

Controlling the Wettability and Adhesion of Nanostructured Poly-(*p*-xylylene) Films

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The hydrophobic surface properties of structured poly-(*p*-xylylene) (PPX) films, as measured by water wettability, are studied as functions of surface chemistry, film composition, and surface roughness. We demonstrate the fabrication of very hydrophobic surfaces and control over adhesion properties via nanoscale modulation of roughness, changes in composition, and alteration of the surface chemistry of PPX films. The formation of superhydrophobic surfaces through the chemisorption of fluoroalkylsiloxane coatings to hydroxyl sites created on the nanostructured PPX surface is also illustrated. The ability to control both hydrophobicity and adhesion using nanostructured PPX films is a promising development because it may lead to a new generation of coatings with applicability ranging from self-cleaning surfaces to robotics.

Introduction

Superhydrophobic surfaces (water contact angle $\theta_w > 150^\circ$) have been widely studied to develop materials with unique properties such as self-cleaning and/or antifouling behavior.^{1,2} Normally, superhydrophobic surfaces have higher contact angles and very low water droplet roll-off angles ($< 5^\circ$). A new class of superhydrophobic but adhesive surfaces has been recently reported.^{3–5} These surfaces are prepared either by surface etching³ or by microscopic structures of hydrophobic materials.⁵ Although these nanostructured surfaces have high water contact angles ($\theta_w > 150^\circ$), a water drop adheres to a surface even if the surface is tilted upside down (i.e., 180°). This strong adhesion has been attributed to van der Waals and/or the capillary force interactions between the nanostructured film surface and water. Similarly, biological structures built using molecular protein machinery in nature also show superhydrophobic and adhesive surface features. For example, the attractive forces that hold geckos to surfaces are van der Waals interactions between the finely divided keratinous fibers ($\sim 5 \times 10^5$ on each foot) and the surfaces themselves.^{6–8}

Hydrophobicity and adhesive properties of nanostructured surfaces are important for many practical applications, such as the handling of small liquid droplets, inducing selective permeability in a membrane, and the operation of wall-climbing robots. The methods of preparing superhydrophobic and adhesive surfaces include chemical etching³ and template-based techniques.⁵ However, the simultaneous control of both wettability

and adhesion properties of superhydrophobic surfaces has not been studied in detail.

We have recently introduced a bottom-up process based on oblique angle deposition as a simple, robust method for controlling the morphology of poly-(*p*-xylylene) (PPX) films.^{9–11} In this process, monomer vapors produced by the pyrolysis of chemically functionalized [2.2]paracyclophane precursors are directed at an oblique angle toward a surface to initiate PPX growth. Inclined deposition induces the isotropic growth of PPX nanofibers as a result of high surface diffusion and geometric shadowing effects, leading to a nanostructured PPX film comprising clusters of ~ 50 – 200 nm diameter nanocolumns. This approach allowed us to tune the chemical properties of the nanostructured PPX surface (via the judicious choice of the functionalized paracyclophane precursor) and film morphology (via control of the film deposition conditions) to control the physicochemical properties of the resulting PPX films, such as hydrophobicity, porosity, and crystallinity.

In this letter, we report the control of adhesive properties of several hydrophobic PPX films deposited by the oblique angle method. We demonstrate multiple ways of tuning the hydrophobicity of the structured PPX surfaces. Our method allows a change not only in the surface roughness but also in the surface chemistry of the material. Furthermore, we demonstrate the fabrication of superhydrophobic films through the chemisorption of fluoroalkylsiloxane coatings to hydroxyl sites created on the PPX film surface and the control of both water wettability and adhesion through appropriate choices of PPX surface chemistry and roughness. The ability to simultaneously control surface chemistry and film morphology shown here makes these nanostructured PPX films viable candidates for use in antifouling and biomedical applications.

Results and Discussion

Wettability measurements using various solvents have long been used as a means to estimate a material's surface energy and understand surface energy variations with changes in the

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Table 1. Static Contact Angle Measurements for PPX Films

substrate type	planar (deg)	structured (deg)	average column size (nm)
PPX-COCF ₃	88 ± 3	135.7 ± 4.0	160 ± 7
PPX-Cl	87 ± 2	119.3 ± 1.2	140 ± 11
PPX-Br	80 ± 2	115.2 ± 1.4	188 ± 10

material's chemistry, composition, and morphology. In particular, the contact angle formed by a sessile water droplet (θ_w) resting on a substrate surface provides a convenient means to assess the relative hydrophobicity of that surface. The value of θ_w is known to depend on both the chemical composition and the roughness of the surface, as described previously by Cassie and Wenzel, respectively.^{12,13} Nanostructured PPX films, as described here, offer the opportunity to vary both surface chemistry and roughness simultaneously and precisely as a means to control the hydrophobicity and adhesive properties of such films. In this study, we illustrate the influence of three parameters in controlling the hydrophobicity and adhesion of PPX films: (i) film roughness, (ii) chemical composition of the film, and (iii) direct chemical modification of the film surface.

On a nanostructured surface, there are three possible wetting states. Because we are concerned with surface hydrophobicity, we restrict our definition of the term "wettability" to refer solely to surface wetting by water in this text. A water drop can fully penetrate into the nanostructures, which is known as the Wenzel state, or the liquid can be suspended on the nanostructures, which is known as the Cassie-Baxter state. The third state is an intermediate state between the Wenzel and Cassie modes. When the wetting behavior changes from the Cassie mode to the Wenzel mode, the liquid droplet will at least partially fill the grooves of the rough substrate with a decrease in the apparent contact angle. Consequently, adhesive forces between the surface and water droplet play a key role in the third state.

To better understand the range of conditions that characterize PPX wetting behavior in these three states, we first probed the effects of film roughness on θ_w using poly(chloro-*p*-xylylene) (PPX-Cl) films of various thicknesses. We measured θ_w (97.9, 103.9, and 111.2°) as a function of surface roughness (8.1, 37.6, and 77.5 nm, respectively; see Supporting Information, Figure S-1) for structured PPX-Cl films. The increase in surface roughness as the film becomes thicker is inherent to oblique angle deposition techniques. The surface hydrophobicity increases (i.e., water wettability decreases) as a function of surface roughness as expected, but the data do not obey the Wenzel or Cassie-Baxter equation. For example, Wenzel behavior is described by eq 1, where r is the measured surface roughness factor and θ_w^p is the contact angle on a planar PPX-Cl surface (i.e., 87°, see Table 1):

$$\cos \theta_w = r \cos \theta_w^p \quad (1)$$

Equation 1 predicts θ_w values of 86.5, 84.7, and 82.5° as the roughness increases. Similarly, Cassie-Baxter behavior is governed by eq 2, where f is the fraction of the water droplet in direct contact with the substrate (i.e., not suspended over air) on the rough surface:

$$\cos \theta_w = f(1 + \cos \theta_w^p) - 1 \quad (2)$$

AFM mapping of the tops of the PPX-Cl fibers is shown in the Supporting Information; Figure S-1 provides f values of 0.63,

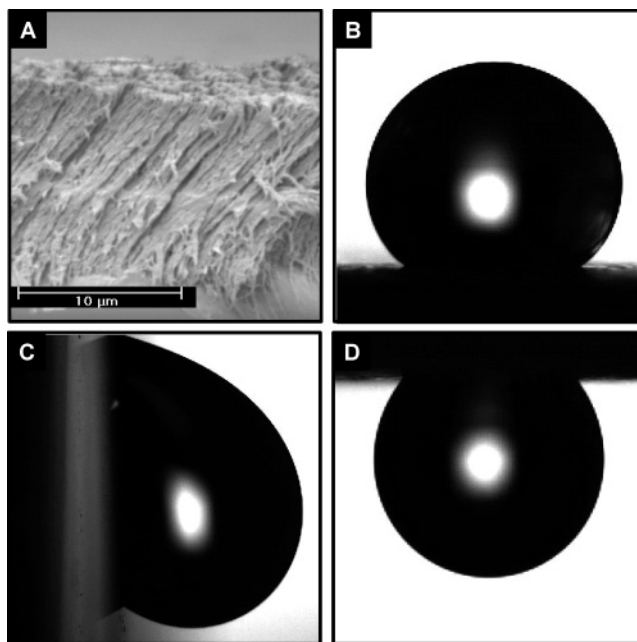


Figure 1. (A) Cross-sectional SEM image of the structured PPX-COCF₃ film. Shapes of water droplets on the structured PPX-COCF₃ film with different tilt angles: (B) 0, (C) 90, and (D) 180°.

0.67, and 0.68 for the same films corresponding to predicted θ_w values of 109.5, 107.4, and 106.3° from eq 2, respectively, that again differ markedly from measured θ_w values. These results suggest that van der Waals and/or capillary forces sufficient to induce wetting behavior associated with the intermediate state are present for the structured PPX-Cl films.

Changes in the chemical composition of the PPX film associated with the use of [2.2]paracyclophanes bearing other hydrophobic substituents, such as the trifluoroacetyl group, also produce nanostructured films capable of exhibiting this intermediate wetting state. For example, Figure 1a shows a cross-sectional scanning electron microscope (SEM) image of a structured poly(trifluoroacetyl-*p*-xylylene) (PPX-COCF₃) film deposited using the trifluoroacetyl-di-*p*-xylylene precursor on a silicon substrate. Very clearly, the SEM images confirm that the structured PPX-COCF₃ film consists of assemblies of parallel columns. The inclination angle of the columns is 61°. Although the structured PPX-COCF₃ film morphology, as indicated by the diameter of its pillars, is similar to that of the PPX-Cl film (Table 1), it is more hydrophobic ($\theta_w = 135.7^\circ$; Table 1 and Figure 1b) than the PPX-Cl film ($\theta_w = 119.3^\circ$, Table 1). However, good adhesion of the water droplet placed on the surface is observed for *both* films. For example, even when we tilted the films vertically or flip them upside down, as shown in Figure 1c,d, respectively, for the PPX-COCF₃ film, the water droplet did not slide from the surface. However, the planar PPX-COCF₃ film has a static contact angle of 88° (Table 1), and the roll-off angle is 25°. The structured PPX-COCF₃ film is composed of approximately $\sim 10^7$ aligned columns (approximately 120–170 nm in diameter) per square millimeter. Clearly, both increased surface hydrophobicity and adhesion are due to nanostructure.

Similar adhesive behavior is also noted for structured poly-(bromo-*p*-xylylene) (PPX-Br) films prepared by the oblique deposition of the dibromo-di-*p*-xylylene precursor at the $\alpha = 10^\circ$ incident angle geometry used for the PPX-Cl and PPX-COCF₃ films, even though the ($\sim 188 \pm 10$)-nm-diameter PPX-Br columns are somewhat larger than those of the other films. Table 1 summarizes the wettability behavior and structural features (i.e., average column diameters) observed for each film.

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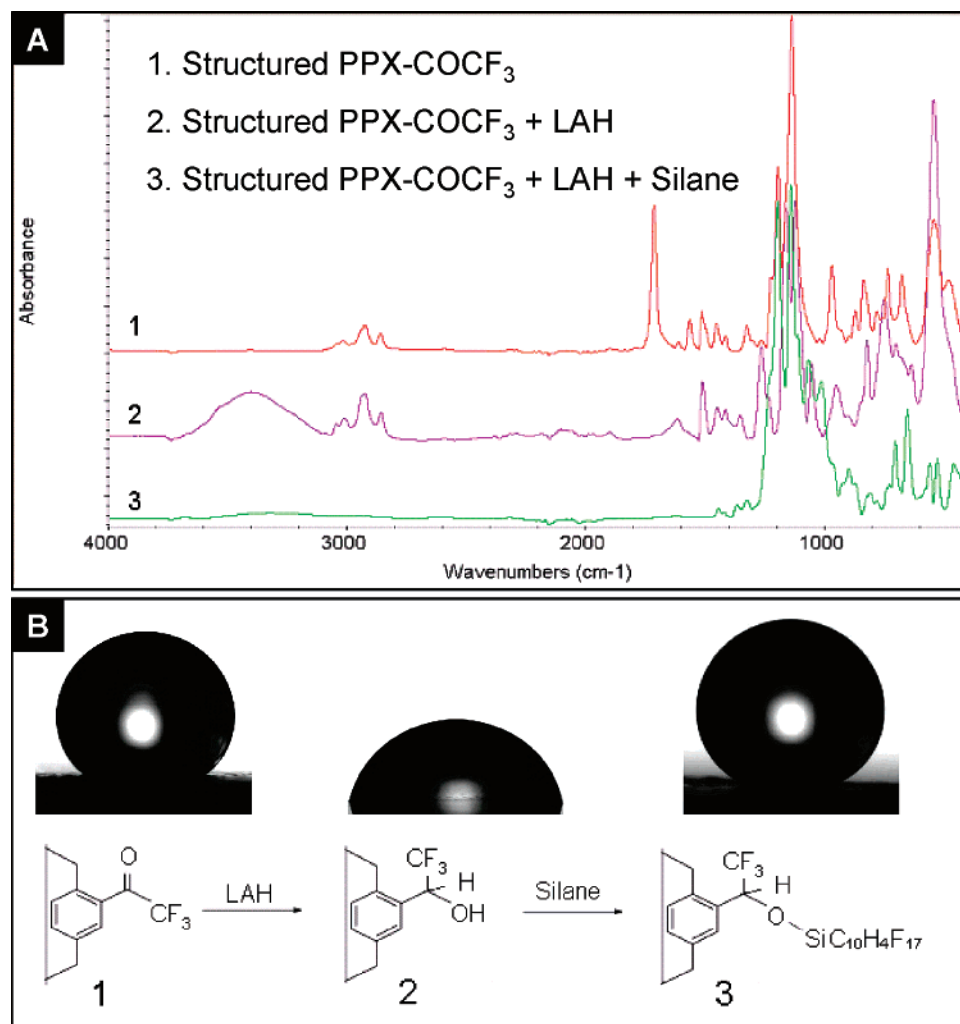


Figure 2. (a) FTIR/ATR spectra of the structured PPX-COCF₃ film are shown for three conditions: (1) before LAH reduction, (2) after LAH reduction, and (3) after 3 h of fluoroalkyltrichlorosilane chemisorption. (b) Water droplets adhere well to the surface for conditions 1 and 2 but become nonadherent (roll-off angle <5°) for condition 3. The contact angles for conditions 1–3 are 136, 78, and 152°, respectively.

Clearly, high surface adhesion is observed even for PPX films having diverse chemical compositions. The hydrophobic natures of the planar as well as structured forms of the PPX-derivative films are exemplified by the contact-angle goniometry results, which range from 80 to ~136° depending on the type of film. In general, every planar film is less hydrophobic than its structured counterparts as a result of the roughness differences; the structured PPX films are very rough compared to the planar PPX films. This is expected because planar films form a conformal surface, and their surface roughness is very small. Additionally, structured PPX-COCF₃ exhibits superior hydrophobicity compared to the remaining five films as a result of the CF₃ group in the polymer and the surface roughness associated with the film's nanostructure. It is noteworthy that all three structured PPX surfaces exhibit good adhesive interactions with water droplets. Such behavior suggests that there exists a range of surface energies, as measured by θ_w (~115–136°) and determined by the PPX surface chemical composition and morphology (Table 1), for the fabrication of hydrophobic, adhesive materials of these types.

Direct chemical modification of the native PPX surface represents an additional means to control the hydrophobicity and adhesive properties using our nanostructured PPX films. For example, it is generally known that the chemisorption of fluoroalkyltrichlorosilanes to hydroxyl groups present on appropriately roughened substrate surfaces provides a convenient

means to fabricate superhydrophobic surfaces.^{14,15} Superhydrophobic surfaces satisfy two important criteria. They exhibit (1) very high θ_w values (>150°) and (2) very low water droplet roll-off angles (<5°).

Given the proximity of the nanostructured PPX-COCF₃ film's θ_w (~136°) to the superhydrophobicity threshold and our desire to explore further the range of conditions conducive to adhesive behavior, we decided to modify the PPX-COCF₃ film surface chemically using the fluoroalkyltrichlorosilane heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane. Therefore, the surface of the nanostructured PPX-COCF₃ film was first reacted with lithium aluminum hydride (LAH) in THF to reduce the carbonyl group to a secondary alcohol. AFM control experiments (Supporting Information, Figure S-2) indicated that PPX-COCF₃ films were not appreciably swollen by THF or structurally degraded by LAH and that their fibrous morphology was maintained. After the reduction, θ_w of the film, referred to hereafter as PPX-COHCFCF₃, was measured to be 78°, which is consistent with the replacement of the ketone by a more hydrophilic hydroxyl group. The IR spectra of the films shown in Figure 2a confirmed the reduction of the ketone to the alcohol. The ketone peak of the untreated PPX-COCF₃ film observed at 1712 cm⁻¹ (spectrum

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1) disappeared, and an OH band at 3500 cm^{-1} (spectrum 2) ascribed to the secondary hydroxyl group appeared after the LAH treatment.

The hydroxyl sites created by the reduction of surface ketone groups of the structured PPX-COCF₃ films by LAH react readily with hexane solutions of heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane to conformally chemisorb this organotrichlorosilane onto the polymer surface. Chemisorption is confirmed by (1) the appearance of a Si 2p signal at $102.7 \pm 0.2\text{ eV}$ associated with the presence of siloxane species¹⁶ in the XPS spectrum of the treated surface (Supporting Information, Figure S-3) and (2) the disappearance of the hydroxyl IR band at 3500 cm^{-1} , as shown in spectrum 3 of Figure 2a. The nature of the fluoroalkylsiloxane films formed during the chemisorption process is known to depend upon the amount of water present on the substrate surface, with multilayer film deposition favored for chemisorption onto highly hydrated surfaces.¹⁷ However, although the good wettability (i.e., $\theta_w = 78^\circ$) measured for our PPX-COHCFC₃ film suggests a well-hydrated surface, we are as yet unable to directly verify the formation of a fluoroalkylsiloxane multilayer in our system (vide infra).

The maximum contact angle for a heptadecafluoro-1,1,2,2-tetrahydrodecyl)siloxane self-assembled monolayer (SAM) film is reported to be 110° on a planar silicon substrate.¹⁸ After the chemisorption of a heptadecafluoro-1,1,2,2-tetrahydrodecyl)siloxane film onto our nanostructured PPX-COHCFC₃ film, the contact angle is measured to be 152° (Figure 2b). Repetition of the heptadecafluoro-1,1,2,2-tetrahydrodecyl)siloxane chemisorption experiment in triplicate for various treatment times (i.e., 1, 3, and 24 h) provides films having θ_w values of 104 , 152 , and 150° , respectively. The heptadecafluoro-1,1,2,2-tetrahydrodecyl)siloxane-coated nanostructured PPX-COHCFC₃ film clearly becomes superhydrophobic ($\theta_w = 152^\circ$; i.e., a 42° increase in θ_w compared to that of the corresponding heptadecafluoro-1,1,2,2-tetrahydrodecyl)siloxane SAM on a planar Si surface) after just an ~ 3 h treatment.

In contrast to the behavior of the nanostructured PPX-COCF₃ film prior to and after LAH treatment (vide infra), however, water droplets do *not* adhere (roll-off angle $\sim 3^\circ$) to the heptadecafluoro-1,1,2,2-tetrahydrodecyl)siloxane-coated nanostructured PPX-COHCFC₃ film. The penetration of the water droplet into the interstitial regions between the nanocolumns required to access the intermediate wetting state associated with adhesive behavior is clearly hindered for this film. Although the low surface energies associated with the CF₂ and CF₃ functional groups present at the outer heptadecafluoro-1,1,2,2-tetrahydrodecyl)siloxane layer certainly contribute to the water repellency, geometric factors may also be involved. Specifically, in previous studies we have shown that columnar spacings within nanostructured PPX films can be as small as ~ 10 – 30 nm , especially for thicker films (i.e., micrometer scale) such as those used here.¹⁹ At such small dimensions, the chemisorption of a multilayer film of several nanometers thickness may also contribute to the exclusion of water through narrowing of the channels separating the nanocolumns. Unfortunately, we are currently unable to distinctly discern hydrophobicity and adhesion contributions because of geometric factors in our system. However, the fact that adherent properties have been previously observed for other

poorly wetted (i.e., $\theta_w > 150^\circ$) surfaces^{3–5} indicates that superhydrophobicity alone is not a sufficient barrier to adhesive behavior and that geometric or other factors specific to our nanostructured PPX films contribute.

Although our fluoroalkylsiloxane surface-modification strategy, as described here, currently limits the observation of adhesive behavior to nonsuperhydrophobic nanostructured PPX films, our experiments indicate that adhesive behavior can readily be observed for nanostructured PPX films having higher surface energies (i.e., lower θ_w) than those shown in Table 1. For example, the PPX-COHCFC₃ film exhibits a relatively high surface energy, as indicated by its low $\theta_w = 78^\circ$, compared to the materials in Table 1. Unlike the superhydrophobic fluoroalkylsiloxane-coated nanostructured PPX-COHCFC₃ film, however, this film exhibits adhesive behavior similar to that observed for the other nanostructured PPX films described in Table 1 and Figure 1. Consequently, adhesive behavior for our nanostructured PPX films can be observed over an extremely wide range of surface energies, presently represented by $\theta_w = 78^\circ$ – 136° . It is interesting that each of these materials possess heteroatom components capable of exhibiting dipolar (e.g., PPX-Cl, PPX-Br, or PPX-COCF₃) or hydrogen bonding (e.g., PPX-COHCFC₃) interactions with water, which are features that may be necessary to promote the intermediate wetting state associated with the adhesive function. We are currently synthesizing PPX films having new functional groups to explore this hypothesis and further understand the chemical and morphological factors influencing adhesion in these model nanostructured polymer systems.

Experimental Section

PPX Film Deposition. The paracyclophane precursor for the poly(chloro-*p*-xylylene) (PPX-Cl) films, dichloro-di-*p*-xylylene, was obtained from Uniglobe-Kisco Inc. The precursors for the poly(bromo-*p*-xylylene) (PPX-Br) film, dibromo-di-*p*-xylylene, and poly(trifluoroacetyl-*p*-xylylene) (PPX-COCF₃) film, trifluoroacetyl-di-*p*-xylylene, were prepared according to the literature method.⁹ The oblique angle vapor deposition method used to fabricate the nanostructured PPX thin films has been described elsewhere.^{9–11} The nanocolumnar PPX films used here were prepared using an $\alpha = 10^\circ$ deposition angle.

Film Characterization. Static contact angles were measured by applying a video microscope interfaced to a computer (FTA-1000) to capture drop images. Deionized H₂O ($10\ \mu\text{L}$, $18\ \text{M}\Omega\ \text{cm}$ resistivity; Barnstead Nanopure II deionizer) was used for contact angle measurements. Surface roughness was measured with a Nanoscope-E atomic force microscope (Veeco Metrology, CA) in ambient air at room temperature, with silicon nitride (SiN) triangular cantilevers having contact mode tips (DNP-20, Veeco Metrology, CA). The rms roughness from $5\ \mu\text{m}$ scans (average of three sets) was calculated using the Nanoscope software without tip deconvolution methods²⁰ as a result of high roughness. Scanning electron microscope (SEM) images were recorded with a Philips XL-40 system after cleaving the samples in liquid nitrogen. The FTIR (Thermo Nicolet IR) and ATR (diamond crystal) data were collected with respect to silicon wafer reference in air and were recorded using Norton-Bear apodization with $4\ \text{cm}^{-1}$ resolution. For each spectrum, 100 scans are co-added.

PPX-COCF₃ Film Reduction by LiAlH₄. Experiments were done in a glove bag in a dry N₂ atmosphere. All chemicals were used without further purification. LiAlH₄ (LAH) was purchased from Alfa Aesar. In a typical experiment, 50 mg of LAH was dissolved in $\sim 25\ \text{mL}$ of THF (Aldrich Sure-Seal, $<0.005\%$ H₂O) in a dry 50 mL round-bottomed flask, and the PPX-COCF₃ film was immersed in this solution for 4 h. The treated PPX-COCF₃ film, designated PPX-COHCFC₃, was removed from the flask, rinsed with fresh THF, removed from the glove bag, and examined by IR. Upon completion

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of the reaction, the IR absorption band of the ketone group at 1712 cm^{-1} disappeared. The reduced PPX-COHCF₃ film was then thoroughly rinsed with water (doubly distilled) and dried under vacuum overnight.

Silane Functionalization. Heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane (Gelest, PA) was reacted with the PPX-COHCF₃ film in the glove bag under dry N₂. A 1% (w/v) solution (10 mL) of the organotrichlorosilane was prepared in hexane. The PPX-COHCF₃ film was immersed in this solution and kept there for 1, 3, or 24 h. Upon completion of the reaction, the film was removed from the organotrichlorosilane solution, washed with hexane, and dried under vacuum overnight.

Conclusions

We have demonstrated that both the hydrophobicity and adhesion of model nanostructured PPX films can be readily varied through control of the film morphology (roughness) as well as the surface chemistry via PPX chemical composition or direct chemical modification of the PPX film surface. The columnar components of our nanostructured PPX films constitute a carpet of densely packed fibers (i.e., 140–200 nm diameter; $\sim(2-3) \times 10^7$ columns mm^{-2}) reminiscent of the naturally occurring adhesive keratinous fibers of a gecko's foot ($\sim 5 \times 10^5$ fibers on each foot). The nanocolumnar morphology of our PPX films promotes strong adhesive interactions with water droplets over a wide range of surface compositions, chemistries, and energies,

as measured by θ_w values ranging from 78 to 136°. Further attempts to reduce wettability via chemisorption of fluoroalkylsiloxane coatings onto nanostructured PPX films produce “truly” superhydrophobic materials exhibiting both poor wettability (i.e., $\theta_w = 152^\circ$) and poor water droplet adhesion (water drop roll-off angle $< 3^\circ$) under our conditions. Nevertheless, the ability to control both hydrophobicity and adhesion using nanostructured PPX films is a promising development because it may lead to a new generation of coatings for applications ranging from self-cleaning surfaces and biomedical implants to robotics. We are continuing our studies of these films, particularly to address means of employing external stimuli to control their hydrophobicity and adhesive behaviors in real time, to realize these applications.

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Supporting Information Available: Surface AFM scans for structured PPX-Cl and PPX-COCF₃ films. X-ray photoelectron spectroscopy of heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane on nanostructured PPX-COHCF₃. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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