value decreases as P(DDTA) > P(*p*PDTA) > P(*m*PDTA). This trend is identical to the one observed for the equilibrium water swelling (*S*) or PA volume fraction ($\phi_p \approx S^{-1}$),¹³ thus suggesting that *k* decreases with ϕ_p , which is consistent with previous works showing that the hydraulic permeability scales with the polymer concentration of the swollen network.¹⁵⁻¹⁷

For polymer networks that swell in an affine manner, the intrinsic permeability can be directly related to the characteristic mesh size of the polymer (ξ). Specifically, the characteristic mesh size can be calculated once the monomer units between crosslink junction (*N*) is known because it has an explicit scaling relationship with *N*.¹⁸ While *N* for these PA networks have been measured *via* swelling studies, it is difficult to calculate the corresponding ξ values because of their inherent low network functionality (f= 3, due to the TMC monomer) that causes these networks to swell in a non-affine manner *via* topological rearrangement.¹³ The

Sample	$\frac{dV}{dt}$ (×10 ⁻¹⁰ m ³ s ⁻¹)	$P_{\rm o}/Ah$ (×10 ¹⁴ N m ⁻³)	$k^{0.5}$ (nm)	S
P(DDTA)	2.03	7.13	0.79 ± 0.20	≈1.50
	1.73	7.74		
	1.83	9.12		
	1.20	6.55		
	1.29	6.29		
	0.84	6.05		
P(pPDTA)	8.7	7.04	0.63 ± 0.05	≈1.16
	8.63	7.04		
	1.27	7.79		
	1.52	7.99		
	1.37	8.65		
	1.53	8.67		
P(mPDTA)	1.06	10.89	0.49 ± 0.01	≈1.08
	1.04	11.18		
	1.16	11.07		
P(oPDTA)	—	—	—	≈1.04

Table 2 Water permeation rate (dV/dt), pore pressure (P_o/Ah) , and intrinsic permeability (k) of the PAs that display poroelastic relaxation.

The swelling ratios (S) are obtained from Chan et al.¹³

alternative measurement approach is to directly quantify their characteristic mesh size *via* scattering, and work is currently underway to compare the intrinsic permeability of these PAs to average network correlation lengths using small angle neutron scattering.

While the intrinsic permeability cannot be directly compared with the characteristic mesh size of the PA networks investigated, it can be compared with the reported average "pore" size measured from positron annihilation lifetime spectroscopy (PALS). Although data for P(*p*PDTA) is not available in literature because it is not a common PA, the reported average "pore" size by PALS for commercial versions of P(DDTA) and P(*m*PDTA) networks are 0.46 nm and 0.35 nm, respectively.¹⁹⁻²¹ These results show that the average "pore" size of the PAs determined by PALS are similar to the intrinsic permeability determined by PRI.

The slightly larger values obtained from PRI can be attributed to measuring the PAs in the swollen state *versus* previous PALS measurements that were done in the dry state. Another origin for deviation can be possibly linked to the different synthetic approaches used to fabricate the PAs in this study *versus* the commercial materials used in previous studies.

Nevertheless, the comparison between the intrinsic permeability and average "pore" size confirms that PRI provides a convenient measurement approach to estimate the characteristic size-scale of the PA network that regulates transport. Additionally, both PALS and our PRI results confirm that the intrinsic permeability for P(DDTA) is greater than that of P(*m*PDTA), which is consistent with empirical data comparing the differences in salt permeation of these two PAs when used as water desalination membranes.²²

Besides the intrinsic permeability, the parameters extracted from PRI can be used to estimate the water permeance of the PA networks with a poroelastic relaxation time. The water permeance is a parameter that was developed to compare the performance of different desalination membranes. Specifically, it is a ratio of the water flux *versus* pressure drop (= $J_w/\Delta p$). For commercial desalination membranes, the water permeance ranges from $\approx 3 \times 10^{-11}$ m² kg⁻¹ s⁻¹ to $\approx 1 \times 10^{-12}$ m² kg⁻¹ s⁻¹.²² From the PRI measurements, the water permeance is estimated by ratio of the volumetric flow rate *versus* the initial compressive stress acting across the area of water transport,

$$\frac{J_{\rm w}}{\Delta p} \approx \frac{P_{\rm o} - P_{\rm f}}{P_{\rm o} \rho_{\rm w} g \tau_{\rm p}} \frac{2\pi a h}{\pi a^2} = \frac{2\Delta \phi_{\rm w} h}{\rho_{\rm w} g \tau_{\rm p} a} \,. \tag{12}$$

Substituting the parameters measured from PRI into eqn (12), the water permeance for P(DDTA), P(*p*PDTA), and P(*m*PDTA) are estimated $\approx 5.2 \times 10^{-12} \text{ m}^2 \text{ kg}^{-1} \text{ s}^{-1}$, $\approx 2.8 \times 10^{-12} \text{ m}^2 \text{ kg}^{-1} \text{ s}^{-1}$, and $\approx 1.6 \times 10^{-12} \text{ m}^2 \text{ kg}^{-1} \text{ s}^{-1}$, respectively. These values are in good agreement with commercial desalination membranes, thus suggesting that the results from PRI can be correlated to traditional performance metrics used in water desalination operations.

Finally, characterizing the permselectivity of water desalination membranes requires quantifying both the water and salt (*i.e.* sodium chloride) diffusion coefficients within the PA selective layer. PRI has been successfully demonstrated for characterizing the diffusion coefficient of two different permeating species for a relatively thick layer of hydrogel.⁷ However, PA ultrathin films pose a significant measurement challenge for quantifying the salt diffusion coefficient because of ultra low concentration of salt (<100 ppm) present in the films, which implies that the mass change due to salt transport is challenging to measure using the current PRI instrument.

Conclusions

This work demonstrated that PRI is able to quantify the water transport properties of ultrathin PA films that are commonly used as water desalination membranes. The experimental parameters obtained from PRI, which includes the poroelastic time, contact radius, initial and final load, can be used to determine the diffusion coefficient and the intrinsic permeability of water through the PA network by applying the established theory of poroelasticity.

The limitation with PRI for characterizing water desalination membranes is that it is not sufficiently sensitive to measure the diffusion coefficient of salt within these ultrathin layers. This is a measurement challenge for the water desalination membrane community in general as little work has been done to quantify salt diffusion. Compared to other techniques that can measure the water dynamics (inelastic neutron scattering, nuclear magnetic resonance) and structure (PALS, small angle neutron scattering) of these ultrathin polymer layers, the key attribute of PRI is that it can measure these properties using only a single ultrathin layer without the need to prepare a multilayer stack of the material in order to increase the sample mass.

One interesting application of PRI is to extract the network parameters of these swollen PA layers. Li and coworkers have provided the theoretical framework and experimental approach of utilizing PRI to quantify the network parameters for bulk polymer gels.²³ This methodology is analogous to measuring the change in osmotic pressure *versus* mechanical deformation of a bulk elastomer specimen submerged in a solvent reservoir in order to solve the equation-of-state. However, the challenge with adapting their approach for ultrathin PA layers lies in detecting the small changes in water concentration as a function of applied deformation.

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