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Full Paper

Partially Fluorinated Poly-*p*-xylylenes Synthesized by CVD Polymerization**

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This paper describes partially fluorinated poly-*p*-xylylenes prepared by CVD polymerization. The synthesis, characterization, and surface modification of two partially fluorinated polymer coatings, namely poly(4,12-dibromo-1,1,9,9-tetrafluoro-*p*-xylylene) (**2**) and poly(4-heptadecafluorononanoyl-*p*-xylylene-co-*p*-xylylene) (**4**), is described. Polymer **2** is synthesized from 4,12-dibromo-1,1,9,9-tetrafluoro[2.2]paracyclophane (**1**), which is fluorinated at the aliphatic bridge, while 4-heptadecafluorononanoyl[2.2]paracyclophane (**3**), which contains a perfluorinated keto group at the aromatic ring, is used to synthesize polymer **4**. Furthermore, the keto-functionalized polymer **4** introduces both extreme hydrophobicity and surface reactivity towards hydrazide-containing ligands.

Keywords: Fluorinated polymers, Poly-*p*-xylylenes, Superhydrophobic surfaces, Surface engineering

1. Introduction

Commercially available, non-functionalized poly-*p*-xylylene (PPX) or parylene coatings have been used in a variety of applications such as biomaterials, sensors, packaging, and in MEMS devices. Based on the Gorham process,[1] CVD polymerization of [2.2]paracyclophanes is commonly used to fabricate PPX coatings.[2] CVD typically provides a solvent-free environment, controllable polymer composition and architecture, good adhesion, and the ability to tailor surface properties to a broad extent.[3] These approaches include a range of microstructuring methods,[4–8] which are applicable to both flat and three-dimensional surfaces.[9,10]

Surface wettability is an important attribute of a coating, determining the suitability of surfaces for a range of different applications. In this respect, fluorinated polymer coatings with low surface energy are particularly attractive due to their water-repellence, inertness, and low coefficient of friction.[11,12] Fluorinated polymer films such as poly(octafluoro-*p*-xylylene) (also known as parylene-AF4) and poly(tetrafluoro-*p*-xylylene) (VT-4), synthesized using CVD polymerization, have exhibited excellent optical properties, low dielectric constants, and high thermal stability.[13,14] Despite these interesting properties, these coatings typically lack reactive functional groups for further surface modification.

Several functionalized PPXs have been synthesized via CVD polymerization of substituted [2.2]paracyclophanes creating a wide range of different reactive polymer coatings.[3,15,16] In order to incorporate the potential advantages of fluorinated polymers with the concept of reactive polymer coatings, fluorinated and reactive moieties can be simultaneously introduced into [2.2]paracyclophanes, which are subsequently deposited via CVD polymerization. This can be achieved either through modification of the aliphatic bridges, or by substitution at the aromatic rings.

Taking the aliphatic route, we intended to synthesize a fluorinated polymer coating, **2**, via CVD polymerization of precursor **1**, which is partially fluorinated at the aliphatic bridge (Scheme 1). This polymer contained bromine at the aromatic ring, which may be further converted into reactive groups providing easy access for subsequent surface modification reactions. In fact, CVD polymerized, brominated-PPX coatings are known to undergo dehydrohalogenation resulting in vinyl and ethynyl moieties.[17] However, post-polymerization modification of the brominated

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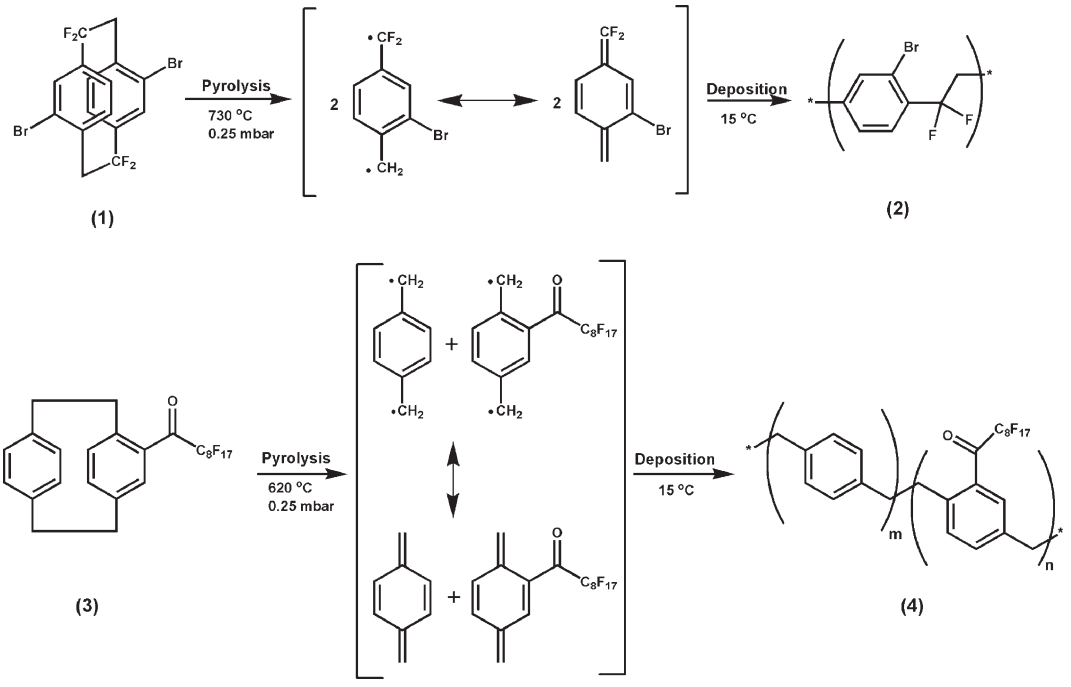

Scheme 1. Mechanism of CVD polymerization of partially fluorinated [2.2]paracyclophanes to yield the corresponding PPXs. Polymer **2** is fluorinated at the aliphatic bridge, whereas polymer **4** contains a fluorinated reactive group at the aromatic ring.

aromatic ring may require harsh chemical conditions so, as an alternative, we explored incorporation of functional groups into the aromatic segments that may combine reactivity with high hydrophobicity. In the past, several PPXs have been synthesized with shorter fluorinated side chains resulting in relatively hydrophobic coatings.[3,18–21] To further investigate this effect, we have now synthesized and CVD-polymerized a [2.2]paracyclophane with a long perfluorinated side chain. Specifically, compound **3** was synthesized and used to prepare ultrahydrophobic coatings of polymer **4** which contained a carbonyl-functionalized derivative with an 8-carbon perfluorinated side chain (Scheme 1). Given the usefulness of non-functionalized, as well as the perfluorinated PPX, for coating applications,[2,13,14,22] widening the scope of CVD polymerization by applying this technique to reactive, yet partially fluorinated paracyclophanes, may significantly advance the field of low-surface energy coatings. Not only do new polymer coatings, such as polymer **4**, possess robust chemical properties, but their reactivity also allows for subsequent surface modifications.

2. Results and Discussion

2.1. Precursor Synthesis and Characterization

Compound **1** was synthesized and characterized as previously described.[23] In principle, the presence of bromine may allow subsequent modifications of the polymer, albeit harsh conditions may have to be employed. On the other hand, compound **3** was synthesized as described previously for similar compounds,[19,24] using Friedel-Crafts acylation of the commercially available [2.2]paracyclophane with heptadecafluorononanoyl chloride in the presence of $AlCl_3$. To control the reaction, the synthesis was carried out at low temperatures (−40 to −30 °C) in dichloromethane. Even slightly elevated temperatures close to 0 °C caused an uncontrollable reaction and resulted in the loss of the paracyclophane and in-solution polymerization, leading to insoluble by-products.

The chemical structure of compound **3** was analyzed using nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry (MS). Both ^1H NMR and ^{13}C NMR confirmed the expected structure of paracyclophane **3**. MS conducted during CVD polymerization further confirmed the structure of compound **3** revealing a mass peak at 654 Da (M+) and characteristic peaks at 550 Da and 104 Da corresponding to the two quinodimethanes ($C_8H_7COC_8F_{17}$+, C_8H_8+), respectively.

2.2. CVD Polymerization and Polymer Characterization

Once the synthesis of functionalized, fluorinated [2.2]paracyclophanes was achieved, we addressed the question of whether they would lend themselves to CVD polymerization without loss of the functional groups. For CVD polymerization, precursor **1** was sublimated under a

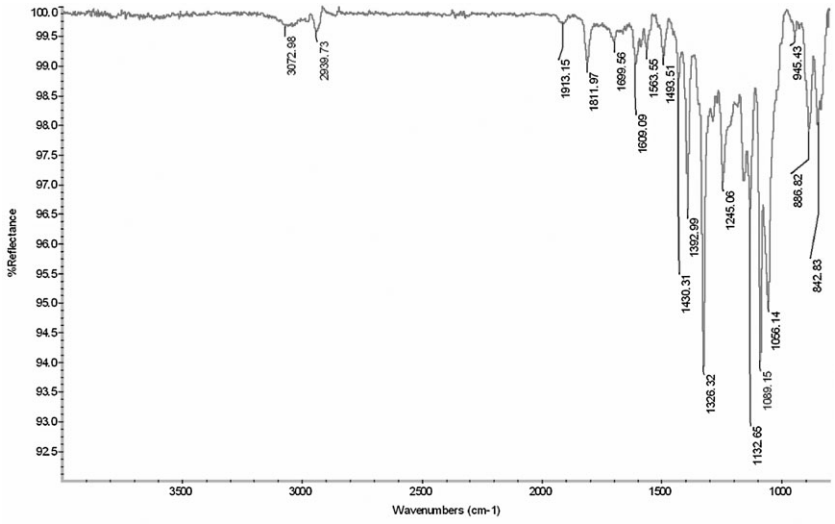

Fig. 1. Grazing angle FTIR spectrum of polymer 2 deposited on a gold substrate.

Table 1. High-resolution C 1s XPS data for polymers 2 and 4.

	Polymer 2			Polymer 4		
	BE [eV]	expt. [%]	calc. [%]	BE [eV]	expt. [%]	calc. [%]
C–C	285	74.1	75	285.3	42.6	49.63
C–Br	285.9	10.7	12.5	–	–	–
C–C=O	–	–	–	286.9	3.7	5.04
C=O	–	–	–	288.8	5.7	5.04
C–F	289.9	11	12.5	–	–	–
$\pi\rightarrow\pi^*$	291.6	4.2	–	291.1	4.1	–
CF_2	–	–	–	292	38.2	35.25
CF_3	–	–	–	294.2	5.7	5.04

reduced pressure of 0.2 mbar and a temperature of 80 °C. The argon carrier gas transported the vaporized precursor **1** into the pyrolysis zone, which was heated to 720 °C to ensure cleavage of the C–C bonds of the bridge, resulting in the corresponding quinodimethanes (monomers). Finally, these monomers were adsorbed on the substrate, which was maintained at 10–15°C, where they spontaneously polymerized. This process resulted in transparent and topologically uniform films of polymer **2** with thicknesses between 20 and 50 nm, as determined by ellipsometry. These polymer films were amorphous, as confirmed by X-ray diffraction (XRD) studies. Moreover, polymer **2** was deposited on a wide range of materials, including polymers (polyethylene, polystyrene), metals (stainless steel, gold), glass, and silicon. The grazing angle Fourier transform infrared (FTIR) spectrum of polymer **2** showed characteristic bands of the C-F stretches from 1056 cm^{-1} to 1132 cm^{-1} (Fig. 1).[25] In addition, the spectrum showed characteristic signals from 2939 cm^{-1} to 3072 cm^{-1} indicative of aliphatic and aromatic C-H bands.

X-ray photoelectron spectroscopy (XPS) was used to ascertain the elemental composition of polymer **2**. The following atomic ratios were calculated from the survey spectrum and high-resolution C 1s spectrum: Br 3p/C 1s: 11.3% (calc: 12.5%), C-Br/C-C: 13.9% (calc: 16.7%), F 1s/C 1s: 17.7% (calc: 25.0%), C-F/C-C: 14.0% (calc: 16.7%) (Table 1 and Fig. 2). These values compare well with the (calc.) theoretical values based on the chemical structure of the corresponding paracyclophanes. The high-resolution C 1s spectrum further revealed characteristic signals for aliphatic and aromatic carbon atoms (C–C, C–H) (normalized to 285.0 eV), carbon attached to bromine (C–Br) at 285.9 eV, carbon-fluorine (C–F) at 289.9 eV, and a signal indicating $\pi\rightarrow\pi^*$ transitions at 291.6 eV. The latter is a characteristic of aromatic molecules and has been previously reported for similar PPXs.[3] The XPS data in conjunction with the FTIR spectrum strongly suggests that the chemical structure of the synthesized CVD polymer film **2** was as expected (shown in Scheme 1).

Polymer **4** was synthesized by CVD polymerization of precursor **3** under conditions similar to those used for the preparation of polymer **2**. Owing to the long fluorinated side chain, precursor **3** possessed a higher molecular weight than other functionalized [2.2]paracyclophanes previously reported;[3] therefore a sublimation temperature between 90 and 100 °C and a lower optimum pyrolysis temperature of 630 °C were used. Characterization of polymer **4**, using FTIR spectroscopy, showed a strong peak at 1713 cm^{-1}

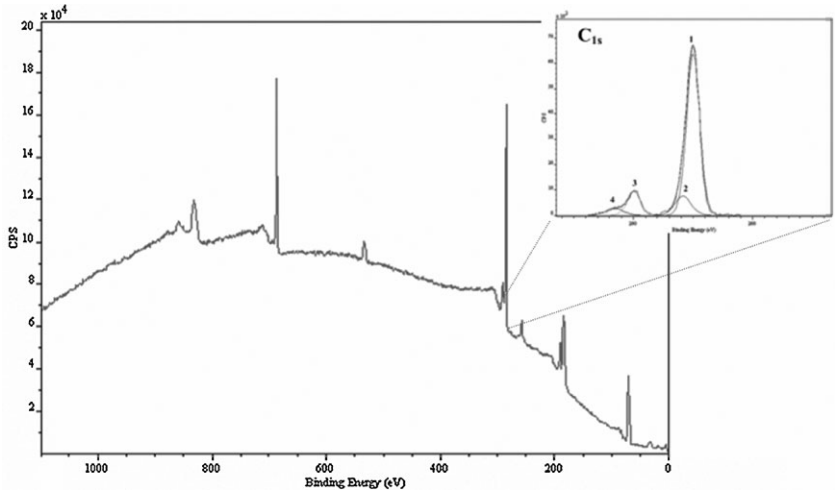

Fig. 2. XPS survey spectrum of polymer 2; inset shows the high-resolution C 1s spectrum.

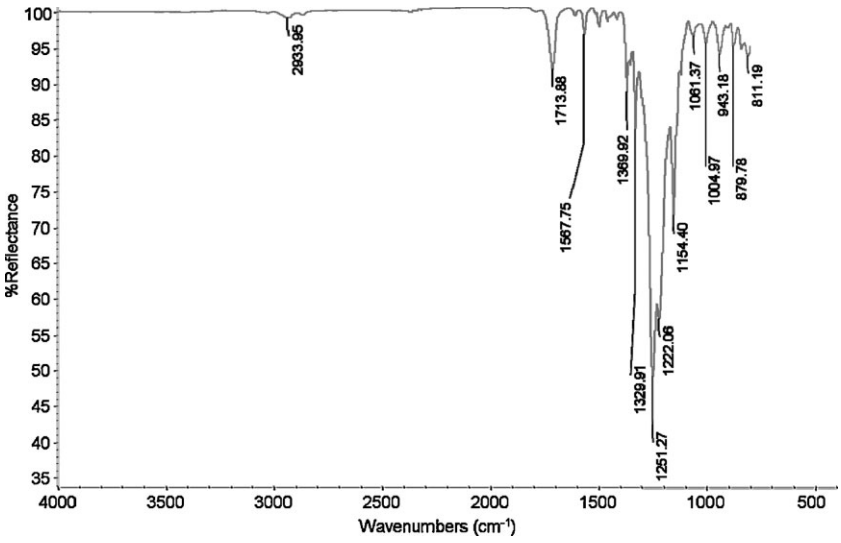

Fig. 3. FTIR spectrum of polymer 4 deposited on a gold surface.

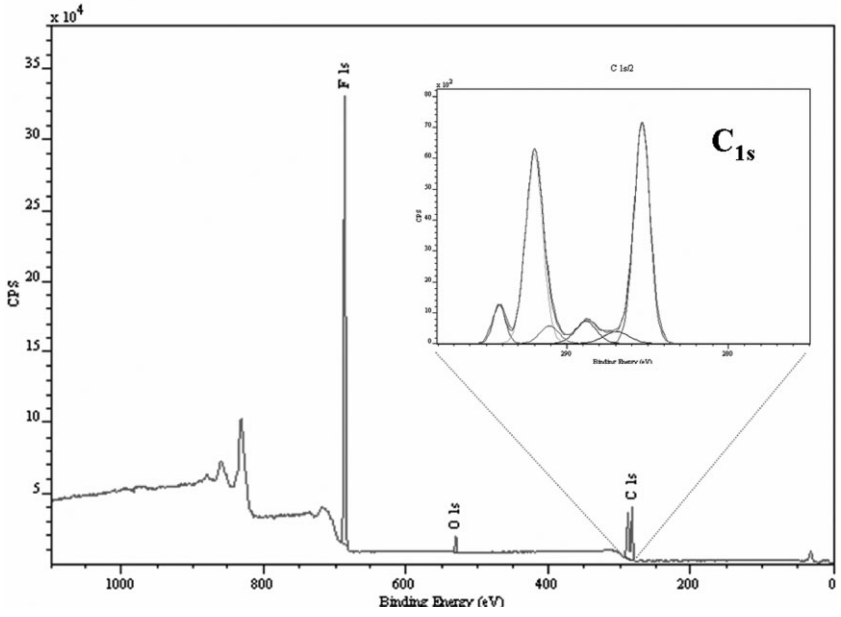

Fig. 4. XPS survey spectrum of polymer 4; inset shows the high-resolution C 1s spectrum.

indicating carbonyl (C=O) stretches confirming the presence of the functional group after CVD polymerization. Also, characteristic signals at 1329, 1251, 1222, and 1154 cm^{-1} signified C-F vibrations (Fig. 3).

Similar to polymer **2**, the XPS-based atomic ratios for polymer **4** were in good agreement with theoretical calculations (Table 1). Figure 4 shows the survey and high-resolution C 1s XPS spectra for polymer **4**. In the high-resolution C 1s spectrum, a binding energy of 288.8 eV indicated the carbonyl carbon (C=O). Furthermore, the ratio of C–F_3 to C–F_2 carbons equals 0.143, which agreed well with the calculated value of 0.149, indicating preservation of the fluorinated ketone. Overall, the high-resolution XPS spectrum confirmed the FTIR results.

Water contact angle measurements of the polymers provided an insight into the degree of hydrophobicity of the polymers. Polymers **2** and **4** were compared to non-functionalized PPX films and two previously reported PPXs with shorter fluorinated side groups, namely, poly-(4-trifluoroacetyl-*p*-xylylene-co-*p*-xylylene) (PPX-$COCF_3$) and poly(4-pentafluoro-propionyl-*p*-xylylene-co-*p*-xylylene) (PPX-COC_2F_5).[18,19,21] Differences in the functionalities and chain lengths influenced the contact angles in such a manner that a greater degree of fluorination increased the contact angle (Fig. 5).

Polymers **2** and **4** were also deposited on a variety of substrates such as gold, silicon, glass, and poly(dimethyl siloxane) (PDMS) on which they showed good adhesion. To ascertain the adhesiveness of the polymers, a piece of Scotch tape was first pressed onto the film and then released by peeling it off.[26] The robustness of the film was examined visually (Fig. 6) and FTIR was used for further confirmation. The films also remained stable after ultrasonication in water for 15–20 min. Moreover, polymers **2** and **4** were stable in aqueous solutions and several organic solvents such as ethanol, acetone, methanol, dichloromethane, chloroform, dimethylformamide, and toluene. This is an important property of the polymer which differentiates it from the precursor as well as other oligomers and low molecular weight polymers, thus indicating the formation of a high molecular weight polymer. However, it was observed that higher pyrolysis temperatures for polymer **4** resulted in coatings which were stable in ethanol but soluble in other organic solvents.

2.3. Surface Modification of Polymer 4

The ability to pattern the surface of low surface energy coatings is an important requirement for surface engineering. The presence of a reactive keto group in polymer **4** provides an opportunity for surface modification. Accessibility of the functional groups was evaluated by using a reaction between the keto group and hydrazide-containing ligands to form hydrazones. The surface reaction between biotinyl hydrazide and polymer **4** was conducted using microcontact printing, as previously described.[26] Briefly, an oxidized PDMS stamp was inked with a biotinamidocaproyl

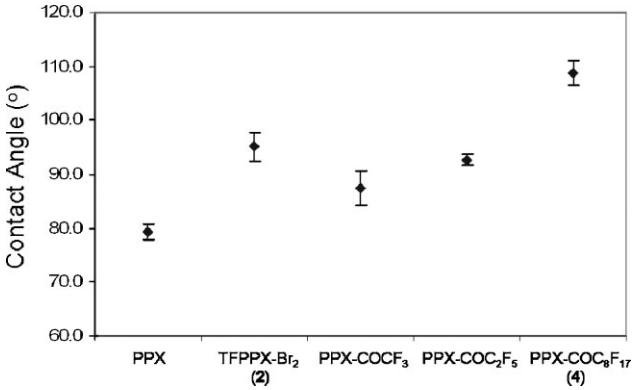

Fig. 5. Comparing contact angles of non-functionalized PPX, polymer 2, PPX-$COCF_3$, PPX-COC_2F_5, and polymer 4.

hydrazide solution, which was then brought into contact with a substrate coated with polymer **4** (Fig. 7a). The biotin-patterned substrate was then visualized by incubating the substrate with rhodamine-labeled streptavidin which bound specifically to the biotinylated regions on the substrates (Fig. 7b). A fluorescence signal from the fluorescently labeled streptavidin was observed predominantly in the regions where the PDMS stamp was brought into contact with the coating. This demonstrates the availability of keto groups on the polymer surface for surface reaction with hydrazide-functionalized moieties.

2.4. Combination of Superhydrophobicity and Reactivity

Superhydrophobicity of a surface is often created by the combination of low surface energy materials in conjunction with a complex hierarchical surface architecture. Typically, superhydrophobic surfaces do not possess any reactivity and therefore cannot be used for further surface modifications. This is because most functional groups tend to render a surface more hydrophilic. If coating **4** is applied to a substrate with a rough topography, the properties of a low surface energy reactive polymer coating will be further enhanced and a reactive, superhydrophobic coating should be prepared. Reactive polymer coating **4** was deposited onto a poly(acrylic acid-co-acrylamide) (P(AA-co-AAm)) surface displaying a rough morphology, which was fabricated using electrohydrodynamic jetting, and stabilized by thermal imidization.[27,28] Briefly, a layer of interconnected P(AA-co-AAm) particles was deposited onto a solid substrate using electrohydrodynamic jetting. After curing the particles for 6 h at 175 °C, a thin film of polymer **4** was coated onto these particles. Scanning electron microscopy (SEM) images of the surface (with and without the CVD polymer layer) revealed that the surface morphology consisted of a random distribution of particles having diameters of 1–2 μm (Figs. 8a,b). Electrohydrodynamic jetting has previously been used to enhance the surface roughness by creating a network of microparticles and nanofibers on flat substrates.[29,30] Contact angle measurements showed that this combined film rendered a superhydrophobic character to the solid surface with a contact angle of >153° (Inset of Fig. 8b). This angle is much higher than the contact angle of the hydrophilic P(AA-co-AAm) surface (~15°; Inset of Fig. 8a) or a smooth surface coated with polymer **4** (108.7° ± 2.3°). Moreover, the water droplet freely rolled off the surface suggesting that the surface has a very low hysteresis, one of the key characteristics of superhydrophobic surfaces.[31–33] Finally, to demonstrate the reactivity of polymer **4**, the surface was reacted with biotinamidocaproyl hydrazide (as previously described in Sect. 2.3) and incubated with Alexa Fluor 633 Streptavidin. Analysis with confocal scanning laser microscopy con-

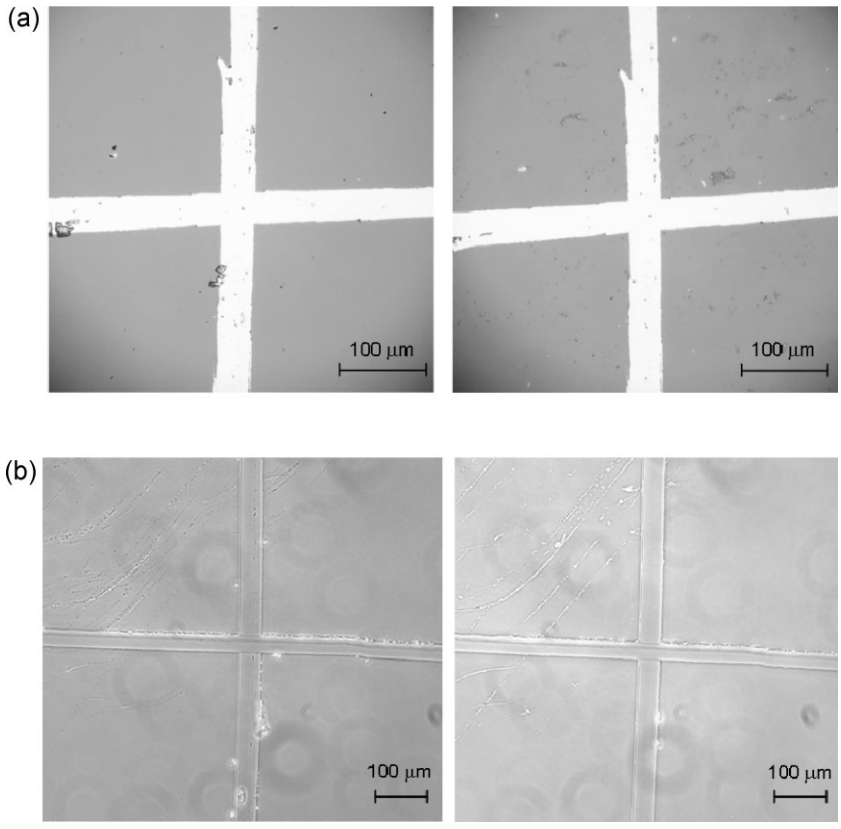

Fig. 6. Adhesion tests of a) polymer 2 and b) polymer 4. The polymer surface was first marked using a sharp object and then Scotch tape was pressed onto the surface. The surface was observed before and after peeling off the tape. Optical micrographs before and after testing are shown on the left and right panels, respectively. IR spectra were identical before and after testing.

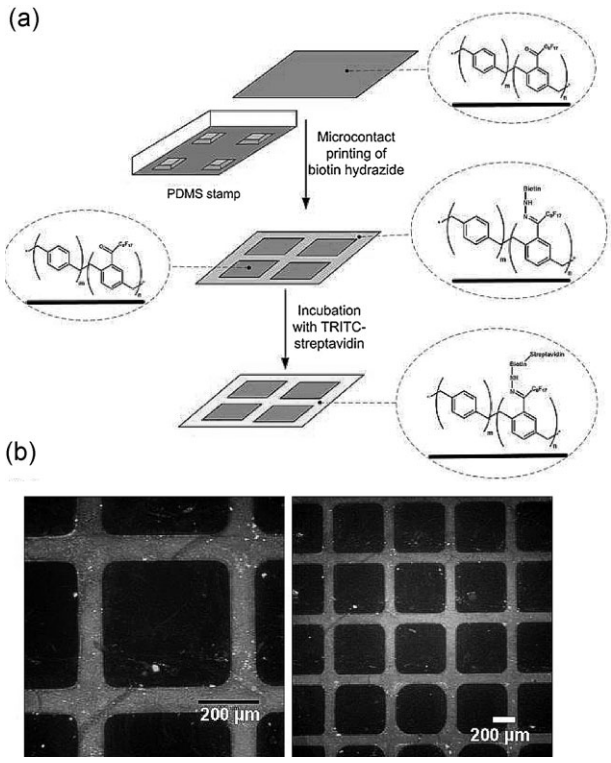

Fig. 7. a) Schematic of the microcontact printing process used to verify the reactivity of polymer 4 with hydrazides. b) Fluorescence micrographs of TRITC-labeled streptavidin immobilized onto patterned biotin hydrazide substrates.

firmed the reactivity of this superhydrophobic surface with hydrazide-containing ligands (Fig. 8c).

3. Conclusions

In summary, we have synthesized and polymerized two partially fluorinated [2.2]paracyclophane precursors with aliphatic or aromatic functionalization. Precursor **1** is fluorinated at the aliphatic bridge and may allow for further functionalization of the aromatic rings because of the presence of bromine groups. Precursor **3** contained a highly fluorinated keto group at the aromatic ring. Deposition of these polymers using CVD yielded coatings **2** and **4** that were stable in a range of organic solvents and aqueous solutions. Polymer **4** was also shown to be reactive with hydrazide-functionalized biotin, which then linked readily with fluorescently labeled streptavidin. Finally, polymer coating **4** was applied in the fabrication of reactive, superhydrophobic coatings. This class of functionalized, fluorinated PPXs could be of great interest as low energy, reactive, vapor-based coatings for applications in such areas as biomedical, automotive industries, and anti-fouling coatings.

4. Experimental

4.1. Precursor Synthesis

Compound **1** was synthesized according to a previously established synthesis chemistry [23]. Precursor **3** was synthesized by Friedel-Crafts acylation of [2.2]paracyclophane with the corresponding acid chloride (heptadecafluorononanoyl chloride 98%, Apollo Scientific Ltd., Cheshire, UK). Aluminum chloride (0.96 g) was dissolved in 30 mL of dichloromethane under inert conditions. The suspension was cooled to −40 °C with constant stirring. The acid chloride (2.5 g, 5.2 mmol) was slowly added into this mixture using a syringe. Dichloromethane (10 mL) was further added to the suspension. After 20 min, [2.2]paracyclophane (1 g, 4.8 mmol) was slowly added to the suspension. The reaction continued with vigorous stirring at −40 °C for 45 min, and then the mixture was allowed to reach 0 °C over a period of 1 h. The reaction was quenched with aqueous HCl, and ethyl acetate was added to the organic phase to increase solubility of the heavy products. The organic layer was separated and subsequently washed with 10 mL each of DI H_2O, 0.5M Na_2CO_3, and 0.5M NaOH. After purification with column chromatography (1:40 ethyl acetate/hexane), the product was diluted with hexane. Hexane was then removed in volumetric increments. After each increment, the unreacted [2.2]paracyclophane was allowed to precipitate, with the final product still in solution. In the final increment, pure precursor **3** (1.1 g) crystallized at the bottom of the flask, while the by-products remained in solution.

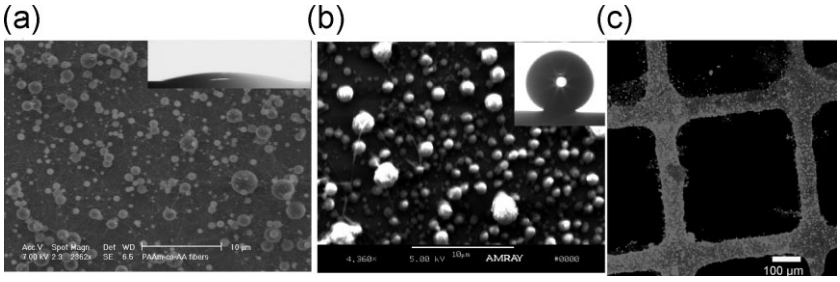

Fig. 8. SEM of the surface a) before CVD coating and b) after CVD coating. Insets show the corresponding water contact angles. c) Confocal image showing binding of fluorescently labeled streptavidin to biotinylated, micropatterned surfaces.

4.2. CVD Polymerization of Precursors

Starting materials, precursors **1** and **3**, were sublimed at 80–90 °C under vacuum and pyrolized into the corresponding quinodimethanes, which spontaneously polymerized upon condensation onto the substrate surface (at 10–15 °C). A constant argon flow of 20 sccm was used as the carrier. Starting material **1** pyrolized at

720 °C, and compound **3** pyrolized at 620 °C. Subsequently, polymerization occurred on a rotating, cooled sample holder placed inside a stainless steel chamber with a wall temperature of 120 °C. The pressure was set at 0.3 mbar or lower.

4.3. Characterization

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded using a Varian Inova 400, ^{1}H NMR (400 MHz), ^{13}C NMR (100.6 MHz), ^{19}F NMR (376 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual non-deuterated solvent as internal standard ($CDCl_3$: ^{1}H: $\delta = 7.22$; ^{13}C: $\delta = 77.00$). IR spectroscopy was performed on a Nicolet 6700 spectrometer utilizing the grazing angle accessory (Smart SAGA) at a grazing angle of 85°. Mass spectra were recorded using a VG (Waters) 70-250-S Magnetic sector mass spectrometer (EI, 70 eV) on a DCI desorption probe. The instrument was scanned from m/z 1000 to m/z 35 and was calibrated with perfluorokerosene-H. XPS data were recorded on an Axis Ultra X-ray photoelectron spectrometer (Kratos Analyticals, UK) equipped with a monochromatized Al Kα X-ray source. In these experiments, pass energy was set to 160.0 eV with an X-ray power of 150 kW, and the aperture was 600 μm × 600 μm. Thickness measurements were recorded at a wavelength of 532 nm using an EP^3-SW ellipsometer (Nanofilm Technologie GmbH, Germany). Nulling experiments were performed at an angle of incidence of 60°, and an anisotropic Cauchy model was used to model the ellipsometric parameters psi and delta. Surface morphology was examined by SEM (Philips XL30 ESEM, high vacuum mode).

Polymer **2**: XPS (atomic ratios): Br 3p/C 1s: 11.3% (calc: 12.5%), C-Br/C-C: 13.9% (calc: 16.7%), F 1s/C 1s: 17.7% (calc: 25.0%), C-F/C-C: 14.0% (calc: 16.7%); FTIR (grazing angle 85°): ν (cm^{-1}) = 842, 886, 1056, 1089, 1132, 1157, 1245, 1326, 1392, 1430, 1493, 1563, 1609, 1811, 2848, 2939, 3037, 3072.

Precursor **3**: ^{1}H NMR (400 MHz, $CDCl_3$): (= 2.9–3.3 (7H, CH2), 3.6 (1H, CH_2), 6.3 (1H, CH), 6.5 (4H, CH), 6.75 (1H, CH), 7.0 (1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): (= 34.90, 34.92, 34.99, 35.85, 107.50, 110.22, 110.52, 110.69, 111.18, 112.93, 115.66, 118.52, 130.87, 131.04, 132.45, 132.70, 132.85, 133.43, 136.61, 138.54, 139.37, 139.79, 139.93, 144.38, 184.84. ^{19}F NMR (376 MHz, $CDCl_3$): (= −80.8, −110.9, −111.9, −112.5, −113.6, −120.6, −120.9, −121.8, −122.7, −126.1. EI (70 eV): m/z (%) = 654.2 (43.8) [M+], 550.1 (7.4) [$C_8H_7COC_8F_{17}$+], 235 (4.7) [$C_{16}H_{15}CO$+], 131.1 (14.8) [C_8H_7CO+], 104.1 (100) [C_8H_8+]. FTIR (grazing angle 85°): ν (cm^{-1}) = 2931, 2852, 1707, 1591, 1549, 1500, 1371, 1329, 1248, 1198, 1146, 1116, 1070, 997, 960, 935, 843.

Polymer **4**: XPS (atomic ratios): F 1s/C 1s: 86.4 (calc. 85.6%), O 1s/C 1s: 5.9% (calc. 5.0%). FTIR (grazing angle 85°): ν (cm^{-1}) = 2934, 1714, 1568, 1498, 1458, 1416, 1370, 1330, 1251, 1222, 1154, 1061, 1005, 943, 880, 811.

4.4. Contact Angle Measurements

A microsyringe was used to place a 5 μL droplet on the substrate, and a picture of the droplet was captured using a digital camera (Canon EOS 20D) after 5 s. An image processing software (Image J) was used to analyze the droplet images and calculate the contact angles.

4.5. Immobilization of Biotinamidocaproyl Hydrazide

PDMS stamps were fabricated as described in literature. The PDMS stamp consisted of square-shaped indentations (400 μm on a side) with 50 μm gaps between the square edges. The PDMS stamp was treated with UV-ozone for 25 min (UV-Ozone Cleaner; Model no. 342, Jelight Company Inc.), then inked with a 10 mM solution of biotinamidocaproyl hydrazide (Pierce Biotechnology, IL) in ethanol at a pH of 5–6. The inked surface was then stamped onto a surface coated with polymer **4**. The stamp was kept in contact with the substrate for 1 min and then the patterned substrate was incubated with rhodamine-labeled streptavidin (50 μg mL^{-1}, Pierce Biotechnology, IL) or streptavidin labeled with Alexa Fluor 633 (50 μg mL^{-1}, Invitrogen, CA) in an aqueous phosphate buffer solution (pH 7.4, Sigma, MO) consisting of bovine serum albumin (0.1% w/v, Sigma, MO) and Tween 20 (0.02% v/v, Sigma, MO) for 1 h. The substrate was washed three times with the incubating buffer and rinsed with DI water. The micropatterns on the substrate were visualized using a Nikon TE200 fluorescence microscope and confocal laser scanning microscope (CLSM) (Olympus FluoView 500, USA).

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