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Quantifying Carboxylic Acid Concentration in Model Polyamide Desalination Membranes via Fourier Transform Infrared Spectroscopy

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Abstract

Carboxylic acid groups impart hydrophilicity and ionizable moieties to polyamide membranes for desalination, hence influencing water and ion transport through the material. Model polyamide films were synthesized via molecular layer-by-layer deposition on planar substrates to study the formation process of these materials and overcome the chemical and topological inhomogeneity inherent to conventional interfacially polymerized polyamide membranes. The carboxylic acid content in these model films was characterized using Fourier transform infrared (FTIR) spectroscopy by quantifying the C=O band at 1718 cm⁻¹. The concentration of carboxylic acid groups decreased as the thickness of the membrane increased, suggestive of an increase in crosslink density as the polyamide network develops. For the thinnest molecular layer-by-layer (mLbL) samples, the carboxylic acid concentration for films on gold was 0.35 mmol g⁻¹, whereas analogous films on silicon had an acid content of 0.56 mmol g⁻¹, indicating a clear influence of the substrate on the initial network formation. As the thickness of the membrane increased, the influence of the substrate and initial layer growth became less significant as the carboxylic acid

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Author Contributions

T.J.Z. and M.A.H. conceived the FTIR analysis and T.J.Z. performed the DFT modeling and IR experiments. C.M.S. conceived the mLbL studies. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: XYZ.

Additional data on IR peak fitting, peak intensities, calculated absorbance of carboxylic acid groups, and calculations of acid content and path length via each IR technique (PDF).

concentration on both substrates reached a value of 0.12 mmol g^{-1} . We demonstrate that FTIR spectroscopy is a practical and accessible way to quantify the carboxylic acid content in these types of extremely thin polyamide membranes to help quantify network formation in these materials.

Graphical Abstract

Keywords

membranes; polyamides; water purification; functional groups; carboxylic acid; FTIR

INTRODUCTION

Current state-of-the-art reverse osmosis and nanofiltration desalination membranes are constructed as a thin film composite: they consist of an extremely thin ($< 100 \text{ nm}$), crosslinked polyamide selective layer that is supported by a porous polysulfone layer atop a non-woven polyester backing. The support layers serve as mechanical reinforcement against the large applied pressures necessary to overcome the osmotic pressure of high salinity feed waters, while the dense active layer performs the separation. These thin film composite membranes are traditionally prepared via interfacial polymerization between an aromatic or aliphatic diamine such as *m*-phenylenediamine (MPD) or piperazine (PIP) and an aromatic polyacyl chloride such as trimesoyl chloride (TMC). In efforts to deduce structure-property-performance relationships of these materials, detailed chemical and structural information of the polyamide selective layer is required.^{1–3} However, the interfacial polymerization process leads to heterogenous, ridge-and-valley structures that make quantitative measurements of the physical properties of this layer extremely difficult.⁴ For example, traditional interfacial polymerization of TMC and MPD leads to a polyamide selective layer that is approximately (150 to 200) nm thick with a root mean square roughness of (80 to 120) nm.⁵ Additionally, it has been shown that the performance of these membranes is highly sensitive to preparation conditions such as monomer concentration or support wetting and processing protocol.⁶ Thus, there is wide variability in performance metrics (water flux and salt rejection) reported in the literature and few fundamental measurements of the intrinsic properties, such as composition and structure, of the active layer.

To enable new insight into the active layer materials, a new paradigm for generating the polyamide selective layer has been reported. Termed molecular layer-by-layer (mLbL) deposition, this process involves the sequential reaction of the triacid chloride and diamine,

with appropriate rinse steps in between each monomer deposition, to grow a crosslinked polyamide from a substrate or support.⁷⁻⁹ The ability to produce polyamide films/membranes with controlled thickness, roughness, and chemistry via mLbL has opened up new possibilities to employ high-fidelity characterization methods to elucidate the structure and properties of these materials.⁹⁻¹³

Of particular interest is the quantification of carboxylic acid groups within the polyamide active layer. The presence of carboxylic acids groups is a direct indication of incomplete crosslinking in the polyamide layer, and therefore provides some indication of the network structure of the membrane. Carboxylic acid groups, however, also impart hydrophilicity and ionizable groups to the membrane.^{5,14,15} For example, Jin et al. used Fourier transform infrared spectroscopy (FTIR) to show that water initially hydrogen bonds with the amide groups (CONH) within the polyamide film before hydrogen bonding with the carboxylic acid groups (COOH).¹⁶ They attributed this preferential interaction to be simply a result of the higher concentration of amide groups within the membrane compared to carboxylic acids. However, they also showed that membranes with a higher content of free carboxylic acid had an order of magnitude larger diffusion coefficient of water within the membrane, which argues that free carboxylic acid groups are highly desirable for enhanced membrane performance.

To obtain quantitative results using FTIR, the peak corresponding to the functional group of interest must be well understood in terms of its position, shape, and width. In this work, we used FTIR spectroscopy to quantify the carboxylic acid concentration in model polyamide films produced using molecular layer-by-layer assembly. Specifically, we leverage density functional theory to aid in peak assignments and to constrain peak positions during fitting of the amide region in FTIR spectra of highly crosslinked polyamides. We then employed a series of commercial (bulk) membranes with varying concentrations of carboxylic acid functionality to determine the molar absorptivity of the carboxylic acid functional group in crosslinked polyamides. With this knowledge, we quantified the carboxylic acid concentration in mLbL films as a function of cycle number (thickness) and on different substrates, which provides a direct measure of the extent of crosslinking within the polyamide network.

EXPERIMENTAL SECTION

General.

Equipment and instruments or materials are identified in the article to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it imply the materials are necessarily the best available for the purpose.

Membranes.

Samples for transmission IR experiments were prepared from uncoated commercial membranes (BWXE, Dow Chemical Company). These membranes were prepared via interfacial polymerization of trimesoyl chloride (TMC) and m-phenylene diamine (MPD),

generating a network structure similar to that shown in Figure 1. The reactions conditions were tailored in such a way as to create polyamide membranes of varying ion exchange capacity (IEC). The free acid [COO⁻] group is the only ionizable group in the material and thus is the only contributor to the measured IEC. IEC was quantified using a RBS technique similar to Coronell and Cahill.^{17,18} The IEC is defined as the milliequivalents of ionic group per gram of material (meq g⁻¹) and values report in this work have an error of $\pm 10\%$ over three replicates.

To isolate the membranes from the support structure, the polyester backing layer was first delaminated from the membrane by peeling the non-woven polyester layer from the membrane, and the polysulfone was removed by dissolution in dimethylformamide, as previously reported.^{5,19} The resulting polyamide film was soaked in an excess of dimethylformamide for 72 h to remove any residual polysulfone before being rinsed by water followed by methanol. The complete removal of polysulfone was confirmed spectroscopically by the disappearance of characteristic polysulfone peaks (O-S-O stretching at $\approx 1150\text{ cm}^{-1}$ and aromatic C=C at $\approx 1585\text{ cm}^{-1}$) as shown in Fig S1. In order to maintain an absorbance between (0.03 and 1) absorbance units, where linearity in the Beer-Lambert law is preserved, the polyamide samples used to prepare the calibration curve were diluted in KBr and compounded to make a pellet for transmission IR measurements. These dilution factors are provided in Table S2.

Model polyamides were synthesized by molecular layer-by-layer (mLbL) assembly, as previously reported.^{7,8} Briefly, trimesoyl chloride (TMC) and *m*-phenylene diamine (MPD) were dissolved in toluene at a concentration of 1 % by mass. TMC was first deposited onto a clean substrate and allowed to adsorb/react, and the excess TMC was rinsed off with fresh toluene. Then, MPD was deposited onto the TMC and allowed to react, and the excess MPD was rinsed off with fresh acetone. One cycle corresponds to one layer of TMC and one layer of MPD, and the cycle was repeated to build a model polyamide network. Samples are referenced by the number of cycles to generate the film. Model polyamides were prepared via mLbL on both the native oxide of silicon and gold-coated silicon wafers (100 nm Au, Platyus Technologies). All substrates were pre-cleaned with ethanol and dried with a stream of nitrogen before placing in a ultraviolet-ozone (UVO) cleaner (Model 42, Jelight Company) for 20 min just prior to mLbL deposition.

IR Measurements.

FTIR spectra were obtained using reflectance absorbance infrared spectrometry (RAIRS) for samples on gold substrates and surface overlayer geometry (SO-ATR) for samples on silicon. RAIRS provides a significantly enhanced signal on metallic substrates enabling the analysis of ultrathin films, while SO-ATR provides a similar enhancement on silicon substrates.^{20–22} All FTIR experiments were conducted using a Bruker Vertex 70 Fourier transform spectrometer (Billerica, MA) equipped with a liquid nitrogen-cooled narrow-band MCT detector collected at an optical velocity of 2.6 cm s^{-1} (40 kHz, HeNe) and a resolution of 5 cm^{-1} .

Transmission experiments using 7 mm KBr pellets containing the commercial interfacially polymerized polyamide film were conducted to generate a calibration curve and derive

optical constants for the polyamide films. The optical constants were derived using a Kramers-Kronig algorithm and used to predict the spectral response of polyamide films in RAIRS and SO-ATR experiments.^{23,24}

RAIRS measurements were carried out on a PIKE VeeMAX II variable angle accessory (Madison, WI) set at an angle of incidence of 72° with a liquid nitrogen-cooled MCT detector. The accessory was aligned and optimized using a pristine gold mirror before each experiment. Samples were placed on a 2 cm sooted specular mask to define the sampling area. Spectra were averaged over 1500 scans.

SO-ATR experiments were performed on a Harrick VariGATR accessory (Pleasantville, NY) at an incident angle of 65° with a constant force of 700 N applied to the sample to achieve intimate contact. Spectra were averaged over 500 scans.

Density Functional Theory (DFT) Calculations.

DFT was used to confirm peak positions and assignment of component bands in the vibrational spectra of the polyamide films. The vibrational spectrum of a small polymer fragment was calculated in the gas phase. The optimal geometries and the Cartesian force fields for all the considered fragments were calculated at the DFT/B3LYP level with the 6–31++G** basis set. A scaling factor of 0.9062 was applied to account for the overestimation of vibrational frequencies and the resultant intensities normalized to the experimental ring mode intensity. This approach has been shown to provide accurate multiparameter-scaled frequencies.^{25,26}

RESULTS AND DISCUSSION

Density functional theory (DFT) calculations were performed on a small polymer fragment with the functional groups representative of the crosslinked polyamide structures obtained in the interfacial polymerization of TMC and MPD. These calculations were used to aid in identifying the vibrational modes that contribute to the peaks observed in the experimentally-measured polyamide fingerprint region, such that the position and shape of any peak(s) associated with unreacted or “free” carboxylic acids could be uniquely identified. While this method of calculating vibrational modes neglects interactions such as hydrogen bonding and may not correctly estimate coupling of vibrational modes, the method used in this work has a distinct advantage in that it optimizes the use of computational resources. Moreover, several researchers have shown that fragment approximation methods yield accurate predictions of atomic displacements and vibrational activities for macromolecules, including proteins that are structurally similar to the polyamides studied here.^{26–28}

For this study, we focused on the amide C=O stretching mode at 1672 cm⁻¹, which is also coupled with the C-C-N deformation mode and the C-N stretching mode, and the carboxylic acid C=O stretching mode at 1718 cm⁻¹.²⁹ However, knowledge of the other vibrational modes is critical in the peak fitting of the amide region and could be used for other structural studies such as orientation measurements.^{22,23,30} For example, the peak at 1492 cm⁻¹ is almost entirely due to MPD ring vibrations and can be used to determine the orientation of

aromatic rings (Figure S2). A representative IR spectrum of the amide region is shown in Figure 2, along with the results of the peak fitting to quantify the free acid peak. The peaks relevant to this study are highlighted in Figure 2, and the remaining combinations of vibrational modes are represented by the dashed lines and summarized in Table 1.^{31–36} It should be noted that the unhydrolyzed acid chloride C=O stretching mode occurs at 1765 cm⁻¹.³⁷ While this peak is observed in the neat TMC spectra (Figure S3), it is unlikely that we would observe this peak in the polyamide.

samples due to the relative ease of hydrolysis of the acid chloride to the carboxylic acid upon exposure to atmospheric moisture. Informed by the DFT calculations of the small molecule amide fragment, we then performed peak fitting of the amide region of a commercial polyamide membrane with the highest IEC. Fitting of the obtained spectrum was performed using a Levenberg-Marquardt^{38,39} algorithm with mixed peak shapes (Lorentz + Gaussian)⁴⁰ between 1811 cm⁻¹ and 1627 cm⁻¹ to delineate the contributions of the multiple bands that overlap in this region. The results of the peak fitting are shown in Figure 2. After peak fitting, the free carboxylic acid peak at 1718 cm⁻¹ is reliably isolated, and the peak height and peak area can be easily quantified.

Next, we applied this approach to the series of commercial membranes with varying IEC. Using the peak fitting strategy described above, the free carboxylic acid peak at 1718 cm⁻¹ could be dependably resolved, as shown in Figure 3a. Figure 3b shows the absorbance of the peak at 1718 cm⁻¹ as a function of the IEC for the five commercial membranes. A linear relationship between the peak height and the carboxylic acid content of the polymer is observed as expected from the Beer-Lambert law:

$$A = \epsilon bC$$

where A is the absorbance, ϵ is the wavelength-dependent molar absorptivity, b is the path length, and C is the concentration of the species of interest (carboxylic acid groups in this case). The absorbance of each sample was divided by the thickness of the pellet to normalize for the IR path length. Using the parameters shown in Table S1, the normalized IR spectra for commercial polyamide samples were fit to yield the components shown in Fig 3a for the highest IEC sample; the complete sample set is shown in Fig S4. The molar absorptivity (ϵ) of the carboxylic acid group can be obtained by dividing the slope of the fit in

Figure 3b (ϵb) by the thickness of the pellets used (b). The absorptivity was found to be 488 M⁻¹ cm⁻¹ at 1718 cm⁻¹, which falls within the range reported in the literature for carboxylates, (300 to 700) M⁻¹ cm⁻¹.⁴¹

We used this empirical relationship to deduce the “free” carboxylic acid content in the mLbL polyamide films by measuring the absorbance of the peak at 1718 cm⁻¹. As noted earlier, unreacted carboxylic acid groups can be thought of as defects in the network. In particular, we studied the effect of the substrate used for growing the mLbL polyamide on the concentration of unreacted carboxylic acid moieties remaining in the film. For these measurements, mLbL polyamide films were prepared on two substrates: silicon with a native oxide layer, and Au-coated silicon. IR measurements of ultrathin films on Au-coated silicon

are relatively straight-forward, while the same measurements on silicon are more challenging. However, many property and performance measurements of mLbL polyamide membranes rely on hydroxyl and amine functional groups as anchor points for the growing film^{9,13}; thus, mLbL films grown on the native oxide of silicon perhaps better represent the polyamide growth and structure in those studies.

Polyamide films of increasing thickness were prepared via mLbL by controlling the number of sequential TMC and MPD deposition cycles. For this study, we prepared mLbL films having (5, 10, 15, 30, and 60) cycles on silicon and Au-coated silicon. Based on previously reported growth rates (0.34 nm/cycle)⁸ for similar deposition conditions, the film thickness ranged from approximately (2 to 20) nm. The IR spectra for these films are shown in Figure 4, and the spectra were normalized to the C=C ring modes at $\approx 1615\text{ cm}^{-1}$. On silicon, we observed a large acid peak at low cycle numbers that decreased as the number of cycles increased; similar behavior was observed on Au substrates. As the number of cycles increases, the relative number of unreacted carboxylic acids is expected to decrease as the network becomes more crosslinked. It is also possible that subsequent cycles could backfill and further react with remaining acyl chlorides left in the network from previous cycles.

We can further quantify the concentration of “free” carboxylic acid groups within the membrane through the molar absorptivity determined previously. These results are shown in Figure 5. In general, the acid content decreases as the cycle number increases, indicative of increased crosslink density for higher cycle number films. This observation agrees with recent swelling measurements on mLbL polyamide films that show the equilibrium swelling ratio decreases with increasing cycle number (i.e. thickness) of the polyamide film.⁴² The IEC in the 5-cycle film on gold was 0.35 mmol g^{-1} , whereas the parallel sample on silicon had an IEC of 0.56 mmol g^{-1} . The increased acid content on silicon may be due to the presence of surface-bound water associated with silanol groups, which can hydrolyze some acid chloride groups [COCl] to the corresponding carboxylic acid [COOH]. Since gold has no associated oxide, the amount of adsorbed water on the surface should be negligible. Furthermore, there is evidence that MPD may displace the first layer of TMC in the first deposition cycle due to preferential binding of amines to gold.⁴³ Thus, there could be a half cycle difference between silicon and gold substrates, causing a slight difference in the cycle number and thickness between substrates. As the cycle number increased beyond 10 cycles, the influence of the initial layer growth became less significant as the crosslink density of the polyamide films on both substrates appeared similar for thicker films. This observation could be rationalized in one of two ways: (1) the initial layers near the substrate contribute less to the overall FTIR signal as the films becomes thicker, or (2) the monomers (TMC/MPD) can reasonably penetrate the growing film and access unreacted groups in the interior of the film (back-filling). The data presented here cannot unequivocally discern which scenario is indeed correct, and this ambiguity presents an interesting topic for future studies.

It is instructive to put the carboxylic acid concentration as measured by FTIR into some perspective. Coronell et al. measured the carboxylic acid content in commercial polyamide reverse osmosis membranes with an average thickness of 111 nm using Rutherford backscattering spectrometry after ion exchange with a heavy ion probe.^{44,45} They determined the carboxylic acid concentration to be $(0.45 \pm 0.25)\text{ mmol g}^{-1}$ for a variety of

reverse osmosis membranes, which is within the range of values obtained via FTIR on mLbL membranes. Sunday et al. used resonant soft x-ray reflectivity on comparable mLbL polyamide films (TMC/MPD, 150 cycles),⁴⁶ and they found the carboxylic acid concentration to be 0.5 mmol cm^{-3} , which equates to 0.38 mmol g^{-1} assuming a density of $\rho = 1.33 \text{ g cm}^{-3}$ for the polyamide. It should be noted that the mLbL films in that study were prepared using a different rinse solvent (isopropanol) compared to the films in this study (acetone). It has been reported that the rinse solvent can dramatically influence the growth rate in mLbL of polyamides, which can be presumed to have a significant impact on the crosslink density and thus the number of unreacted carboxylic acid groups. The use of isopropanol leads to a higher growth rate in mLbL when compared to acetone,⁷ which could be argued would result in a lower crosslink density when isopropanol is used as a rinse solvent. Alternatively, one can calculate the carboxylic acid concentration for several acid-containing polymers from the polymer density (ρ) and the molar mass of a repeat unit. For example, poly(acrylic acid) (molar mass = 72.1 g mol^{-1} , $\rho = 1.41 \text{ g mol}^{-1}$) has a carboxylic acid concentration of 19.6 mmol g^{-1} , whereas poly(glutamic acid) (molar mass = $129.11 \text{ g mol}^{-1}$, $\rho = 1.41 \text{ g mol}^{-1}$) has an acid concentration of 10.9 mmol g^{-1} . These comparisons confirm that the polyamide selective layer is indeed highly crosslinked with a small fraction of unreacted carboxylic acid groups. Future studies could examine how changes in the mLbL process (e.g., choice of solvent, co-monomers, post-fabrication annealing) affect the measured carboxylic acid content of the films now that this quantitative FTIR method has been established.

CONCLUSIONS

We demonstrated a technique to measure the residual carboxylic acid content in thin polymer films and membranes. In particular, we examined the acid content in thin polyamide films which are at the heart of reverse osmosis desalination membranes. Leveraging DFT calculations to decompose the amide-I region into five principle vibrational components, we placed bounds on the peak position and peak shape of the carboxylic acid component and used those bounds to quantify the residual carboxylic acid content in five prototype membranes with varying ion exchange capacity. A linear relationship was found between the absorbance of the carboxylic acid peak in the IR spectra and acid content determined via IEC measurements. Armed with this knowledge, we then synthesized model polyamide films via molecular layer-by-layer deposition to overcome the chemical heterogeneity and roughness inherent to conventional interfacially polymerized polyamide membranes. FTIR enabled the determination of carboxylic acid content in these mLbL polyamide membranes by interpolation of C=O band intensities onto the experimentally determined calibration line for acid content. The results of this work show that at low thicknesses, the mLbL films have a high free acid content, which can be ascribed to incomplete network formation and dangling network chain ends. At greater thicknesses, the free acid content asymptotes to a constant value of approximately 0.12 mmol g^{-1} , which we put into context with other measurements of acid content in polyamide membranes such as RBS and RSoXR. We believe these results, combined with the wide-spread availability of FTIR, provide a robust measurement platform for quantifying residual carboxylic acid concentrations in thin polymer films and membranes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Chemical structures of the monomers used in the synthesis of fully aromatic polyamide membranes. The reaction between trimesoyl chloride and *m*-phenylene diamine results in a highly crosslinked network, where incomplete reaction results in residual carboxylic acid groups.

Figure 2. Deconvolution of the experimentally observed mLbL polyamide mid-IR vibrational spectrum. Peak position and peak shape was informed by the DFT calculations of the polyamide fragment.

Figure 3.

(a) Peak fitting of the amide region of a commercial, high ion exchange capacity (IEC) polyamide membrane, showing a resolved free carboxylic acid peak at $\approx 1720 \text{ cm}^{-1}$; (b) resulting calibration curve that relates the peak intensity of the band at 1718 cm^{-1} to the free carboxylic acid concentration as measured by the ion exchange capacity (IEC) of each membrane. The error bars represent one standard deviation of the data ($n = 3$), which is taken as the experimental uncertainty of the measurement.

Figure 4.

Overlay of the amide FTIR region of mLBL polyamide films of increasing cycle numbers on (a) silicon and (b) gold, showing a decrease in the carboxylic acid peak at $\approx 1720\text{ cm}^{-1}$ as the number of cycles increases.

Figure 5. Concentration of carboxylic acid as a function of mLbL cycle number on silicon (closed circles) and on gold (open circles) substrates. The error bars represent one standard deviation of the data ($n = 3$), which is taken as the experimental uncertainty of the measurement. Some error bars are smaller than the symbol.

Table 1.

Fingerprint region peak assignment of polyamide system

Peak	Position (cm ⁻¹)	DFT	Assignment	Ref
1	1765	1772	C=O stretch free acid chloride on TMC	32, 33,
2	1718	1757	C=O stretch from the COO ⁻ group on TMC	32,33,
3	1672	1682	C=O stretch (mostly) coupled with C-C-N deformation and C-N stretch	27, 28,29
4	1612	1600	combination of E2g (also known as vibration 8) derived C=C ring vibrations on TMC and MPD	34,35,36
5	1546	1541	N-H in plane bending and C-N stretch for Amide group in a trans configuration	27,28,29
6	1492	1496	B1 bending stretch mode of a meta bi functionalized ring	31,34,35,
7	1448	1438	A1 ring vibration in MPD, overlaps with E' ring vibration of TMC	31,35, 37
8	1425	1429	Aromatic C-N stretching (mostly). This peak overlaps with tri-substituted E' derived (C=C) ring mode	34,35,36
9	1325	1320	In plane =C-H deformations on MPD ring	31,34,35
10	1306	1295	Amide C-N-C stretch	27,28,29
11	1287	1282	in plane =C-H deformations on TMC ring	34,36,37
12	1246	1238	Interaction of N-H bending and C-N stretching in amide bond	27,28,29
13	1168	1187	CH vibration on MPD ring	31,34,35