Orientation of Thin Polyamide Layer-by-Layer Films on Non-Porous Substrates

Tawanda J. Zimudzi,† Sarah E. Sheffield,§ Kathleen E. Feldman,‖ Peter A. Beaucage,‖, ‖‖ Dean M.
DeLongchamp,‖ Douglas I. Kushner,§ Christopher M. Stafford,‖\* and Michael A. Hickner †,§\*

† Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania, 16802, USA

§ Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania, 16802, USA

‖ Materials Science and Engineering Division, ||NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

**Corresponding Authors**

\* E-mail (MAH): hickner@matse.psu.edu

\* E-mail (CMS): chris.stafford@nist.gov

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ABSTRACT

The orientation of polyamide thin films on non-porous substrates was investigated using Fourier transform infrared (FTIR) spectroscopy and corroborated by near edge X-ray absorption fine structure (NEXAFS) measurements. Polyamide films comprised of *m*-phenylene diamine and trimesoyl chloride were synthesized via a layer-by-layer deposition process on both gold and silicon substrates, where the number of sequential monomer deposition steps (cycles) determines the overall polyamide film thickness. These films represent model materials for metrology development that can be applied to understand the selective polyamide layers in reverse osmosis (RO) membranes. Using the fingerprint region in the infrared spectrum for the *m*-phenylene diamine-trimesoyl chloride (MPD-TMC) system, peaks were identified that could be used as diagnostic modes for molecular orientation analysis. At extremely low cycle numbers, FTIR measurements suggest the MPD-derived aromatic rings exhibited a tilt angle of ≈6° from the surface parallel while the carbonyl group of the amide was similarly oriented with an average tilt angle of ≈17°. The FTIR insights are in agreement with NEXAFS results, which indicate that the aromatic rings in the first half layer-by-layer cycle are oriented parallel to the surface. Both FTIR and NEXAFS measurements further show high anisotropy in the materials at low cycle numbers. As the films approach 60 cycles (≈13 nm films), the films become isotropic and no orientation was detected.

INTRODUCTION

The formation of stable thin films with well-defined and predictable water transport properties has long been of interest for water purification and reverse osmosis applications.1 The inextricable tie between structure and properties in these materials makes it imperative to first understand the molecular structure of these thin films before any strides can be made in improving their transport properties for large scale applications. Currently, thin film composite reverse osmosis (RO) membranes are built on polyamide (PA) thin films fabricated by interfacial polymerization of an aromatic polyamine, e.g., *m*-phenylenediamine (MPD) with an aromatic polyacyl halide, e.g., trimesoyl chloride (TMC). Interfacially polymerized films suffer from chemical inhomogeneity and high surface roughness making the characterization of structure-property relationships difficult in most cases.2 To this end, molecular layer-by-layer (mLbL) synthesized RO membranes have been developed with controllable chemical composition and significantly lower surface roughness, and the performance of such membranes have begun to be characterized.3–8 The development of mLbL films with controlled thicknesses opens new possibilities to employ high-fidelity characterization methods to elucidate the structure of these materials. We recently demonstrated that Fourier transform infrared (FTIR) spectroscopy is a practical and accessible way to quantify the carboxylic acid content in extremely thin (< 60 nm) mLbL polyamide films to help quantify network formation in these materials.9 The most widely used RO membrane characterization methods include X-ray photoelectron spectroscopy (XPS), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), near edge X-ray absorption fine structure (NEXAFS) spectromicroscopy, atomic force microscopy (AFM), and ellipsometry.10,11 While methods such as XPS, AFM, and ellipsometry can give information about film thickness and chemical composition, these methods cannot provide the direct determination of molecular orientation required to fully understand film properties.

FTIR can provide detailed molecular orientation information and is routinely employed to determine orientation parameters, such as dichroic ratios, in films and adsorbed layers on ATR crystals. For thin films or molecules adsorbed on planar substrates, it has been well-established that infrared spectroscopy can be used to calculate the angle between surface normal and the dynamic dipole of a given function group when provided with a measurement of an isotropic sample with the same chemical composition, thickness, and on the same substrate material.12 Unemara, et al. proposed an approach where the isotropic sample spectrum is obtained from a film deposited on an IR element, such as a ZnSe crystal.13 Unfortunately, the Unemara, et al. method is not always practical because it is often impossible to experimentally eliminate all substrate effects and obtain an isotropic sample spectrum. Iida, et al. developed a strategy that eliminated the need for an isotropic spectrum, provided it is possible to observe three peaks whose transition moments are mutually perpendicular.14 These three peaks would essentially define the *x*, *y*, and *z* axes that are needed in determining molecular orientation. Allara, et al. reported a method to obtain quantitative orientation information from reflection absorption infrared spectroscopy (RAIRS) spectra combined with spectral simulations.15 This approach involves comparing the RAIRS spectrum of the sample to that of the calculated isotropic film, of identical thickness on the same substrate.12 The isotropic spectrum is calculated as a parallel-layer multi-slab system, where the optical properties and thickness of each layer is defined by the experimental geometry and sample thickness.15 The most widely accepted method of deriving optical constants from an isotropic bulk film is to use transmission measurements on a sample with a known thickness to obtain the imaginary component of the refractive index (*k*) and a Kramers-Kronig transform to obtain the real component of the refractive index (*n*).16,17 For this analysis to be successful, it must be applied to the diagnostic modes, which are vibrational modes with clearly resolvable peaks and clearly definable transition dipole moment directions. For the case of aromatic polyamides, the diagnostic modes correlate to the peaks in the amide region, referred to as amide I. The ensuing discussion describes optical constants derived for the mLbL system and used to simulate isotropic film spectra on gold and silicon substrates. Orientation was calculated by taking the obtained experimental spectra and dividing this by three times the theoretical spectra prior to calculating the tilt angle. The diagnostic peaks identified were used to calculate the tilt angle of the C=O and MPD derived aromatic rings.

 Similarly, NEXAFS provides information about orientation and electronic structure by probing electronic transitions from occupied to unoccupied molecular orbitals of the bonds to neighboring atoms in a particular atomic species selected by x-ray wavelength.18 Distinct peaks are observed in the electron yield at energies that can be assigned to particular bond systems in the material being probed. When polarized X-rays are used in a NEXAFS experiment, the orientation of the X-ray excitation couples with the orientation of the underlying bond system to allow determination of molecular/bond orientation by rotating the sample in what is known as the “search light effect”; in short, the intensity of an observed peak scales with the number of bonds meeting the orientation condition. For example, for aromatic systems like the polyamides presented here, the C=C 1s -> π\* transitions are oriented out of the plane of the ring, causing an increase in the observed intensity of that transition peak when the ring normal and beam polarization are aligned. NEXAFS was used in this fashion by Peng, et al. to measure the orientation of alkyl-aromatic polyamide films formed via molecular layer deposition.19

In this work, we demonstrate the use of FTIR, aided by density functional theory (DFT) calculations, to provide a direct measure of orientation as a function of film thickness in model polyamide films prepared the mLbL process. The FTIR results are supported by orientation measurements via NEXAFS on similar mLbL films. In this demonstration, FTIR provided molecular orientational information of both the MPD-derived phenyl rings and the amide carbonyl, while NEXAFS provided a measure of all phenyl rings in the system.

EXPERIMENTAL SECTION

Equipment and 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 that the materials are necessarily the best available for the purpose.

The mLbL films were prepared as described by Johnson, et al. on gold and double-sided polished silicon surfaces for orientation analysis.4 Smooth gold substrates were prepared on undoped silicon wafers using a direct line-of-sight approach on a Semicore E-Gun Thermal Evaporator with titanium as an adhesion layer. Silicon wafers were mounted on a planetary holder with Kapton tape and the chamber pumped down to a pressure of 1 × 10−7 Torr (1.33 × 10-5 Pa). A titanium adhesion layer was evaporated at a rate of (0.5 to 1.0) A˚ s−1 at a pressure ≈1 × 10−6 Torr
(1.33 × 10-4 Pa) until a 20 nm layer had been deposited. Gold was evaporated at a rate of (0.1 to 0.3) A˚ s−1 at ≈1 × 10−6 Torr (1.33 × 10-4 Pa) until a 50 nm layer had been deposited.

Thickness values for mLbL films were measured using a J.A. Woollam Alpha-SE spectroscopic ellipsometer (Lincoln, NE). The wave amplitude (Ψ) and phase shift (Δ) were measured at 188 wavelengths over a spectral range of 360 nm to 900 nm (1.377 eV to 3.44 eV) at 65°, 70°, and 75° for 30 s at each angle. The samples were modeled as a stacked multilayer system with the substrate being either gold or silicon, where silicon was modeled to have a native oxide whose thickness was fit prior to thin film deposition. The polymer thin film was then modeled as a uniform Cauchy layer with no surface roughness, where the thickness (*t*) and model coefficients (*A* and *B*) were fit to the amplitude and phase shift.

All FTIR measurements were conducted on a Bruker Vertex 70 spectrometer (Bruker, Billerica, MA) equipped with liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector under a CO2-free dry air purge. A ZnSe wire grid polarizer was used to maintain *p*-polarization for all measurements.

RAIRS measurements were conducted with a VeeMax external reflection accessory (Pike Technology, Madison, WI) at an incident angle of 80° with a 1.5 cm specular mask coated in soot. Reported spectra represent the average from 300 scans at a resolution of 6 cm-1.

 Substrate overlayer attenuated total reflection (SO-ATR) FTIR measurements were conducted on a VariGATR accessory (Harrick Scientific Products, Inc. NY) at an incident angle of 65°.20 The applied pressure on each sample for ATR measurements was monitored by a force sensor and kept constant at 700 N to ensure reproducible contact.

Optical constants for PA films were determined from transmission experiments using KBr pellets containing interfacially polymerized polyamide harvested from commercial RO membranes. The PA layer was harvested by physically separating the PA/polysulfone layers from the polyester backing. The polysulfone/PA layers (about 25 cm × 25 cm) was immersed in 80 mL of dimethylformamide (DMF). The polysulfone dissolves in DMF, leaving the insoluble crosslinked PA suspended in solution. The solution was pressure filtered through a 47 mm diameter, 1.0 µm pore size Advantec PTFE membrane filter using a KST 47 pressure filter holder (Advantec MFS Inc, Dublin, CA). The residue was washed with 20 mL of methanol. A 1.87 % mass fraction PA in KBr pellet was made by mixing 3.2 mg of PA with 167.8 mg of KBr, which was ground for 400 seconds in a Wig-L-Bug grinding mill (Patterson Dental, St. Paul, MN) to minimize grinding effects on absorption values. The sample mixture was pressed into several 7 mm pellets at a load of 2 tons (1814 kg) in a hydraulic press. The transmission spectra were collected immediately after pellet preparation. IR spectra of blank KBr pellets of similar thickness were collected at humidity conditions identical to PA samples to improve baseline quality.21 After spectra collection, the thickness of each pellet was measured to obtain the path length for Beer-Lambert calculations of the *k*-spectra.12 The same program used to calculate the isotropic RAIRS and SO-ATR spectra of desired thicknesses was also used to determine orientation.

Polarized NEXAFS spectroscopy measurements were performed at Brookhaven National Laboratory’s National Synchrotron Light Source beamline U7A. Data was collected at the carbon K-edge in Partial Electron Yield (PEY) mode with a grid collection bias of -50 V across five incident angles ranging from 20° to 70° (10 cycles) and at two incident angles of 33° and 70° (0.5 cycle to 5 cycles). The data was pre-edge normalized to an intensity of zero between 275 eV and 280 eV and post-edge normalized to an intensity of 1.0 between 325 eV and 330 eV. Orientation of the 1s→pi\* resonance, appearing at ≈285.5 eV, was fit to the vector orbital formalism, as described in Stöhr.22

RESULTS AND DISCUSSION

**IR Peak Assignments and Orientation Analysis**

Peak assignments for this system were made in agreement with the previously published work5 by the authors on polyamide thin films.23–39 DFT calculations were used to confirm some peak assignments and identify vibrational modes, which were considered diagnostic peaks and could be used for orientation analysis. The aromatic ring tangential carbon-carbon stretching vibrations, known as ring breathing modes 8 and 19 in the Varsanyi nomenclature30, are prominent in the 1000 cm-1 to 1800 cm-1 frequency range where amide I vibrations occur, as seen in the RAIRS spectrum of a mLbL film on gold (60 mLbL cycles, Figure 1).



**Figure 1**. RAIRS spectrum of mLbL PA film on gold (60 cycles), showing the fingerprint region from 1000 cm-1 to 1800 cm-1, with Varsanyi nomenclature vibrations 8 and 19 labeled.

The dipole changes seen from ring breathing modes 8 and 19 are sensitive to the symmetry of the ring, hence these distinct peaks are obtained for both a 1,3,5-substituted ring and a meta-substituted ring, regardless of the identity of the substituents.28,29 This allows us to distinguish between MPD and TMC as free monomers or when incorporated in the polymer network. Both ring breathing modes 8 and 19 are split to give rise to distinct vibrational modes, depending on the symmetry of the substituent on the benzene ring. The ring breathing modes 8 and 19 in MPD are split into degenerate vibrations, labeled as A and B in Figure 2, creating four distinct vibration modes for MPD.

B2

A1

A1

B2

19a

19b

8a

8b

**Figure 2.** Breathing modes 8 and 19 of MPD rings, occurring between 1350 cm-1 and 1650 cm-1, split into two degenerate vibrations.

Fitting these four modes into the experimental MPD monomer spectrum produced a good fit and provided a fifth peak, attributed to the N-H bend (N-H), to ensure the accuracy of the fit (Figure 3). Details pertaining to the measurement and fitting of the MPD spectrum are provided in the supporting information. As the wavenumber position of these bands is largely governed by the number and position of substituents and does not change after polymerization, we believe it is a fair assumption that the assigned band positions are valid for the mLbL system.



**Figure 3**. Fit of the MPD spectrum between 1350 cm-1 and 1800 cm-1 showing the positions of the major peaks of breathing modes 8 and 19.

From the MPD spectrum in Figure 3, it is clear that the peak at 1492 cm-1 is due to the combination of the degenerate ring breathing modes 19a and 19b. There is minimal overlap from the N-H mode at 1500 cm-1, so this band can be used for orientation/quantitative analysis of MPD rings, provided it is clearly resolvable in the polymer spectrum. When the di-substituted MPD is replaced with a tri-substituted monomer, 1,3-diaminobenzoic acid (1,3-DABA), the resultant polymer contains only tri-substituted rings. This results in the complete disappearance of the 1492 cm-1 peak in the tri-substituted monomer spectrum, as shown in Fig 4. The 1492 cm-1 peak is clearly resolvable in the MPD-TMC system and can be ascribed solely to vibrations 19a and 19b of a meta-disubstituted benzene ring. The dipole change of the 19a vibration is perpendicular to the plane of the aromatic ring, and was used to as a diagnostic peak to determine the orientation of MPD rings in the system. It should be noted that the dipole change of the 19b vibration which contributes 11 % of the peak area under isotropic conditions orthogonal to the 19a dipole change which introduces some error to the quantitative angle reported, as summarized in the supporting information.

a)

b)

**Figure 4.** a) Chemical structures of di-substituted monomer, MPD, and tri-substituted monomer, 1,3 DABA and (b) Spectra of TMC-1,3 DABA and TMC-MPD, showing the presence of the peak at 1492 cm-1 in the TMC-MPD spectrum.

The diagnostic peak selected for the carbonyl, C=O, bond orientation analysis was the amide I peak, which consists primarily of the amide C=O stretch at 1672 cm-1. The amide I peak has routinely been used to determine secondary structures in proteins by the deconvolution of the various vibrational modes that overlap within the peak.40 In the mLbL system, there is a minor contribution from the C-N stretch, which is coupled to the C=O stretch, resulting in the shifting of the orientation of the dipole of the C=O bond plane (Fig 5). This shift has been demonstrated to be approximately 18° to 20° out of the double bond plane31 and is consistent with reported dipole orientation found in some aromatic amide systems. In the ensuing discussion the molecular orientation is described as the angle between the surface and molecular plane i.e, ring plane in case of MPD and C=O plane in the case of amide I (Fig 5).



**Figure 5**. The orientation of the dipole changes for a) the di-substituted MPD aromatic ring and b) the amide I vibration of the aromatic polyamide membranes; c) the orientation of the aromatic ring described by the angle between the surface and ring plane.

**Orientation**

The intrinsic scalar optical constants were obtained by analyzing the material’s optical response in the bulk phase where, on average, molecules assume random orientations. This was accomplished by generating a random dispersion of small polyamide flakes in an inert KBr matrix. The KBr sample provided the basis for determining isotropic scalar optical functions from the analysis of a normal incidence transmission IR spectrum, using a pressed pellet of known thickness and concentration of dispersed material. The transmission experiment provided a good first approximation of the absorption constants of the polyamide from a Beer-Lambert type of relationship (Equation 1).

 $\frac{I}{I\_{0}}= e^{-4πkvt}$ (1)

Here, the set of wavelength dependent *k* values, termed a “*k* spectrum”, appears identical to an absorbance spectrum. Each value of the *k* spectrum was used in the Kramers-Kronig transformation to generate a corresponding set of *n* values. After choosing an initial guess for the *k* spectrum, the *n* and *k* values were refined through an iterative process until the absorbance spectrum obtained from the final *n* and *k* set matched the original experimental spectrum. As a final check, two additional KBr samples of different thicknesses were generated, analyzed, and compared to the spectra simulated from the final set of *n* and *k* values. The optical constants for polyamide determined by this method are shown in Fig 6.



**Figure 6.** The *n* and *k* spectra in the mid-infrared region from the spectral simulation which are used as accepted optical constants.

 For surface-oriented molecules in an external reflection geometry, there is electric field amplitude at infrared frequencies normal only to the surface of the substrate. As a result, the absorbance for a vibrational band is proportional to the square of the electric field amplitude at the surface, the magnitude of the transition dipole moment (μ), and the tilt angle (*θ*) of the transition dipole moment from surface normal, as given by Equation 2:

$A∝E^{2}µ^{2}cos^{2}θ$ (2)

Due to the anisotropy of the surface electric field amplitude, the absorbance of any mode with a transition dipole moment oriented along surface normal will be three times as large as the integrated absorbance of the same vibrational band of identical molecules in a thin film of equivalent thickness and molecular density. Thus, the tilt angle of a given transition dipole moment is calculated using Equation 3:

 $\frac{I\_{obs}}{3I\_{cal}}=cos^{2}θ$ (3)

where *Iobs* is the experimental absorbance of the diagnostic mode, *Ical* is the simulated absorbance of the same mode, and *θ* is the tilt angle between the dipole change of the mode and the electric field vector.

 In both SO-ATR and RAIRS experiments, the electric field is surface normal, hence *θ* is the tilt angle between the dipole change and the substrate normal. Experimental spectra were obtained using a SO-ATR geometry on silicon substrates, as it provided superior sensitivity compared to Brewster’s angle experiments and the electric field is exclusively *z*-polarized in the thickness regime of the mLbL samples analyzed. RAIRS experimental geometry was used for all samples on gold.



**Figure 7.** The tilt angle of the C=O bond of the amide group, with respect to surface normal on gold and silicon surfaces, as a function of the number of mLbL cycles the polyamide film. The error bar represents one standard deviation of the data (n = 3), which is taken as the experimental uncertainty of the measurement.

The tilt angles obtained for the C=O group per number of mLbL cycles used to form the polyamide thin film are presented in Fig 7. From cycle numbers 5 to 15, the average angle, with respect to surface normal, was approximately 16° to 18° with little deviation in the measured angle. However, larger variations in average tilt angle were observed for higher cycle numbers. For 60 mLbL cycles of films on silicon, the average tilt angle was 44± 5° while at 10 cycles it was 17° ± 1°, where the error represents one standard deviation of the data (n = 3). We attribute this difference to an increase in local sample heterogeneity as the cycle number increases and to an increase in the isotropy of the film. While the amide C=O peak provides a reasonable approximation of the molecular order of the film, the overlap of the free acid band and its sensitivity to hydrogen bonding increases the uncertainty in the values obtained. These sources of uncertainty do not exist, however, for the peak at 1492 cm-1, which we ascribed solely to the ring breathing mode of the meta di-substituted benzene ring.35,38 Hence, this vibration was used to determine a more accurate measure of the orientation for the rings in the polyamide system. The dipole change for this vibration is in-plane of the aromatic ring, thus it can be used to directly obtain the tilt angle of the aromatic rings with respect to surface normal. As with the C=O group, there was little deviation in the tilt angle for the (5, 10, and 15) cycle films but a large deviation in cycle numbers above 15. Since some of the calculated tilt angles for the film at 60 cycles were close to the magic angle of 54.73°, we believe that these films contain very little order. The calculated tilt angle for (5, 10, and 15) cycle films was 84°, with respect to surface normal. Figure 8 shows the average tilt angle for the MPD ring, with respect to the surface, and also demonstrates that at low cycle numbers the aromatic ring is close to surface parallel with an average tilt angle close to 6° which gradually becomes more perpendicular as the film grows and becomes more isotropic.

 

**Figure 8.** Tilt angle of the di-substituted MPD aromatic ring with respect to surface parallel on gold and silicon substrates, per number of mLbL cycles of the polyamide film. The error bar represents one standard deviation of the data (n = 3), which is taken as the experimental uncertainty of the measurement.

To further quantify the orientation of the films and corroborate the IR measurements, partial electron yield (PEY-NEXAFS) spectra were collected as a function of tilt angle of the film in the beam (Fig 9a) for mLbL layers on silicon at (0.5, 1, 1.5, 2, 5, and 10) cycles, as shown in Fig 10. The spectra show clear shifts in the intensity of the C 1s  π\* resonance at 285.5 eV in addition to the orthogonal shifts in the intensity of the broad 1s σ\* transitions between 300 eV and 325 eV. The magnitude of these intensity differences was determined by the Gaussian fitting of the spectrum to the vector symmetry formalism22 (Fig 9b). The intensities are consistent with a decrease in tilt angle from aromatic rings nearly coplanar to the substrate in very thin layers to roughly isotropic above 2 cycles. It should be noted that the penetration depth for soft NEXAFS is substantially smaller than that of FTIR, so these results are consistent with the FTIR observations of a rapid decrease in orientation at higher cycle numbers.

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**Figure 9:** a) Schematic of the NEXAFS geometry of the angle-dependent partial electron yield measurement. The sample is rotated to align to sample normal in the beam polarization direction. b) Fit of the anisotropy from Figure 10 to the vector orbital symmetry formalism (ref. 17, eq. 9.16a), where alpha is the aromatic ring tilt, defined as the angle between the ring normal vector (the 1s → pi\* transition dipole of the aromatic system) and the substrate plane, which shows extreme in-plane alignment in the first half-cycle and gradually progresses to a lack of orientation in thicker films.



**Figure 10:** NEXAFS measurements of thin mLbL polyamide films. Normalized spectra for various cycle numbers ranging from 0.5 cycles to 20 cycles. The difference between the 70° and 33° spectra, particularly in the strong peak near 285.5 eV, is attributed to the orientation of the aromatic components in the film. The decreasing orientation is seen above a few cycles, suggesting that the strongest orientation is in the first few layers of the polyamide film.

The C=O bond and aromatic rings are not shown to be coplanar; hence more work is required to relate the two observed angles to each other by considering the bond angles and torsion within the polymer molecule. This analysis is hindered by the accuracy of tilt angle obtained for the C=O bond, which was influenced by changes in the free acid in the film and by the difficulty in accurately calculating the bond angles and torsion in these polymer systems. NEXAFS analysis was unable to distinguish between the tri-substituted and di-substituted rings in the polymer network, while FTIR could only accurately probe the di-substituted rings. A direct quantitative comparison of the tilt angles provided by these two methods is only valid under the assumption that the two rings are co-planar. As it is not possible to experimentally validate this assumption, computational work on the orientation of functional groups, with respect to each other and a surface, would provide interesting complimentary information to the work presented here.

CONCLUSIONS

Infrared spectroscopy can be used to quantitatively determine the orientation of amide C=O groups and di-substituted aromatic rings in model aromatic polyamide membranes. The average tilt angle for the MPD ring, with respect to the surface, demonstrates that at low cycle numbers the aromatic ring is close to surface parallel with an average tilt angle close to 6. This tilt angle gradually became more perpendicular to the wafer surface as the film thickness increases and becomes more isotropic. These results are supported by NEXAFS measurements, which show the aromatics rings being nearly coplanar to the substrate in very thin layers and transitioning to nearly isotropic above 2 cycles. The C=O group follows a similar trend where the average angle, with respect to the surface normal, being approximately 16° to 18° with very little deviation in the measured angle below 15 cycles, while exhibiting bigger variations for higher cycle numbers where the film was more isotropic.

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ASSOCIATED CONTENT

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

Details of the DFT simulations; details on assigning the aromatic ring vibrational modes; sample thickness and orientation data in table format

REFERENCES

(1) Fritzmann, C.; Löwenberg, J.; Wintgens, T.; Melin, T. State-of-the-Art of Reverse Osmosis Desalination. *Desalination* **2007**, *216* (1–3), 1–76. https://doi.org/10.1016/j.desal.2006.12.009.

(2) Petersen, R. J. Composite Reverse Osmosis and Nanofiltration Membranes. *J. Memb. Sci.* **1993**, *83* (1), 81–150. https://doi.org/10.1016/0376-7388(93)80014-O.

(3) Johnson, P. M.; Yoon, J.; Kelly, J. Y.; Howarter, J. a.; Stafford, C. M. Molecular Layer-by-Layer Deposition of Highly Crosslinked Polyamide Films. *J. Polym. Sci. Part B Polym. Phys.* **2012**, *50* (3), 168–173. https://doi.org/10.1002/polb.23002.

(4) Chan, E. P.; Lee, J.-H.; Chung, J. Y.; Stafford, C. M. An Automated Spin-Assisted Approach for Molecular Layer-by-Layer Assembly of Crosslinked Polymer Thin Films. *Rev. Sci. Instrum.* **2012**, *83* (11), 114102.

(5) Mulhearn, W. D.; Oleshko, V. P.; Stafford, C. M. Thickness-Dependent Permeance of Molecular Layer-by-Layer Polyamide Membranes. *J. Memb. Sci.* **2021**, *618*, 118637. https://doi.org/https://doi.org/10.1016/j.memsci.2020.118637.

(6) Mulhearn, W. D.; Stafford, C. M. Highly Permeable Reverse Osmosis Membranes via Molecular Layer-by-Layer Deposition of Trimesoyl Chloride and 3,5-Diaminobenzoic Acid. *ACS Appl. Polym. Mater.* **2021**, *3* (1), 116–121. https://doi.org/10.1021/acsapm.0c01199.

(7) Gu, J.-E.; Lee, S.; Stafford, C. M.; Lee, J. S.; Choi, W.; Kim, B.-Y.; Baek, K.-Y.; Chan, E. P.; Chung, J. Y.; Bang, J.; et al. Molecular Layer-by-Layer Assembled Thin-Film Composite Membranes for Water Desalination. *Adv. Mater.* **2013**, *25* (34), 4778–4782. https://doi.org/10.1002/adma.201302030.

(8) Chowdury, M. R.; Steffes, J.; Huey, B. D.; McCutcheon, J. R. 3D Printed Polyamide Membranes for Desalination. *Science* **2018**, *361* (6403), 682–686. https://doi.org/10.1126/science.aar2122.

(9) Zimudzi, T. J.; Feldman, K. E.; Sturnfield, J. F.; Roy, A.; Hickner, M. A.; Stafford, C. M. Quantifying Carboxylic Acid Concentration in Model Polyamide Desalination Membranes via Fourier Transform Infrared Spectroscopy. *Macromolecules* **2018**, *51* (17), 6623–6629. https://doi.org/10.1021/acs.macromol.8b01194.

(10) Tang, C. Y.; Kwon, Y.-N.; Leckie, J. O. Effect of Membrane Chemistry and Coating Layer on Physiochemical Properties of Thin Film Composite Polyamide RO and NF Membranes. *Desalination* **2009**, *242* (1–3), 149–167. https://doi.org/10.1016/j.desal.2008.04.003.

(11) Tang, C.; Kwon, Y.; Leckie, J. Probing the Nano- and Micro-Scales of Reverse Osmosis Membranes—A Comprehensive Characterization of Physiochemical Properties of Uncoated and Coated Membranes by XPS, TEM, ATR-FTIR, and Streaming Potential Measurements. *J. Memb. Sci.* **2007**, *287* (1), 146–156. https://doi.org/10.1016/j.memsci.2006.10.038.

(12) Chalmers, J.; Griffiths, P. *Handbook of Vibrational Spectroscopy*; 2001.

(13) Umemura, J.; Kamata, T.; Kawai, T.; Takenaka, T. Quantitative Evaluation of Molecular Orientation in Thin Langmuir-Blodgett Films by FT-IR Transmission and Reflection-Absorption Spectroscopy. *J. Phys. Chem.* **1990**, *94* (1), 62–67. https://doi.org/10.1021/j100364a009.

(14) Iida, K.; Imamura, Y.; Liao, C.; Nakamura, S.; Sawa, G. Evaluation of Molecular Orientation in Aromatic Polyimide Films by FT-IR Reflection Absorption Spectroscopy. *Polym. J.* **1996**, *28* (4), 352-356.

(15) Parikh, A. N.; Allara, D. L. Quantitative Determination of Molecular Structure in Multilayered Thin Films of Biaxial and Lower Symmetry from Photon Spectroscopies. I. Reflection Infrared Vibrational Spectroscopy. *J. Chem. Phys.* **1992**, *96* (2), 927. https://doi.org/10.1063/1.462847.

(16) Myers, T. L.; Francis, R. M.; Banach, C. A.; Burton, S. D.; Oeck, A. M.; Johnson, T. J.; Furstenberg, R.; Kendziora, C. A. Obtaining the Complex Optical Constants n and k via Quantitative Absorption Measurements in KBr Pellets. In *Chemical, Biological, Radiological, Nuclear, and Explosives (CBRNE) Sensing XX*; Guicheteau, J. A., Howle, C. R., Eds.; SPIE, 2019; Vol. 11010, pp 131–137. https://doi.org/10.1117/12.2519503.

(17) Musfeldt, J. L.; Tanner, D. B.; Paine, A. J. Method for the Determination of the Optical Properties of Highly Conjugated Pigments. *J. Opt. Soc. Am. A* **1993**, *10* (12), 2648–2657. https://doi.org/10.1364/JOSAA.10.002648.

(18) Hahner, G. Near Edge X-Ray Absorption Fine Structure Spectroscopy as a Tool to Probe Electronic and Structural Properties of Thin Organic Films and Liquids. *Chem. Soc. Rev.* **2006**, *35* (12), 1244–1255. https://doi.org/10.1039/B509853J.

(19) Peng, Q.; Efimenko, K.; Genzer, J.; Parsons, G. N. Oligomer Orientation in Vapor-Molecular-Layer-Deposited Alkyl-Aromatic Polyamide Films. *Langmuir* **2012**, *28* (28), 10464–10470. https://doi.org/10.1021/la3017936.

(20) Zimudzi, T. J.; Hickner, M. A. Signal Enhanced FTIR Analysis of Alignment in NAFION Thin Films at SiO 2 and Au Interfaces. *ACS Macro Lett.* **2016**, *5* (1), 83–87. https://doi.org/10.1021/acsmacrolett.5b00800.

(21) Allara, D. L.; Nuzzo, R. G. Spontaneously Organized Molecular Assemblies. 2. Quantitative Infrared Spectroscopic Determination of Equilibrium Structures of Solution-Adsorbed n-Alkanoic Acids on an Oxidized Aluminum Surface. *Langmuir* **1985**, *1* (1), 52–66. https://doi.org/10.1021/la00061a008.

(22) : Stöhr, J. *NEXAFS Spectroscopy*, 1st ed.; Springer-Verlag Berlin Heidelberg, 1992. https://doi.org/10.1007/978-3-662-02853-7.

(23) Elzein, T.; Brogly, M.; Schultz, J. Quantitative Calculation of the Orientation Angles of Adsorbed Polyamides Nanofilms. *Polymer (Guildf).* **2003**, *44* (13), 3649–3660. https://doi.org/10.1016/S0032-3861(03)00293-3.

(24) Kwon, Y.-N.; Leckie, J. O. Hypochlorite Degradation of Crosslinked Polyamide Membranes: II. Changes in Hydrogen Bonding Behavior and Performance. *J. Memb. Sci.* **2006**, *282* (1–2), 456–464. https://doi.org/10.1016/j.memsci.2006.06.004.

(25) Abbott, N. B.; Elliott, A. Infra-Red Spectrum and Dichroism of Crystalline Acetanilide. *Proc. R. Soc. London A Math. Phys. Eng. Sci.* **1956**, *234* (1197), 247–268.

(26) Mahalakshmi, G.; Balachandran, V. FT-IR and FT-Raman Spectra, Normal Coordinate Analysis and Ab Initio Computations of Trimesic Acid. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2014**, *124*, 535–547. https://doi.org/10.1016/j.saa.2014.01.061.

(27) Cheam, T. C.; Krimm, S. Infrared Intensities of Amide Modes in N‐methylacetamide and Poly(Glycine I) from Abinitio Calculations of Dipole Moment Derivatives of N‐methylacetamide. *J. Chem. Phys.* **1985**, *82* (4).

(28) Katritzky, A. R.; Simmons, P. 414. Infrared Absorption of Heteroaromatic and Benzenoid Six-Membered Monocylclic Nuclei. Part VIII.-Meta-Disubstitiuted Benzenes. *J. Chem. Soc.* **1959**, No. 0, 2058–2062. https://doi.org/10.1039/JR9590002058.

(29) Katritzky, A. R.; Jones, R. A. 416. Infrared Absorption of Substituents in Aromatic Systems. Part II. Acylamino-Compounds. *J. Chem. Soc.* **1959**, No. 0, 2067–2071. https://doi.org/10.1039/JR9590002067.

(30) Varsanyi, G. *Vibrational Spectra of Benzene Deivatives*; Academic press: London, 1969.

(31) Tsuboi, M.; Kubo, Y.; Akahane, K.; Benevides, J. M.; Thomas, G. J. Determination of the Amide I Raman Tensor for the Antiparallel β-Sheet: Application to Silkworm and Spider Silks. *J. Raman Spectrosc.* **2006**, *37* (1–3), 240–247. https://doi.org/10.1002/jrs.1452.

(32) Wu, S.; Zheng, G.; Lian, H.; Xing, J.; Shen, L. Chlorination and Oxidation of Aromatic Polyamides. I. Synthesis and Characterization of Some Aromatic Polyamides. *J. Appl. Polym. Sci.* **1996**, *61* (3), 415–420. https://doi.org/10.1002/(SICI)1097-4628(19960718)61:3<415::AID-APP3>3.0.CO;2-L.

(33) Larkin, P. *Infrared and Raman Spectroscopy; Principles and Spectral Interpretation*; 2011.

(34) Katritzky, A. R.; Sinnott, M. V; Tidwell, T. T.; Topsom, R. D. Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. V. Ortho- and Meta-Disubstituted Benzenes. Nu16 Band near 1600 Cm.-1. *J. Am. Chem. Soc.* **1969**, *91* (3), 628–636. https://doi.org/10.1021/ja01031a019.

(35) Scherer, J. R. Group Vibrations of Substituted Benzenes—II. Planar CH Deformations and Ring Stretching and Bending Modes of Chlorinated Benzenes. *Spectrochim. Acta* **1965**, *21* (2), 321–339. https://doi.org/10.1016/0371-1951(65)80013-3.

(36) Scherer, J. R. Group Vibrations of Substituted Benzenes—I. *Spectrochim. Acta* **1963**, *19* (3), 601–610. https://doi.org/10.1016/0371-1951(63)80124-1.

(37) Miyazawa, T.; Shimanouchi, T.; Mizushima, S. Normal Vibrations of N‐Methylacetamide. *J. Chem. Phys.* **1958**, *29* (3).

(38) Green, J. H. S. Vibrational Spectra of Benzene Derivatives—VIII: M-Disubstituted Compounds. *Spectrochim. Acta Part A Mol. Spectrosc.* **1970**, *26* (7), 1523–1533. https://doi.org/10.1016/0584-8539(70)80213-6.

(39) Green, J. H. S.; Harrison, D. J.; Kynaston, W. Vibrational Spectra of Benzene Derivatives—XI1 1,3,5- and 1,2,3-Trisubstituted Compounds. *Spectrochim. Acta Part A Mol. Spectrosc.* **1971**, *27* (6), 793–806. https://doi.org/10.1016/0584-8539(71)80158-7.

(40) Barth, A.; Zscherp, C. What Vibrations Tell about Proteins. *Q. Rev. Biophys.* **2002**, *35* (4), 369–430. https://doi.org/10.1017/S0033583502003815.