

# Spatially Organized Free-Standing Poly(*p*-xylylene) Nanowires Fabricated by Vapor Deposition

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Thin films of poly(chloro-*p*-xylylene) (PPXC) grown by the pyrolysis and evaporation of chloro-[2.2]paracyclophane in an evacuated chamber contain free-standing, slanted, parallel columns that are 50  $\mu\text{m}$  long and are assemblies of 50- to 100-nm-diameter nanowires, which thus can have an unprecedented aspect ratio as high as 1000:1. The nanostructured thin films organize spatially with a chemical structure similar to that of planar PPXC thin films, but the former also possess nanostructured morphology. Nanostructured thin films of poly(*p*-xylylene) (PPX) and its derivatives shall be useful as functionalized interfaces for antifouling coatings and biomedical devices.

[2.2]Paracyclophane was first prepared in 1949 by Brown and Farthing<sup>1</sup> and systematically investigated by Cram and co-workers from 1951 onward.<sup>2</sup> Chemically, [2.2]paracyclophane is a dimer of two *p*-xylylene groups (a layered  $\pi$  system) that have an unusual 3D aromatic structure compared to that of the planar benzene ring. Applications of [2.2]paracyclophane include molecular machines realized through supramolecular assembly<sup>3</sup> and polymeric thin films (poly(*p*-xylylene)) of cyclophanes for biomedical purposes.<sup>4</sup>

Only a few examples of nanostructured poly(*p*-xylylene) (PPX) films have been described in the literature, including PPX polymer brushes<sup>5</sup> and template PPX fibers.<sup>6</sup> In this letter, we demonstrate that highly porous thin films of PPX, comprising free-standing, slanted, parallel columns containing nanowires, can be fabricated (Figure 1). These PPX thin films can be 50  $\mu\text{m}$  thick and contain 50-nm to 100-nm-diameter nanowires, which thus *can* have an unprecedented aspect ratio (to our knowledge) as high as 1000:1. The production technique does not require any mask, lithography method, or surfactant for deposition.

The nanostructured PPX thin films have two advantages over planar (flat) PPX thin films. First, the nanostructure enhances the surface area, thereby increasing the efficiency of functionalization. Second, novel chemical properties can be obtained by the co-deposition of two or more types of PPX monomers with different side groups ( $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  in Figure 1), which can be esters, ketones, amines, lactones, and so forth.

Our nanostructured PPX thin films are deposited on a stationary substrate from a directional vapor source in an evacuated chamber.<sup>7</sup> The substrate is oriented obliquely relative to the vapor flux, typically at an angle  $\alpha \leq 10^\circ$  in Figure 1, which creates a porous, low-density thin film of columns inclined at an angle of  $\phi \geq \alpha$ . The growth of nanoporous columnar thin films is governed by three mechanisms: (i) geometrical self-shadowing, (ii) surface diffusion along the sub-

strate of incoming adatoms constituting the vapor, and (iii) bulk diffusion leading to oriented crystallization.<sup>8</sup> Such thin films of metals, semiconductors, and a few organic dielectrics have been deposited by oblique-angle vapor deposition methods.<sup>8,9</sup> Similar thin films of polymers have been grown by an oblique-angle molecular beam deposition method<sup>10</sup> on the atomistic length scale but not on larger length scales. The formation of our nanostructured PPX thin films must have been influenced by a combination of nucleation (common in thin films<sup>11,12</sup>) with bond formation (i.e., polymerization), in addition to the aforementioned three mechanisms.

Poly(chloro-*p*-xylylene) (PPXC) was selected as the initial compound for thin-film deposition ( $R_1 = R_2 = \text{Cl}$  and  $R_3 = R_4 = \text{H}$  in Figure 1). Physical and chemical properties of PPXC films (i.e., crystallinity, structure, surface energy, and surface topography) were qualitatively assessed by scanning electron microscopy (SEM), atomic force microscopy (AFM), glancing angle X-ray diffraction (XRD), contact angle measurements, and infrared (IR) spectrophotometry. We intend to grow thin films of other PPX derivatives in due course.

Figure 2 shows a cross-section SEM image and a top-surface AFM image of a nanostructured PPXC thin film fabricated by deposition for 10 min on a silicon substrate. Very clearly, the SEM image (Figure 2a) confirms that nanostructured PPXC thin films are assemblies of parallel, slanted, free-standing columns. Furthermore, the AFM image (Figure 2b) shows that the columns are assemblies of nanowires that are 50 to 100 nm in diameter. Thus, the nanostructured PPXC thin films contain nanowires having an aspect ratio (i.e., thickness/diameter) as high as 1000:1.

Transmission infrared (IR) spectroscopy was used to compare the nanostructured PPXC thin films qualitatively with planar PPX thin films (which are conventionally deposited<sup>4</sup> and do not possess nanostructured morphology). The IR analysis over the 500 to 4000  $\text{cm}^{-1}$  frequency range shows features for CH stretching (2800–3000  $\text{cm}^{-1}$ ), aromatic CH stretching (3026

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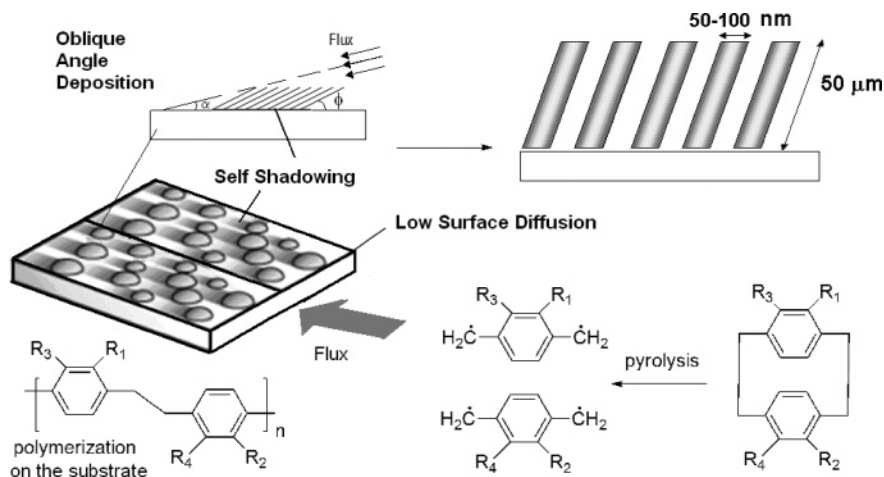
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**Figure 1.** Flow chart of the deposition of nanostructured poly(*p*-xylylene) (PPX) thin films showing the paracyclophane chemistry together with the vapor deposition technique. Nanowires grow at an inclined angle  $\phi$  when the vapor flux is directed at an angle  $\alpha \leq \phi$ . Side groups  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  can be esters, ketones, amines, lactones, and so forth.

$\text{cm}^{-1}$ ), CH deformation ( $1340 \text{ cm}^{-1}$ ), C deformation ( $1401 \text{ cm}^{-1}$ ), and benzene breathing ( $950 \text{ cm}^{-1}$ ) in Figure 2c for both nanostructured and planar PPXC thin films. This indicates that the chemical structure of the nanostructured PPXC thin films is the same as that of the planar counterparts.

The hydrophobic nature of the nanostructured PPXC thin films is shown by the optical image in Figure 2d of a water drop on the top surface of a film. The shape of the water drop on the resulting surface has an apparent contact angle of  $100 \pm 5^\circ$ , according to a standard static contact-angle measurement system. The surface roughness and porosity of nanostructured PPXC film were measured with an AFM to be 60 nm and 50%, respectively. Hence, the contact angle for the nanostructured PPXC thin film is predicted by the Wenzel formula<sup>13</sup> to be  $94^\circ$ , which is slightly higher than the  $87^\circ$  value measured<sup>14</sup> for the planar PPXC thin film.

The semicrystalline behavior of polymers is of great importance to the physical and chemical properties exhibited by the material.<sup>15</sup> Planar PPXC thin films produced conventionally are typically only about 50–60% crystalline.<sup>14</sup> At temperatures below the melting point of the crystallites, the planar PPXC thin films cannot be dissolved, but a slight swelling is observed as the solvent attacks the amorphous phase: 0% for water and 1 to 3% for dichlorobenzene.<sup>14</sup> The measured X-ray diffraction (XRD) pattern in Figure 2e shows that nanostructured PPXC thin films are also semicrystalline. The diffraction pattern of PPXC was also calculated using Mercury software<sup>16</sup> based on a monoclinic unit cell (Figure 2f) with  $a = 596 \text{ pm}$ ,  $b = 1269 \text{ pm}$ ,  $c$  (chain axis) =  $666 \text{ pm}$ , and  $\beta = 135.2^\circ$ .<sup>17</sup> A chloro-substituted ring represents the repeat unit along the polymer chain. Two major peaks, (020) and  $(-110)$ , are identified from the XRD data based on the computed diffraction pattern.

In conclusion, the work described in this letter concerns a novel method of deposition of free-standing PPX nanostructures in thin films. The nanostructured PPXC thin films were found

to organize spatially with chemical structure similar to that of planar PPXC thin films, but their morphology is different. Nanostructured PPX thin films offer the possibility of fabricating novel free-standing columnar materials by systematically varying and controlling the chemistry (i.e.,  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$ ) and substrate topology (i.e., patterned substrates). The demonstrated deposition of nanostructured PPX thin films is a simple and potentially versatile method for the functionalization of surfaces. Therefore, it is of great importance in fabricating interfaces for advanced antifouling coatings and biomedical devices,<sup>18,19</sup> a prospect that inspires further work on controlling the surface chemistry and nanostructured morphology of these films.

## Experimental Section

**Nanostructured Poly(chloro-*p*-xylylene) Deposition.** The fabrication of the nanostructured PPXC thin film starts with a chloro-paracyclophane dimer (commercially known as parylene-C, SCS Coatings, Inc.), which is placed in an evacuated chamber and converted to a reactive vapor of monomers by pyrolysis. The deposition rate and the deposition pressure are controlled by the evaporation temperature ( $175 \text{ }^\circ\text{C}$ ) of the dimer and the pyrolysis temperature ( $690 \text{ }^\circ\text{C}$ ). Depositions are made in a reactor that was modified to combine chemical and physical vapor deposition processes specifically for direct one-step fabrication of PPXC films. The substrate is held fixed in a specific orientation ( $\alpha = 10^\circ$ ). The dimer (0.5 g) is inserted into the vaporizer for each deposition, and the vapor pressure is maintained at approximately 10 mTorr. The deposition process takes 10 min after the required vacuum level has been achieved. The thin films are deposited on both glass and silicon substrates.

**Characterization Methods.** Transmission infrared spectra (IR, Bruker) are collected with respect to a silicon wafer reference in air. Spectra are recorded using Norton-Beer apodization with  $1 \text{ cm}^{-1}$  resolution, and for each spectrum, 400 scans are co-added. The spectra are analyzed using OPUS 5.5 software. The surface roughness is quantified by AFM (Nanoscope E, Veeco) in a liquid chamber using silicon nitride cantilevers in contact mode. Column dimensions are calculated with Nanoscope software (Veeco Metrology, CA) using the grain size tool. Contact-angle measurements (DFTA 1000, First Ten Angstroms, Inc.)

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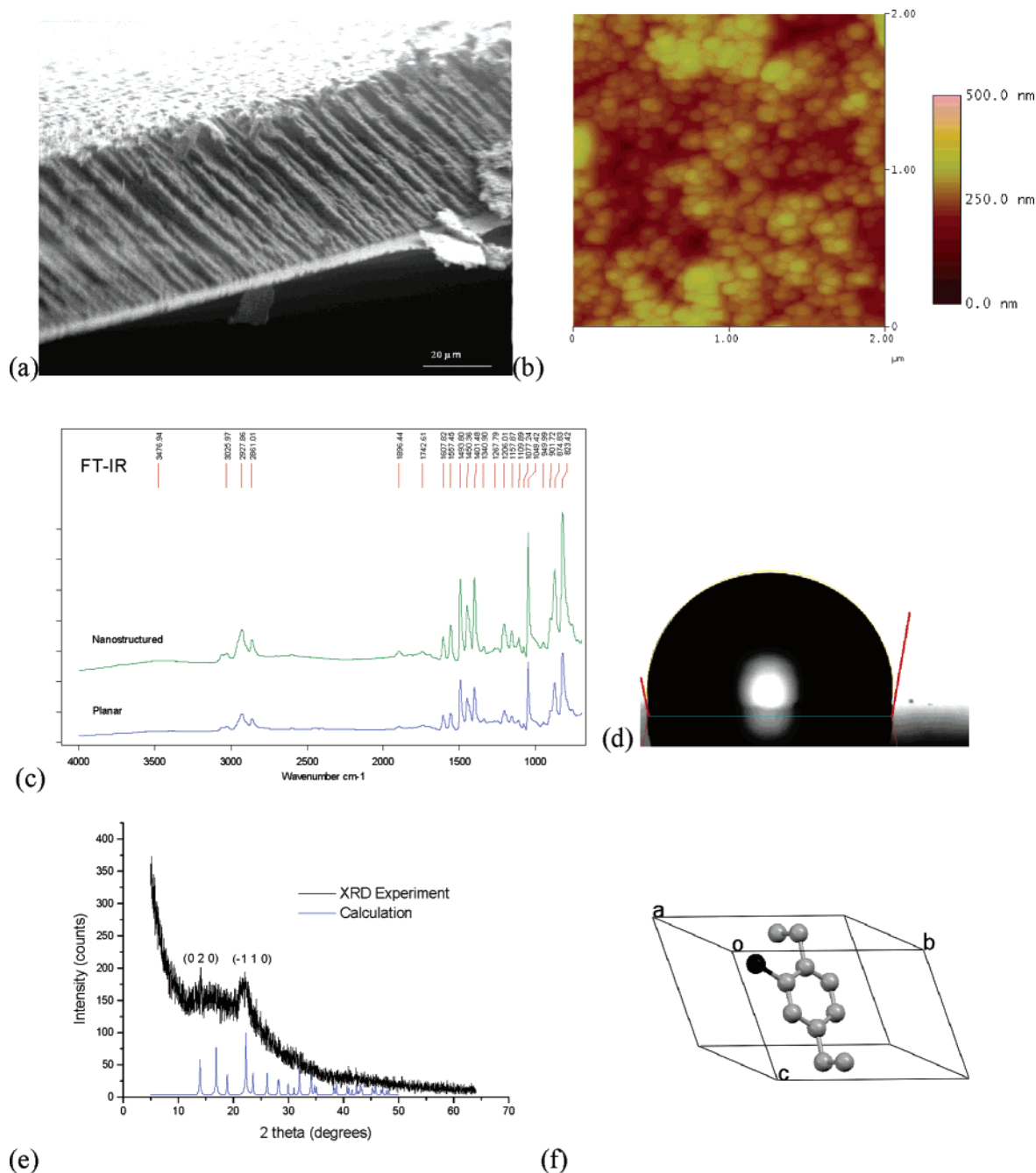
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**Figure 2.** (a) Cross-sectional SEM micrograph of a nanostructured PPXC thin film (scale bar  $20\ \mu\text{m}$ ). (b) Top-surface AFM image of the same film showing nanowires that are approximately 50–100 nm in diameter (color scale shows the height). (c) Transmission IR spectra of a nanostructured PPXC thin film and a planar PPXC thin film. (d) Optical image of a water drop on the top surface of a nanostructured PPXC thin film, the apparent contact angle being  $100^\circ$ . (e) Measured and calculated diffraction patterns of a nanostructured PPXC thin film. (f) Crystal structure of PPXC, wherein hydrogen atoms are not shown for clarity, and the first and last carbon atoms in the crystal lattice represent the repeat unit along the polymer chain (carbon and chlorine shown in gray and black respectively).

are carried out with a video microscope interfaced to a computer. The glancing angle XRD pattern of a nanostructured PPXC thin film deposited on a glass substrate is measured (Scintag Pad V). Samples for scanning electron microscopy (JEOL 6700F FE-SEM) images are prepared by cleaving the thin films in liquid nitrogen.

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