

In Situ Nanoscale Characterization of Water Penetration through Plasma Polymerized Coatings

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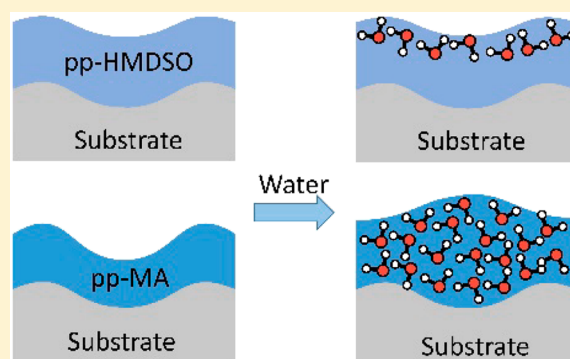
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Supporting Information

ABSTRACT: The search continues for means of making quick determinations of the efficacy of a coating for protecting a metal surface against corrosion. One means of reducing the time scale needed to differentiate the performance of different coatings is to draw from nanoscale measurements inferences about macroscopic behavior. Here we connect observations of the penetration of water into plasma polymerized (PP) protective coatings and the character of the interface between the coating and an oxide-coated aluminum substrate or model oxide-coated silicon substrate to the macroscopically observable corrosion for those systems. A plasma polymerized film from hexamethyldisiloxane (HMDSO) monomer is taken as illustrative of a hydrophobic coating, while a PP film from maleic anhydride (MA) is used as a characteristically hydrophilic coating.

The neutron reflectivity (NR) of films on silicon oxide coated substrates shows that water moves more readily through the hydrophilic PP–MA film. Off-specular X-ray scattering indicates the PP–MA film on aluminum is less conformal with the substrate than is the PP–HMDSO film. Measurements with infrared–visible sum frequency generation spectroscopy (SFG), which probes the chemical nature of the interface, make clear that the chemical interactions between coating and aluminum oxide are disrupted by interfacial water. With this water penetration and interface disruption, macroscopic corrosion can occur much more rapidly. An Al panel coated with PP–MA corrodes after 1 day in salt spray, while a similarly thin (~30 nm) PP–HMDSO coating protects an Al panel for a period on the order of one month.



■ INTRODUCTION

Plasma enhanced chemical vapor deposition (PECVD)¹ is a versatile technique used to deposit plasma polymerized thin films on various substrates for a wide range of applications, including surface modifications,^{2–4} biomedical sensors,^{5–7} and protection of metal against corrosion.^{8–13} During the deposition process, organic monomers are vaporized and flow into a vacuum chamber. When the vaporized monomers are energized using a high-frequency electric field to form a plasma, they are fragmented into radicals, ions, and electrons which react with each other to form a thin film on a substrate with which the stream of activated species collides. Compared to conventional polymer coatings, plasma polymerized coatings have higher cross-link densities and better adhesion to substrates.¹ In addition, PECVD is not a conventional organic solvent based process, so it has much lower VOCs emissions and is more environmentally friendly. To bring the potential of plasma polymerized coatings to bear on the important problem

of corrosion,^{8–13} it is necessary to better understand their detailed structures and interactions with water.

When a corrosion-resistant coating is exposed to a humid environment or water, water molecules can penetrate to the coating/metal interface through the bulk coating or along the interface.^{14,15} The incorporation of water at the interface decreases adhesion and causes coating failure by interrupting the interfacial interactions between the coating and substrate.¹⁶ Understanding the interface between the coating and substrate under both dry and wet conditions is important for designing improved protective coatings and adhesive joints. Previous research has focused on measuring corrosion resistance of plasma polymerized coatings with electrochemical impedance spectroscopy (EIS)^{8,9,17} and the salt spray test.^{18,19} Vautrin-Ul et al.⁸ considered protecting iron panels using plasma

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polymerized coatings from a widely studied precursor, hexamethyldisiloxane (HMDSO), mixed with oxygen in four ratios and characterized their effectiveness with EIS. EIS and salt spray measurements are time-consuming and do not resolve where the water is and what the structure of the water is (e.g., its coordination through hydrogen bonding). Moreover, EIS experiments are sensitive to tiny flaws in the coating, which can cause large errors when the coatings are thin. Only a few studies^{20,21} have been done on the water transport through plasma polymerized coatings on a nanoscale, and these have not investigated the structure of interfacial water between the plasma polymerized coating and the substrate.

Neutron reflectivity (NR) is exquisitely sensitive to film structure in the direction normal to the substrate. Furthermore, NR is suitable to investigate deuterated water (D_2O) penetration into the plasma polymerized films on smooth Si substrates because of the high contrast between the film and D_2O . Nelson and co-workers²⁰ used NR to investigate the water response of hydrophilic allylamine (AA) and hydrophobic HMDSO plasma polymerized coatings deposited on oxide coated Si wafers. They found that the hydrophilic PP-AA swelled by approximately $\sim 5\%$ in thickness when in contact with D_2O , and the hydrophobic PP-HMDSO had no thickness change. While the scattering length density (SLD) of the PP-HMDSO increased when in contact with water, they attributed this change to a small degree of proton exchange, but not penetration of water into the film. Blanchard et al.²¹ also investigated with NR the response in a humid environment of plasma polymerized coatings deposited with HMDSO and HMDSO/ O_2 mixtures on oxide coated Si wafers. The incorporation of oxygen monomer with HMDSO caused the PP film character to change from hydrophobic to hydrophilic and caused the water to penetrate more readily into the film as the chemical structure of the film more closely approximated that of PP-SiO_x.

In reflectivity studies, the incident angle, θ , with respect to the surface is equal to the angle of detection with respect to the surface. We probe the “specular” scattering. Because in the measurement of the specular reflectivity the scattering vector is always normal to the surface, the variation in specular reflectivity with incident angle provides the laterally averaged depth profile of the sample structure and composition along the surface-normal direction. Reflectivity measurements do not provide direct information on the structure of a film in the in-plane direction. The in-plane structure can be probed using off-specular scattering, a general term encompassing several techniques in which the incident and exit angles are varied to access scattering vectors with a nonzero in-plane component.^{22–27} Off-specular scattering has the following advantages over techniques commonly used to study in-plane structure by surface imaging. First, it provides global statistical information about the surface, and second it can provide such information about buried interfaces. Sinha et al.²⁴ monitored the development of electrochemically induced pitting on a Cu electrode in an electrolyte solution with off-specular X-ray scattering. They saw that the scattering adjacent to the specular peak broadened with time and inferred that the density of pits increased with time. Stamm and co-workers²⁶ examined the dewetting of polymer thin films on silicon substrates at various temperatures using off-specular X-ray scattering. Detector scans, in which the incident angle was held constant and the scattering at various detector angles measured, showed fringes for films as spun-cast, indicating conformality of the films with

the underlying substrates. These fringes vanished after heating above the polymer’s glass transition temperature, indicating a loss of conformality.

The structure of water at interfaces that is critical for understanding adhesion and corrosion has been characterized with sum frequency generation spectroscopy (SFG),²⁸ which is a second-order nonlinear and interface sensitive technique.²⁹ Under the dipole approximation, SFG is only active where there is a breakdown in inversion symmetry such as at surfaces and interfaces. Briefly, SFG spectroscopy involves two incident beams: a visible beam and a tunable IR beam overlapping temporally and spatially on the sample and generating a sum frequency signal at the interface. The intensities and positions of peaks in an SFG spectrum from an interface provide information on the chemistry and orientation of molecules at that interface. Chen et al.³⁰ investigated the interface between an epoxy layer and a polymer layer with SFG and correlated the interfacial structures probed by SFG with the adhesion strengths measured for the corresponding interfaces. Jing and co-workers²⁸ have probed with SFG the water structure at an interface between polyurethane and sapphire (aluminum oxide) upon exposure to liquid water or water vapor as a function of relative humidity. When the sample was exposed to liquid water, the interfacial water existed in the form of a hydrogen-bonded water network and disrupted film/substrate interactions evidenced by the SFG spectrum before exposure to water.

In this study we consider plasma polymerized films from two quite different precursors. The first, HMDSO, provides films already widely considered as impermeable coatings and used in many applications where barrier properties are required.^{8–13} Plasma polymerized films of maleic anhydride (MA), on the other hand, are of particular interest in the biomaterials area due to the reactive functional groups in the structure.^{31,32} Films of the first precursor are relatively hydrophobic, and those of the second are hydrophilic; this difference would be expected to result in quite different behavior in the management of water coming to the film. The penetration of water through these two types of PP films is characterized on the nanoscale on relatively short time scales on model oxide coated silicon substrates using NR to take advantage of the particularly clear features (fringes) in the reflectivity curves seen with PP films on these very smooth silicon substrates. The aluminum films that could be deposited on silicon wafers in this work have microroughnesses large enough that fringes in the reflectivity curves are strongly obscured. However, this same microroughness leads to stronger scattering in off-specular X-ray scattering, making it easier to see with that technique in-plane structure changes. The aluminum films always have their native oxide when the PP film is deposited, and measurements with SFG, which focus on chemistry at the interface, rather than morphology, are also done for PP film/aluminum oxide interfaces using sapphire substrates. The insights into the water behavior on the nanoscale are then successfully correlated to the macroscopic corrosion behaviors of the PP-HMDSO and PP-MA films on Al panels.

■ EXPERIMENTAL SECTION

Substrates. Ultraflat, single-crystal silicon wafers (3 in. diameter, 5 mm thick), purchased from El-Cat, were used for reflectometry measurements. Smaller, 2×1 cm² wafers, 0.7 mm thick, were used as substrates for X-ray photoelectron spectroscopy (XPS) and water contact angle characterization. Plasma polymerized coatings for off-

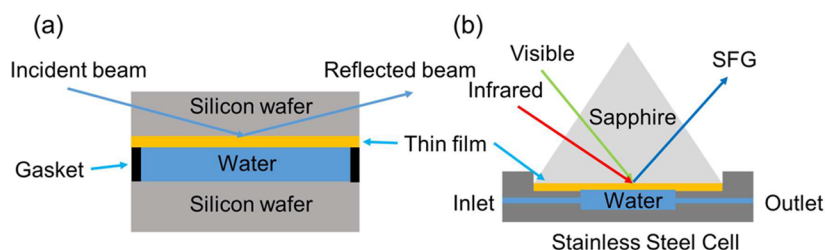


Figure 1. Water cells for (a) NR measurement and (b) SFG measurement. For both cells, liquid water can only penetrate through the coating surface, not through the coating edge.

specular X-ray measurements were deposited on silicon wafers covered with 45 nm thick Al layers deposited using dc magnetron sputtering at the NIST Nanofab. Sapphire (aluminum oxide) prisms with the *c*-axis parallel to the prism face were purchased from Meller Optics. Plasma polymerized coatings deposited on sapphire were used for SFG experiments. Both silicon wafers and sapphire prisms were cleaned with boiling piranha³³ solution (70 vol % H₂SO₄ in concentrated H₂O₂) for 30 min. The substrates were thoroughly rinsed with DI water and blown dry with nitrogen gas.

Plasma Polymerization. Two different plasma coatings were deposited in a custom-built, inductively coupled and rf-driven ($f = 13.56$ MHz) reactor.³⁴ The cylindrical vacuum chamber (reactor) was wound around by a coil which was connected to the generator through an impedance matching network. A roughing pump was connected to the vacuum chamber through a liquid nitrogen cold trap. A pressure gauge at the outlet of the chamber monitored the vapor pressure. The base pressure in the chamber was less than 2 Pa. The liquid precursor reagent was contained in a glass tube connected to the reactor chamber through a manually controlled valve. For HMDSO (Sigma-Aldrich), this valve was opened so that HMDSO vaporized and moved into the chamber to bring the chamber vapor pressure to 27 Pa. This pressure was held for 10 min while continuing to pump the chamber so that a sufficient fraction of the gas in the chamber vapor was HMDSO. The plasma was ignited after the pressure was reduced to about 8 Pa by partially closing the valve on the precursor supply. The input power for plasma polymerization was 35 W, and deposition occurred over 20 min. After deposition, the pressure in the chamber was kept at 8 Pa for another 5 min by continuing to provide HMDSO vapor into the chamber to prevent reaction between unreacted radicals in the film and air. For deposition of a different film from the monomer MA (Sigma-Aldrich), the pressure in the chamber was adjusted to 12 Pa. The input power for plasma polymerization was 35 W, and the treatment time was 20 min. After deposition, the chamber pressure was kept at 11 Pa for another 5 min by continuing to provide MA vapor to prevent reaction between air and unreacted radicals.

X-ray Photoelectron Spectroscopy and Infrared Spectroscopy. The XPS spectra were obtained using a Versa Probe II Scanning XPS Microprobe from Physical Electronics (PHI) under ultrahigh vacuum (2.0×10^{-6} Pa). Automated dual beam charge neutralization was used during sample analysis to reduce surface charging. The analyzer pass energy was 117.4 eV for the survey spectra. Survey scans in the range 0–1000 eV were used to evaluate the percentage of different atoms present on the surfaces of the samples. Each spectrum was collected using a monochromatic Al *Kα* X-ray beam ($E = 1486$ eV) over a 200 μm diameter probing area with a beam power of 50 W.

Infrared spectroscopy measurements were performed using a Thermo Nicolet 6700 Fourier transform infrared spectrometer (FTIR) equipped with a mercury–cadmium–tellurium (MCT) detector. The spectrum for PP–HMDSO was collected using transmission geometry with the PP–HMDSO thin film deposited on CaF₂. The spectrum for PP–MA was collected using an ATR geometry with the PP–MA thin film deposited on a silicon crystal.

Reflectometry Measurements. X-ray reflectometry (XR) data were obtained on a spectrometer mounted on a rotating anode source³⁵ (Rigaku, RA-HF 18) using a wavelength of 1.54 Å. The

scattering vector had only a component in the *z* direction, q_z , which is normal to the sample surface. The spectrometer resolution in q_z was 0.01 nm^{-1} . Background scattering was measured using longitudinal diffuse scans and subtracted from the overall measured intensity to yield specular intensity.

NR data were measured at fixed neutron wavelength ($\lambda = 5.001 \pm 0.003$ Å) on the MAGIK³⁶ spectrometer at the National Institute of Standards and Technology National Center for Neutron Research in Gaithersburg, MD. Specular neutron reflectivity was measured from $q_z = 0$ to 0.2 Å^{-1} . Background scans were collected over the same range of q_z . The data were reduced using programs from the Reflpack suite³⁷ and analyzed with Motofit.³⁸ Plasma polymerized films deposited on silicon wafers with their native oxide layers were measured first in the “as-deposited” state with XR and NR. For the experiments of water penetration through the plasma polymerized coatings, the samples were assembled in a wet cell, shown in Figure 1a, and then measured with NR. The assembled sample cell was mounted with a vertical orientation. The incident beam was collimated with slits which were opened with increasing θ to keep the illuminated sample surface area approximately constant and directed through the silicon substrate before the beam impinged on the PP film/silicon interface. The detector acceptance angle was determined with slits that were similarly opened with increasing θ to permit detection of all specular scattering.³⁶

Sum Frequency Generation Spectroscopy. SFG is a second-order nonlinear optical technique sensitive to the orientation and concentration of interfacial molecules. SFG spectra were acquired with a picosecond Spectra-Physics laser system producing a tunable IR beam over 2000–3800 cm^{-1} with 1 ps pulse width, 1 kHz repetition rate, and a beam diameter of 100–200 μm , together with a visible beam of 800 nm, 1 ps pulse width, 1 kHz repetition rate, and diameter of 1 mm.³⁹ The SFG spectra were measured by scanning the IR range from 2000 to 3800 cm^{-1} . A 200 nm thick film of uncured polyurethane (PU) purchased from Sigma-Aldrich was spun-cast on the plasma coated sapphire to obtain a total sample thickness so that the signal came from the desired interface.²⁸ Water penetrated this 200 nm thick PU film easily in a previous study,²⁸ so resistance to movement of water through the PU coating did not dictate the outcome of our experiments. Based on calculations using Snell’s law for total internal reflection, an incident angle with respect to the surface normal of the sapphire prism face of 5° was used to probe specifically the plasma polymerized coating/sapphire interface. The polarization combination used for spectra reported here was PPP (p-polarized SFG output, p-polarized visible input, and p-polarized IR input). The resulting spectra were fit using the Lorentzian equation

$$I_{\text{SFG}} \propto \left| \chi_{\text{eff, NR}} + \sum \frac{A_q}{\omega_{\text{IR}} - \omega_q - i\Gamma_q} \right|^2 \quad (1)$$

where $\chi_{\text{eff, NR}}$ describes the nonresonant contribution. A_q , Γ_q , ω_{IR} , and ω_q are the amplitude, damping constant, scanning frequency of the incident IR beam, and angular frequency of the q^{th} vibrational resonance, respectively.

A wet cell for SFG experiments, shown in Figure 1b, was used previously to study water penetration through polyurethane.²⁸ The stainless-steel cell was cleaned by sonicating in toluene and ultrapure

water for 1 h and dried with N_2 gas. The apparatus prevents water incursion into the sapphire interface from the edge and loss of water during experiments.

Off-Specular X-ray Scattering. Off-specular X-ray scattering scans were performed using a wavelength of 1.03 Å at the 33-BM beamline⁴⁰ at the Advanced Photon Source of the Argonne National Laboratory. Measurements of “dry” samples were done before exposing samples to water. Measurements of “wet” samples were performed by exposing sample to liquid water for 12 h, drying them off with nitrogen gas, and then measuring in air. The “detector scans” were performed with a fixed beam incident angle. The scattering over a range of exit angles was captured with a CCD camera. For these off-specular scattering measurements, both q_z and a scattering vector value in the sample surface plane along the direction of the beam, q_{xz} were defined. A line cut was performed for each 2-D scattering pattern along the q_z direction for $q_{xz} = 0$ using a MATLAB program.⁴¹

Salt Spray Test-ASTM B117. The plasma polymerized coatings were deposited onto Al 3003 panels (Q-lab) for the salt spray test. Before deposition, the Al panels were cleaned with acetone (ACS grade) three times. The thicknesses of the coatings were around 30 nm, similar to those of coatings used for NR and SFG study. The salt spray test was performed according to the ASTM B117 standard using a sodium chloride concentration of 5 wt %, temperature of 35 °C, and flow rate of 0.7 L/h.

RESULTS AND DISCUSSION

Chemical Structure of Plasma Coatings. XPS, FTIR, and water contact angle results show clear differences in the compositions and surface characters of the two plasma polymerized coatings. The XPS results for two films deposited on silicon wafers are summarized in Table 1. Analysis of the

Table 1. Dry State Film Atomic Compositions for PP-HMDSO and PP-MA Films and Calculated Compositions of the Corresponding Precursors

sample	atomic % composition		
	C 1s	O 1s	Si 2p
HMDSO monomer ^a	66.7	11.1	22.2
PP-HMDSO ^b	54.2 ± 0.5	27.3 ± 0.4	18.5 ± 0.1
MA monomer ^a	57.1	42.9	
PP-MA ^b	66.2 ± 0.5	33.9 ± 0.5	

^aCalculated from monomer structure. ^bErrors represent one standard deviation.

XPS data reveals that the chemical composition of each plasma polymerized film differs from that of its monomer. While the C/O and C/Si ratios for HMDSO monomer are 6 and 3,

respectively, for the PP-HMDSO film the ratios are around 2 and 3, respectively. FTIR results shown in Figure 2a provide information on the film's bulk structure and reveal that the PP-HMDSO coating has –OH bonds, as indicated by vibrations at 3350 and 1620 cm^{-1} . The oxygen incorporation during the plasma polymerization may be due to some residual air or water left in the reactor chamber and postplasma oxidation reactions upon exposure of the film to ambient atmosphere.⁴² The FTIR spectrum shows that the bulk structure of PP-HMDSO has Si–O–Si bonds, corresponding to the strong band at 1060 cm^{-1} , Si(CH₃)_x groups, identified through bands at 1260 and 800–900 cm^{-1} , and –CH₃ and –CH₂–, evidenced by bands at 2850–2950 cm^{-1} .¹⁷ The differences between the chemical compositions of the film and precursor suggest that methyl abstraction is a major fragmentation/activation pathway during plasma polymerization. The water contact angle for PP-HMDSO is $92 \pm 2^\circ$, so the coating is hydrophobic. For our purposes here we take the transition from hydrophilic to hydrophobic to correspond to 90° .⁴³

While the C/O ratio from XPS is 1.3 for the MA monomer, it is 2 for the PP-MA film. The FTIR spectrum (Figure 2b) shows that the PP-MA film is rich in carbonyl groups (1730 cm^{-1}) and CH₂ groups (2950 cm^{-1}).⁴⁴ The water contact angle for PP-MA is $42 \pm 2^\circ$, so the film is hydrophilic. These two plasma polymerized coatings have distinctly different surface and bulk structures and characters.

Characterization of Dry Plasma Polymerized Films.

While XPS only probes the top 10 nm of the plasma films and FTIR gives only information on bulk composition, XR and NR measurements assess the whole scattering length density depth profiles of these plasma polymerized films. The XR and NR results for dry PP-HMDSO and PP-MA are shown in Figures 3a and 4a, respectively. These curves have features common to all the reflectivity curves collected and analyzed in this study. The fringes observed are called Kiessig fringes and are caused by interference of X-ray or neutron beams reflected at different interfaces. The spacing of these Kiessig fringes varies inversely with the thickness of the plasma polymerized film, while the amplitude of the fringes is related to the contrasts at the interfaces.^{22,45} The low-amplitude fringes in the PP-MA result from low neutron scattering contrast between the PP-MA film and air.

Details of the film structure are obtained from each curve by nonlinear regression of the data. The reflectivity curve calculated from an assumed model is compared to the data,

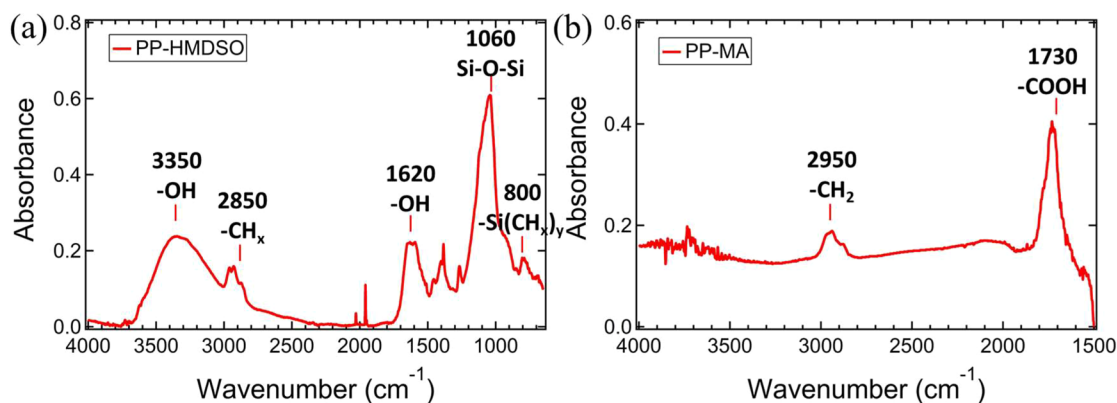


Figure 2. FTIR results for (a) PP-HMDSO film and (b) PP-MA film.

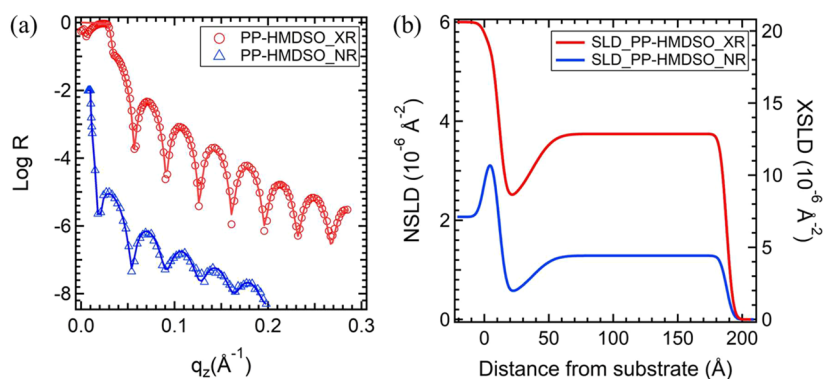


Figure 3. (a) XR (circles) and NR (triangles) results for dry PP-HMDSO, with model fits shown as solid curves. (b) SLD depth profiles corresponding to the fits to the XR (XSLD for X-ray scattering length density) and NR (NSLD for neutron scattering length density) curves shown in (a).

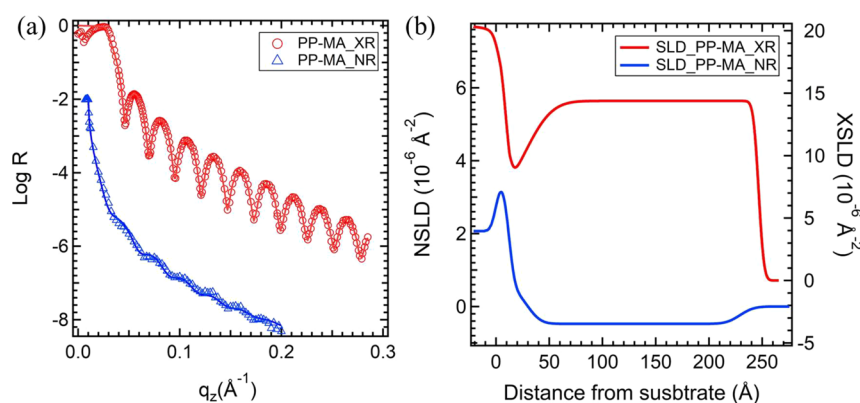


Figure 4. (a) XR (circles) and NR (triangles) results for dry PP-MA, with model fits shown as solid curves. (b) SLD depth profiles corresponding to the fits to the XR (XSLD for X-ray scattering length density) and NR (NSLD for neutron scattering length density) curves shown in (a).

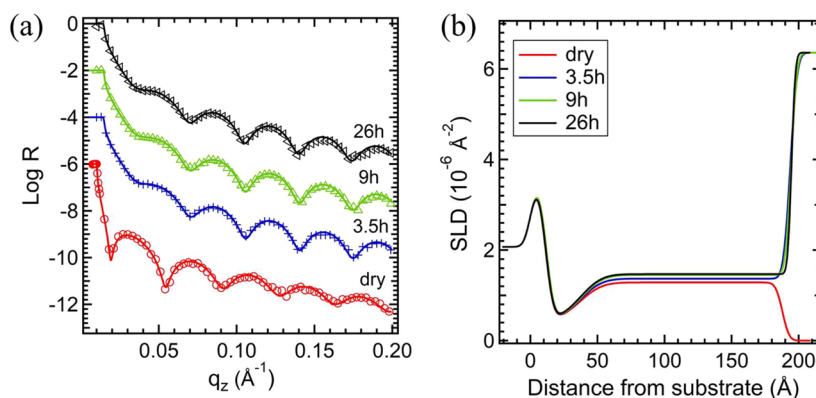


Figure 5. (a) NR curves for a PP-HMDSO film exposed to D_2O for different times (data are open symbols with solid lines represent best model fits), with (b) the SLD depth profiles corresponding to the model fits in (a). The reflectivity curves are offset for clarity.

and then the parameters in the model varied until the best agreement between model and data is achieved.²² The fitting provides a model of the film structure expressed in the form of a one-dimensional profile of SLD as a function of depth. The SLD depth profiles corresponding to the XR and NR are shown in Figures 3b and 4b. Two steps are used in building the SLD profile. First, an approximate “box” model is constructed by assuming the film to be a stack of ideal layers, with each layer having a uniform SLD. The interface between each pair of ideal layers is infinitely sharp. To account for the microroughness at each interface MOTOFIT uses the approach of Nevot and Croce⁴⁶ to attenuate the calculated reflection to a degree

parametrized using the roughness parameter σ . For both films and both the XR and NR curves, using just one layer (as shown in Supporting Information Figure S1) to represent the plasma polymerized coating did not fit the data well. Self-consistently fitting the XR and NR data provided multiple pieces of information. First, it allowed us to infer the empirical compositions and density for the “bulk” portion of each film. For the PP-HMDSO film the empirical composition was $\text{Si}_{20}\text{C}_{60}\text{O}_{30}\text{H}_{104}$ and mass density 1.43 g/cm^3 . For the PP-MA film, the composition was $\text{C}_{20}\text{O}_{10}\text{H}_{58}$ and the density was 1.5 g/cm^3 . Second, fitting XR and NR self-consistently showed a thin transition layer in the film at the substrate surface was

required.³⁵ The film was not perfectly uniform with depth. Thus, the model was composed of silicon substrate, native silicon oxide layer, transition layer, “bulk” plasma coating layer, and dry air. This bilayer model is similar to that used by Blanchard et al.,²¹ who required three layers to fit their dry PP-HMDSO films’ experimental data. Kim and co-workers³⁵ have reported that PP-octafluorocyclobutane coatings also have a molecularly thin transition layer next to the substrate due to a transient in the deposition before steady-state plasma polymer deposition is established. It was not possible to rationalize the transition layer simply as a region of reduced mass density. Reducing the density in the same way for models of both data sets from the bulk value did not fit the SLD profiles. Thus, probably the material in the transition layer varies both in composition and in density.

Water Penetration through Plasma Polymerized Films. The behaviors of the two plasma polymerized coatings in water were characterized *in situ* using NR with the samples against liquid D₂O at ambient temperature. NR results for a PP-HMDSO film exposed to D₂O are shown in Figure 5a, with the SLD depth profiles for the PP-HMDSO coating exposed to D₂O for different times shown in Figure 5b. In the models for the PP-HMDSO film exposed to D₂O, the thickness and SLD of the bulk layer were varied to obtain the best fits. The thicknesses and SLDs of the bulk PP-HMDSO layer after different exposure times are summarized in Table 2.

Table 2. Parameters of PP-HMDSO Thin Films after Exposure to Water for Various Times^a

	thickness of PP-HMDSO (nm)	SLD of PP-HMDSO ($10^{-6} \text{ \AA}^{-2}$)	χ^2
dry	15.06 ± 0.04	1.28 ± 0.02	0.005
3.5 h	15.65 ± 0.02	1.37 ± 0.06	0.003
9 h	15.66 ± 0.02	1.45 ± 0.08	0.005
26 h	15.74 ± 0.03	1.47 ± 0.08	0.006

^aErrors represent one standard deviation.

Both the SLD and thickness of the PP-HMDSO bulk layer increase over 26 h, indicating the D₂O (with SLD of $6.36 \times 10^{-6} \text{ \AA}^{-2}$) diffuses into the film. In principle, the SLD increase may also result from exchange of hydrogen by deuterium within the film, but since the film thickness increased slightly, it is clear that water does go into the coating. Our results may be compared to those of Nelson et al.,²⁰ who looked at a PP-HMDSO film next to water with NR. Their plasma

polymerization conditions were quite different, and thus the structure of their film differs from that of ours. The C/Si ratio for their PP-HMDSO film was 1.4 and for our film was 3. They concluded that in their case after an unspecified period of exposure to D₂O there was no change in coating thickness, and therefore the entire increase in SLD was attributed to an exchange of 6% of hydrogens in the entire film, without allowing for any D₂O to remain in the film. In our case the SLD increased by ca. 15%, but also the thickness increased by around 5%. Because the increase in SLD is higher than that in thickness, we propose that a small amount of water diffuses into porosity inside the cross-linked network of PP-HMDSO. Nonetheless, the thickness and SLD changes over 26 h are small, suggesting a small rate of water penetration into the PP-HMDSO.

The NR results and corresponding SLD profiles for a PP-MA coating exposed to D₂O for different times are shown in Figures 6a and 6b, respectively. The Kiessig fringes in the NR curve for PP-MA exposed to water in Figure 6a are not distinct due to the low contrast between the wet PP-MA film and D₂O and the much greater width of interface with D₂O after exposure. After the PP-MA sample was exposed to water for just 4 h, the bulk SLD and thickness have increased considerably compared with the case of PP-HMDSO, as shown in Figure 6b. The SLD in the “bulk” of the film and the PP-MA film thickness have reached a plateau and stopped increasing after 4 h. The PP-MA film absorbs water and swells very rapidly. The final film thickness is 1.5 times larger than the dry thickness, and the SLD is consistent with a D₂O content of 70 vol %.

Characterizing Water Structure at the Film/Substrate Interface. SFG provides details of the water structure at the coating/substrate interface, which is critical for understanding interfacial adhesion and corrosion. For the SFG measurements the substrate surface is that of sapphire, which is a form of aluminum oxide similar to the oxide on the Al metal substrate. Figure 7 shows the SFG spectra for the PP-HMDSO/sapphire interface with and without water present. There are four characteristic peaks at 2800, 2860, 2900, and 2960 cm^{-1} in the hydrocarbon region of the spectrum from the PP-HMDSO/sapphire interface, as shown in Figure 7a. These peaks are assigned to $\alpha\text{-CH}_2(\text{s})$ stretching, $\text{CH}_2(\text{s})$ stretching, $\text{CH}_3(\text{s})$ stretching, and $\text{CH}_3(\text{as})$ stretching, respectively.^{28,47} The intensities of the peaks in the hydrocarbon range have increased significantly after exposure to water due to a change

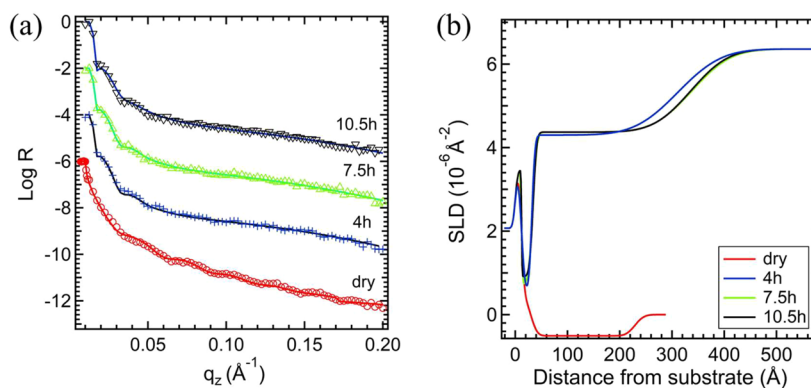


Figure 6. (a) NR curves for a PP-MA film exposed to D₂O for different times (data are open symbols with solid lines represent best model fits), with (b) the SLD depth profiles corresponding to the model fits in (a). The reflectivity curves are offset for clarity.

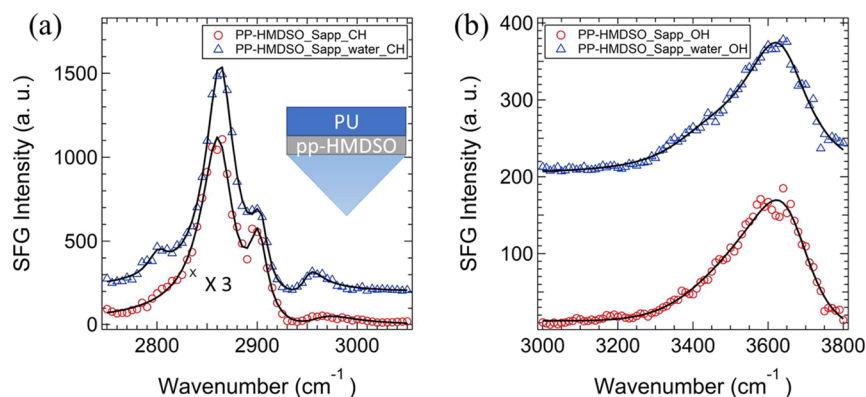


Figure 7. *In situ* SFG spectra for the PP-HMDSO/sapphire interface when the sample is dry (circles) and when sitting next to water (triangles): (a) CH region, (b) OH region. The solid lines are fits to the data points using eq 1. The spectra are shifted vertically for clarity. The sample geometry is shown in the inset.

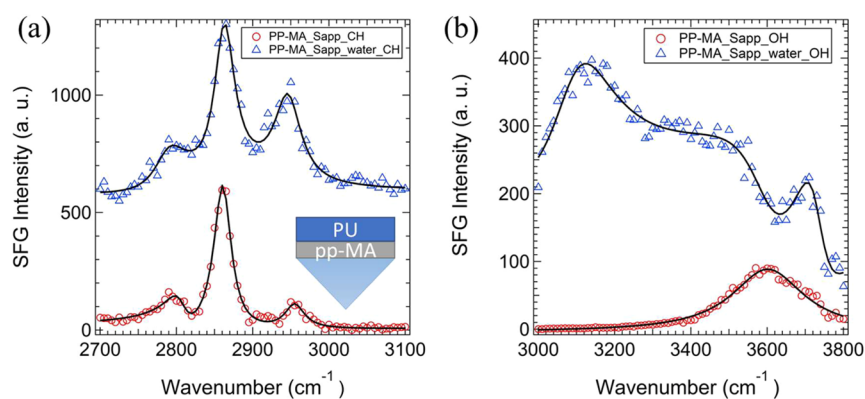


Figure 8. SFG results for the PP-MA/sapphire interface when the sample is dry (circles) and when it is sitting next to water (triangles): (a) CH region; (b) OH region. The solid lines are fits to the data points using eq 1. The spectra are shifted vertically for clarity. The sample geometry is shown in the inset.

in the Fresnel coefficient, but no change in structure is indicated. In Figure 7b are shown data for the OH region of the PP-HMDSO/sapphire interface in the dry state. The curve is fitted with two peaks at 3400 and 3600 cm^{-1} . The shoulder at 3400 cm^{-1} is tentatively assigned to the Si-OH group in PP-HMDSO. The 3600 cm^{-1} peak corresponds to the surface -OH groups of sapphire. The non-hydrogen-bonded free sapphire -OH peak is at 3720 cm^{-1} , so the shift of this peak to lower wavenumbers for the PP-HMDSO/sapphire interface is due to the acid-base interactions between the acidic surface -OH groups and the basic groups in the plasma polymerized film.⁴⁸ The SFG spectrum of the plasma coating/sapphire interface in the presence of water is also shown in Figure 7b. There are no peaks corresponding to water between 3000 and 3400 cm^{-1} , which means there is no water at the PP-HMDSO/sapphire interface. In addition, the fact that the peaks at 3400 and 3600 cm^{-1} are the same after exposure to water indicates that the acid-base interactions between PP-HMDSO and sapphire have not been disrupted by water. The result from SFG that no water has penetrated through the PP-HMDSO film to the interface is consistent with the results from NR, indicating that PP-HMDSO prevents water penetration to the interface over the time scale considered here.

The SFG spectra for the PP-MA/sapphire interface when the sample is dry and when it is sitting next to water are shown in Figure 8. In Figure 8a, the three peaks at 2800, 2860, and

2920 cm^{-1} in the hydrocarbon region are assigned to α -CH₂(s) stretching, CH₂(s) stretching, and CH₂(as) stretching modes, respectively.^{28,49} As in the case of the PP-HMDSO/sapphire interface, the intensities of the peaks in the hydrocarbon region during exposure to water have increased due to changes in the Fresnel coefficient. For the spectrum in Figure 8b for the dry state of the PP-MA/sapphire interface, the 3600 cm^{-1} peak corresponds to the surface -OH groups of sapphire in contact with the plasma film. The OH region for the SFG spectrum of the PP-MA/sapphire interface after the cell was filled with liquid water appears in Figure 8b. Two new peaks appear in this OH region at 3150 and 3450 cm^{-1} . They are assigned to strongly tetrahedrally coordinated H₂O and loosely coordinated H₂O hydrogen-bond stretches, respectively.⁵⁰⁻⁵³ The appearance of these peaks indicates that liquid water has penetrated through the plasma coating to the PP-MA/sapphire interface. Previous SFG studies^{28,54} of silica have shown that the hydrogen bonds between water and silanol (SiOH) groups on the silica contribute to the ordering of water. We propose that there are hydrogen bonds formed between water and the polar groups in PP-MA, such as the carboxyl groups, which enhances the magnitude of the 3150 cm^{-1} water peak with respect to the 3450 cm^{-1} water peak from the PP-MA/sapphire interface. In addition, the peak shifting from 3600 cm^{-1} back up to 3700 cm^{-1} represents the disruption by water of the acid-base interactions between the plasma coating and sapphire. This evidence for the presence of

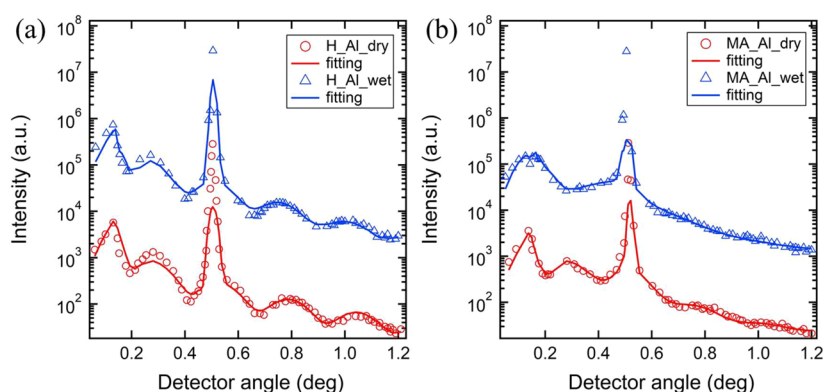


Figure 9. Off-specular X-ray scattering detector scans for (a) PP-HMDSO before and after exposure to water and (b) PP-MA before and after exposure to water. Solid line represents best fit in each case.

liquid water at the coating/substrate interface is consistent with the results from NR showing that water penetrates through the PP-MA coating to the coating/substrate interface.

Correlation between Surface and Substrate. While neutron specular reflectivity is sensitive to variation in water content of the sample perpendicular to the coating/substrate interface, off-specular scattering measurements probe the structure of the outer surface and the coating/substrate interface in the direction parallel to the interface.^{22,23,26,55}

The much higher flux available for X-rays than for neutrons makes X-ray off-specular measurements easier. Off-specular data from “detector scans” for the hydrophobic PP-HMDSO coating on Al coated silicon before and after exposure to water are shown in Figures 9a. The “Yoneda” peak at a detector angle of about 0.15° results from a resonance enhancement of the scattering from the roughnesses of the air surface and the coating/aluminum interface.²⁷ The sharp peak at a detector angle of about 0.5° is from the specular scattering, the radiation reflected from the surface at an angle equal to the incident angle. On either side of the specular peak in Figure 9a are fringes related to interference between radiation scattered from the outer surface and from the coating/aluminum interface, with the spacing of the fringes resulting from the coating thickness.²²

The “detector scan” curves can be analyzed quantitatively by fitting them with a distorted wave Born approximation model of the off-scattering that accounts for the lateral correlation of the interface height modulations within one interface and also accounts for the vertical correlation of the interface heights of two different interfaces.⁵⁶ We made the assumption that the air/plasma film interface and plasma film/aluminum oxide interfaces are the two key interfaces because the scattering contrasts across these two interfaces are the strongest. We further made the simplifying assumption that the roughness of each interface can be described using a self-affine random roughness model. In this case the function describing the height–height correlations between the two self-affine rough interfaces j and k is given as

$$C_{jk}(R) = \sigma_j \sigma_k \exp\{-(R/\xi)^{2h}\} \exp\{-|\mu_j - \mu_k|/\xi_{jk,\perp}\} \quad (2)$$

where R is the distance in-plane, σ_j and σ_k are the root-mean-square roughnesses, and μ_j and μ_k are the mean locations of interfaces j and k , respectively. The Hurst parameter, h , describes the jaggedness of the interface. Small values of h correspond to more jagged surfaces, while values of h

approaching unity model smooth surfaces. The quantity ξ is the lateral correlation length within the interface. For the interfaces here we find it has a value of order $10000 \text{ \AA}$. The quantity $\xi_{jk,\perp}$ is a vertical correlation length. If $\xi_{jk,\perp}$ is much larger than the distance $|\mu_j - \mu_k|$ between the two interfaces, they are perfectly correlated. The fitted curves are shown in Figure 9, and the corresponding model parameters summarized in Table 3. The overall shapes of the curves, the spacing of

Table 3. Model Parameters for Best Fits to “Detector Scans” for PP-HMDSO and PP-MA Films

sample	h	$\xi_{jk,\perp} (\mu\text{m})$	$\sigma (\text{\AA})$
PP-HMDSO dry	0.75 ± 0.13	>1	23.5
PP-HMDSO wet	0.35 ± 0.07	>1	22.3
PP-MA dry	0.18 ± 0.06	>0.1	18.2
PP-MA wet	0.17 ± 0.06	>0.01	19.1

the fringes, and the decay in amplitude of the fringes from below the specular peak to above the specular peak are captured well. There is no attempt in the modeling done here to fit the specular peak.

The definition of the fringes due to correlation between interfaces in the case of the dry PP-HMDSO coating is very good. The experimental data show a fringe to the left of the specular peak with fringe amplitude even somewhat stronger than that in the model. This good definition of the fringes indicates that the outer coating surface is highly conformal with the underlying aluminum surface,¹⁹ which has a roughness of about $20 \text{ \AA}$ rms. We are not able to provide a precise value of the vertical correlation parameter, $\xi_{jk,\perp}$, but we can determine the value of a lower bound for each fit. This is illustrated by the model curves for various values of $\xi_{jk,\perp}$, shown in Figure S2. For the dry PP-HMDSO coating $\xi_{jk,\perp} > 1 \mu\text{m}$, and after exposure to water the lower bound for $\xi_{jk,\perp}$ is the same. The fit to the data is very sensitive to the value of the Hurst parameter, as shown in Figure S3. Although the curve for PP-HMDSO after exposure to water does not seem to have changed much qualitatively from that for the dry sample, this sensitivity of the curve shape to the value of h is seen in a significant decrease in h needed to fit the PP-HMDSO data after exposure. Apparently, at least one of the two film interfaces has become jagged. Presumably the change is also readily seen because the original dry sample has relatively smooth interfaces.

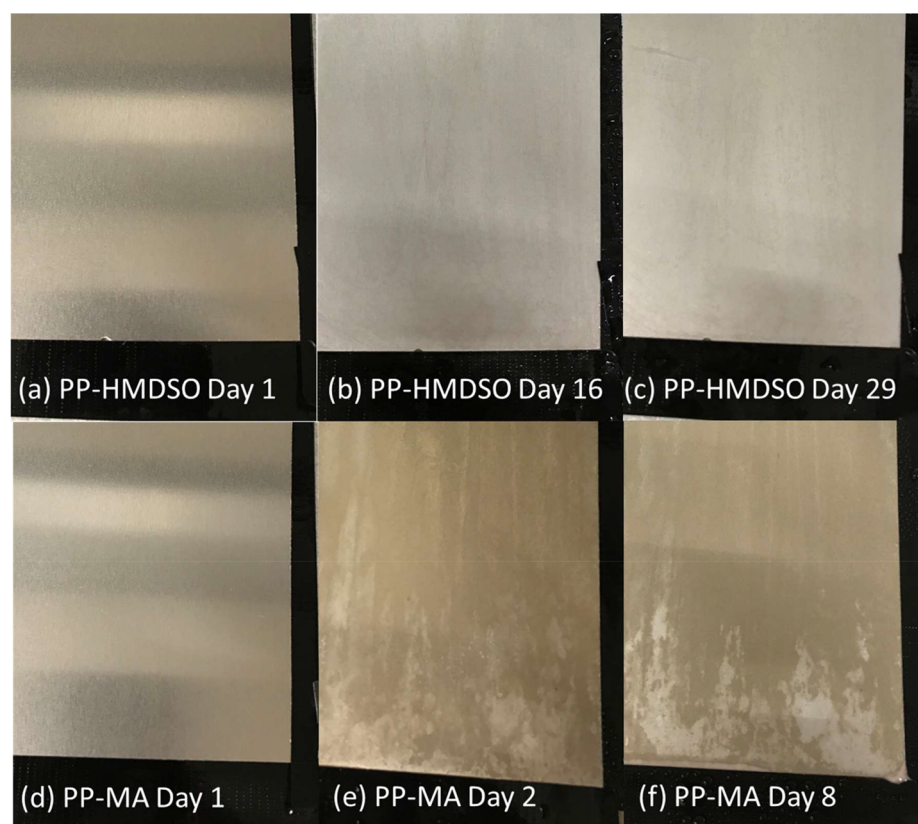


Figure 10. PP-HMDSO coating on Al panel at (a) day 1, (b) day 16, and (c) day 29 of salt spray exposure. PP-MA coating on Al panel at (d) day 1, (e) day 2, and (f) day 8 of salt spray exposure.

As in the case of the PP-HMDSO film, the scan for PP-MA on Al in the dry state presented in Figure 9b shows a Yoneda peak when the detector angle is near the critical angle and shows fringes between the Yoneda peak and the specular reflection. The fringes in the scan for the dry PP-MA, however, are not so clear as those seen for dry PP-HMDSO. These less well developed fringes indicate less conformality for the PP-MA film on Al. Indeed, the fits shown in Figure 9b and Figure S4 indicate that the original film has interfaces that are more jagged than those for PP-HMDSO (h of 0.18 rather than 0.75) and that the lower limit on $\xi_{jk,\perp}$ is lower for the PP-MA film, perhaps $0.1\ \mu\text{m}$. We conjecture that the conformalities of these films may depend on differences in the details of the deposition processes for these two monomers such as the degree to which reaction occurs in the gas phase versus on the surface of the substrate.⁵⁷ In Figure 9b, the scan for PP-MA on Al after exposure to water differs markedly from the scan obtained in the dry state. This change is primarily due to a drop in thickness of the PP-MA film with exposure to water and subsequent drying, presumably due to loss of material. Fitting suggests that the jaggedness of the interfaces changes little with exposure to water, but the degree of conformality appears to have degraded some with this exposure as the lower bound on the value of $\xi_{jk,\perp}$ does drop (see also Figure S4). The more jagged PP-MA film/oxide interface and less conformality between surface and underlying interface suggest a lower quality interface between protective coating and aluminum oxide that could give less corrosion protection to the Al substrate.

Determining Resistance to Corrosion. Plasma polymerized coatings deposited on Al panels were tested at the

macroscopic level in a salt spray chamber for a month. Before the samples were put into the chamber, both the PP-HMDSO and PP-MA film coated samples presented in Figures 10a and 10d were shiny and metallic in appearance. The very thin 30 nm plasma polymerized layers were not visible. The PP-HMDSO protected Al panel did not present any evidence of corrosion after 16 days of salt fog exposure, as shown in Figure 10b. In contrast, the PP-MA coated Al sample corroded only after 1 day exposure in the salt spray chamber, as shown in Figure 10e. The PP-HMDSO coated sample shown in Figure 10c lasted to day 29 without obvious corrosion. In that sense the salt spray test, which probes the behavior on a macroscopic scale, is consistent with the results of the nanoscale characterization of the water penetration using NR, SFG, and off-specular X-ray scattering at much shorter times. Water penetrates easily through the PP-MA coating and disrupts the interface bonding and morphology, so the PP-MA coated Al is easily corroded. In contrast, the 30 nm thick PP-HMDSO coating strongly hinders water penetration to the metal interface, such that no macroscopic corrosion on the Al substrate can be observed after a month.

CONCLUSION

To protect a metal against corrosion, strong interfacial interactions between the polymer and the substrate are important. Upon exposure to water, the diffusion of water to the coating/substrate interface can disrupt this strong interaction, which could cause coating delamination and accelerate corrosion. Preventing water penetration is of interest in many industrial applications, especially for corrosion resistance coatings. Characterization of water penetration

with NR, SFG, and off-specular X-ray scattering provides an integrated picture for understanding corrosion phenomenon on a nanoscale. Both NR and SFG techniques show that no water penetrates through a PP-HMDSO coating and accumulates at the coating/substrate interface within the time considered in this study. Also, the conformality of the PP-HMDSO coating to the substrate is not changed after exposure to water. In contrast, water diffuses readily through the PP-MA coating to the interface, changes the surface/interface morphology, and disrupts the interfacial interaction between coating and substrate. The direct observation of the water penetration and the water structure at the buried interface on the nanoscale provides a new level of detail in our picture of water's role in the corrosion of metal and in the loss of adhesion at coating/metal interfaces. The nanoscale details seen here are consistent with the results from a macroscopic corrosion test. While a thin hydrophilic PP-MA coating fails in a day, a thin hydrophobic PP-HMDSO coating protects Al up to a month in a salt spray test. Understanding water penetration through plasma polymerized coatings and disruption of the coating/substrate interface morphology and bonding will help in designing novel, environmentally friendly plasma polymerized coatings for protecting metals against corrosion. In the future, we will extend our work to the penetration of electrolyte, such as salt solutions, to more closely simulate the real corrosion environment.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.langmuir.8b01646](https://doi.org/10.1021/acs.langmuir.8b01646).

NR data for dry PP-HMDSO on silicon substrate with fit attempted with one-layer model and comparison of off specular X-ray scattering detector scans with model curves for different vertical correlation lengths and values of the Hurst parameter (PDF)

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Notes

The authors declare no competing financial interest.

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