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Growth of nanostructured thin films of poly(*p*-xylylene) derivatives by vapor deposition

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Abstract

Nanostructured thin films of poly(*p*-xylylene) derivatives are deposited by oblique angle vapor deposition method under low-vacuum conditions. We showed deposition of columnar nanostructured poly(chloro-*p*-xylylene) and poly(bromo-*p*-xylylene) thin films, and co-deposition of nanostructured poly(*o*-trifluoroacetyl-*p*-xylylene-*co*-*p*-xylylene) thin film. Characterization of both the nanostructured and planar thin films of poly(*p*-xylylene) are performed with different experimental methods. We developed a generalized strategy towards depositing nanostructured poly(*p*-xylylene) derivatives and thus promise a new generation of thin films suitable for biomedical and antifouling applications.

Keywords: Nanostructured thin films; Paracyclophane; Poly-*p*-xylylene

1. Introduction

Nanoporous films have generated great interest due to their unusual physical and chemical properties arising from their high surface area and nanoscale spatial dimension. A nanoporous film is defined as a continuous connected structure with porosity in at least one dimension being in the nanometer range. A wide variety of nanoporous structures (e.g. wires, membranes and fibers) have been develop in the last two decades [1–4].

Nanoporous columnar thin films are assemblies of parallel, inclined nanowires generally grown by vapor deposition techniques [5,6]. Upright nanowires grow on a substrate that is kept perpendicular to the flux of source vapor. For oblique angle deposition, the substrate is tilted with respect to the incident vapor flux, thereby exciting a self-shadowing process. If the incident vapor flux is directed, on average, at an angle α to the substrate plane, the straight nanowires grow at an angle $\beta \geq \alpha$ to the same plane, as shown schematically in Fig. 1 for a columnar thin film of poly-*p*-xylylene (PPX). [2.2]Paracyclophane [7] is first converted to a reactive vapor of monomers by pyrolysis. The vapor flux of *p*-xylylene is then directed towards a tilted substrate where polymerization occurs on the substrate. Thus, the formation of nanostructured PPX columnar thin films is influenced by a combination of nucleation common in thin films [8] with bond formation (i.e., polymerization), in addition to geometrical self-shadowing, surface diffusion along the substrate of incoming monomers, and bulk diffusion leading to oriented crystallization [9–11].

We showed earlier that nanoporous helical structures of poly(chloro-*p*-xylylene) (Cl-PPX) can be grown using oblique angle deposition technique [9–11]. In this paper, we expanded the deposition technique to other PPX derivatives and showed co-polymerization of two PPXs. Particularly, we showed the deposition of poly(bromo-*p*-xylylene) (Br-PPX) and poly(chloro-*p*-xylylene), and co-deposition of poly(*o*-trifluoroacetyl-*p*-xylylene-*co*-*p*-xylylene) (F-PPX). PPX films are characterized with various experimental methods. Results for these nanostructured thin films are compared with planar PPX thin films. We have introduced a generalized

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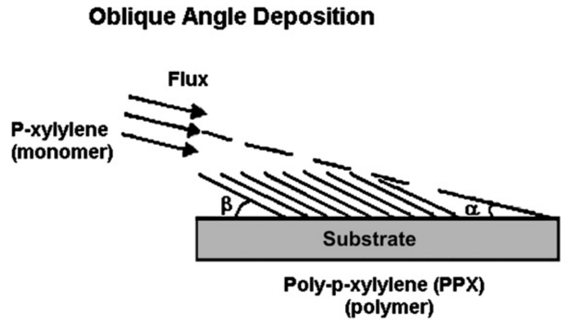

Fig. 1. Schematic of oblique angle deposition combined with pyrolysis of *p*-xylylene. The deposition process starts with [2.2]paracyclophane dimer and then converted to the poly(*p*-xylylene) film on a substrate at an oblique angle ($\alpha = 10°$).

process for nanostructured PPX polymerization based on oblique angle deposition, which is simple and inexpensive method for coating of surfaces at an industrial scale.

2. Experimental

2.1. Paracyclophane synthesis

We adopted the methods of Reich et al. [12] and Lahann et al. [13] to synthesize dibromo[2.2]paracyclophane and 4-trifluoroacetyl[2.2]paracyclophane, respectively (Fig. 2a). Briefly, bromination of [2.2]paracyclophane leads to four isomeric dibromides with 45% yield, whereas trifluoroacetyl-PPX is synthesized by Friedel–Crafts acylation of [2.2]paracyclophane with trifluoroacetic acid anhydride using an excess of $AlCl_3$ (90% yield).

2.2. Substrate preparation

A fresh Si (100) wafer is cleaned by successive immersions in HCl/CH_3OH (1:1 v/v), deionized water, and concentrated H_2SO_4. Adherence of the PPX film to the silicon substrate surface is increased by a self-assembled organosilane monolayer. Styrylethyltrimethoxysilane (Gelest, PA) monolayer is formed on the silicon substrate by using methods described elsewhere [14]. The substrate is baked on a hotplate at 120 °C for 4 min to complete the dehydration reaction that forms the siloxane bond between the organosilane and the silicon substrate. The SAM uniformity and thickness is measured by nanoshaving AFM technique [15].

2.3. PPX thin film deposition

Deposition of a PPX-derivative columnar thin film started with dimers, which are placed in an evacuated chamber and converted to a reactive vapor of monomers by pyrolysis (Fig. 2b). The deposition rate and the deposition pressure are controlled by the evaporation temperature (150–175 °C) and the pyrolysis temperature (650–690 °C) of the dimer. The substrate is held fixed in orientation at $\alpha = 10°$. 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 took 10 min after the required vacuum level has been achieved. The thin films are deposited on silicon substrates.

2.4. Characterization

A Philips XL-40 scanning electron microscope (SEM) is used for cross-sectional analysis of samples prepared by cleaving thin films in liquid nitrogen. All surface measurements are performed with a Nanoscope-E atomic force microscope (Veeco Metrology, CA). Topography images are collected in ambient air at room temperature, with silicon nitride (SiN) triangular cantilevers having contact mode tips (DNT-20, Veeco Metrology, CA). The FT-IR (Bruker Optics, MA) data were collected with respect to a silicon wafer reference in air. Spectra are recorded using Norton–Beer apodization with 4 cm^{-1} resolution, and for each spectrum 400 scans are co-added. The spectra are analyzed using OPUS 5.5 software.

3. Results

There are many [2.2]paracyclophane derivatives which have the same basic molecular architecture but with the aromatic or aliphatic hydrogen atoms replaced by other atoms or chemical groups (e.g. amines, ketones, lactones and esters) [16]. Three hydrophobic paracyclophane derivatives are selected for the current work. We synthesized dibromo[2.2]-paracyclophane and 4-trifluoroacetyl[2.2]paracyclophane based on methods of Reich et al. [12] and Lahann et al. [13], respectively. Dichloro[2.2]paracyclophane is purchased from SCS-coating, IN. Molecular structures and flow charts of the syntheses are given in Fig. 2a. Deposition process of nanostructured thin film is same for three PPX derivatives and it is discussed in detailed earlier [9–11]. Fig. 2b describes the pyrolysis of the paracyclophane, which is followed by polymerization on the silicon substrate during vapor deposition.

Thin films of PPX have a wide range of usage [17] such as chemical and corrosion resistant coatings, capacitor dielectrics, moisture barriers, electrical insulators dry lubricants and anti-friction layers in MEMS [18,19], but those are not nanostructured PPX. Instead, those films may be called "planar films", as they do not have any morphology or structure; in contrast, our PPX films are nanostructured with columnar morphology.

Fig. 3 shows cross-sectional SEM images and corresponding surface topography of the three PPX nanostructured columnar thin films deposited obliquely on silicon substrates at an angle $\alpha = 10°$. Surface topography is characterized by an atomic force microscope (AFM). Each film is an assembly of inclined columns having a length of 10–20 μm. The nanostructured columns grow at an angle $\beta = 55°$. Microscopic features of films from three different substrates appear to have close similarity. The surface AFM images presented also in Fig. 3 indicate the columns are about 50–200 nm in cross-sectional diameter.

Table 1 shows the measured columns size, roughness and surface area for three nanostructured columnar thin films in

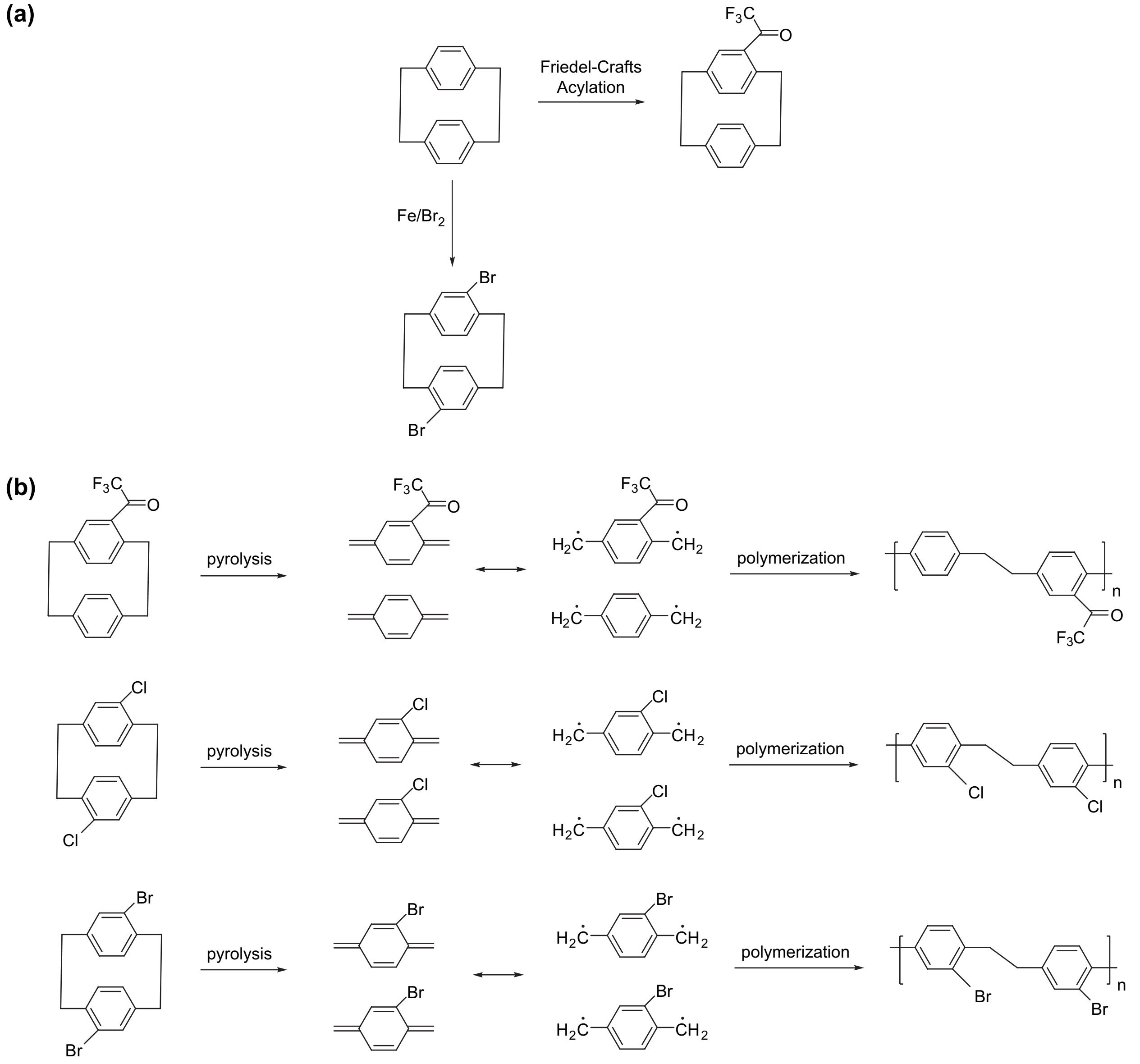

Fig. 2. (a) Synthesis of dibromo[2.2]paracyclophane and 4-trifluoroacetyl[2.2]paracyclophane, and (b) Polymerization of poly(bromo-p-xylylene) (Br-PPX) and poly(chloro-p-xylylene) (Cl-PPX), and co-polymerization of poly(o-trifluoroacetyl-p-xylylene-co-p-xylylene) (F-PPX) are shown.

comparison to their planar counterparts. PPX films are composed of ~40×10^6 aligned columns per square millimeter. Surface roughness data show that the nanostructured films are 3–15 times rougher compared to the planar films. This is expected since planar films form a conformal surface and their surface roughness is very small. Surface area, column size and roughness of PPX films are calculated with the Nanoscope Software (Veeco Metrology, CA).

The nanostructured films are also characterized by infrared (IR) spectroscopy (Fig. 4). The IR spectroscopy for the nanostructured Br-PPX and the Cl-PPX films indicates similar peaks for CH stretching (2800–3000 cm^{-1}), aromatic CH stretching (3026 cm^{-1}), CH deformation (1340 cm^{-1}), C-deformation (1401 cm^{-1}), and benzene breathing (950 cm^{-1}). IR spectra of F-PPX show significant differences below 2000 cm^{-1}. Specifically, the ketone (C=O) peak at 1712 cm^{-1} and alkyl halide peak (C–F) at 1135–1194 cm^{-1} are observed for F-PPX Fig. 4.

4. Conclusions

A general strategy to fabricate nanostructured PPX thin films by oblique angle vapor deposition is presented. We demonstrated deposition of poly(chloro-*p*-xylylene) and poly(bromo-*p*-xylylene) as well as co-deposition of poly(*o*-trifluoroacetyl-*p*-xylylene-*co*-*p*-xylylene) nanostructured thin film.

Nanostructured PPX films are currently deposited to 2.5 cm × 2.5 cm silicon substrates in a 30 cm diameter deposition chamber. We note that industrial scale deposition can be achieved by designing a larger deposition system. Additionally, the nanostructured PPX production technique does not

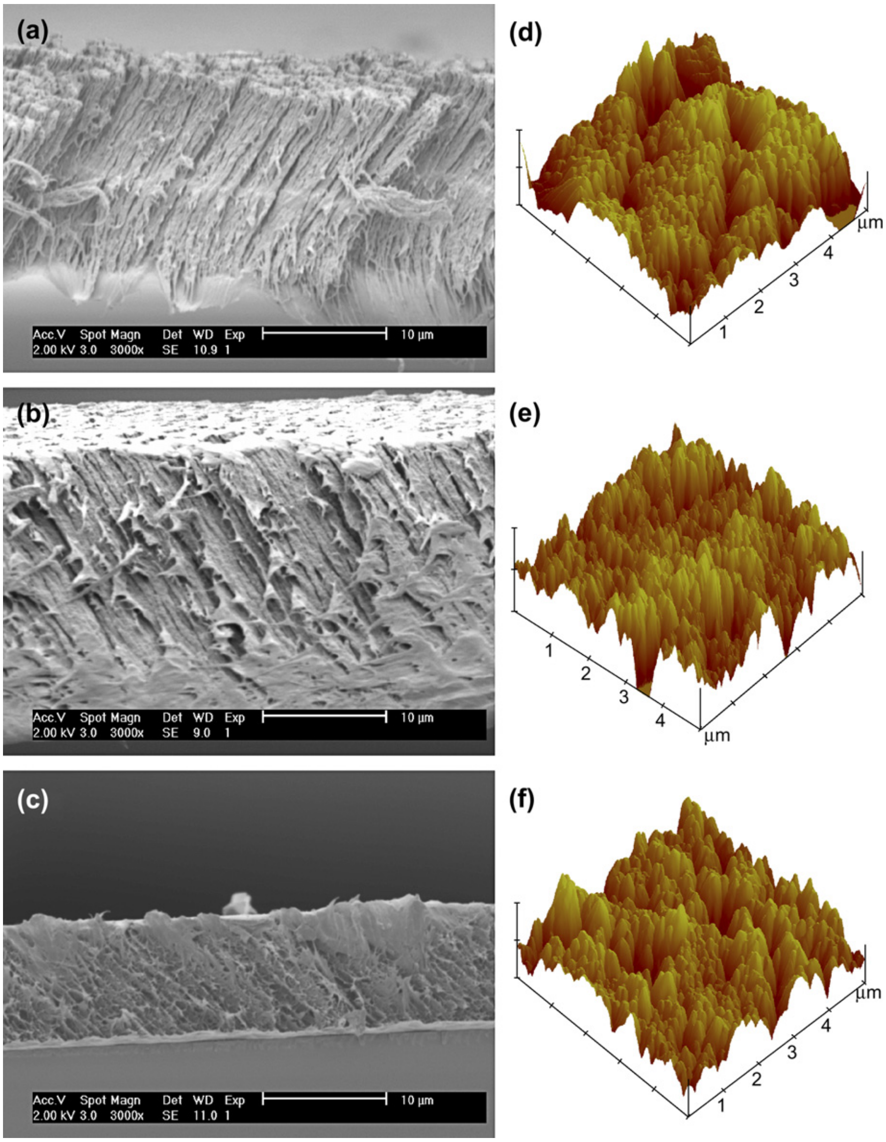

Fig. 3. Cross-sectional SEM images of columnar nanostructured. (a) F-PPX, (b) Cl-PPX, and (c) Br-PPX and corresponding surface images obtained by contact mode-AFM (scale bars for AFM scans: *X*: 1 μm/div, *Y*: 1 μm/div, *Z*: 350 nm/div).

require any mask, lithography method, clean room environment or a surfactant for deposition. Therefore, the nanostructured PPX deposition may be utilized in industrial applications as an inexpensive wide area manufacturing technique.

Table 1
Measured column size, roughness and surface area on a 2 μm × 2 μm top section of PPX thin films

Film type	Number of columns	Surface area (μm^2)	Surface roughness (nm)
Nanostructured F-PPX	152 ± 19	5.20 ± 0.14	62.9 ± 8.1
Nanostructured Cl-PPX	150 ± 6	5.13 ± 0.06	46.3 ± 5.0
Nanostructured Br-PPX	181 ± 20	5.17 ± 0.06	68.0 ± 14.5
Planar F-PPX	N/A	4.18 ± 0.05	17.6 ± 2.3
Planar Cl-PPX	N/A	4.07 ± 0.01	7.9 ± 0.8
Planar Br-PPX	N/A	4.02 ± 0.01	4.8 ± 1.3

The standard deviation is measured on five different sample sections.

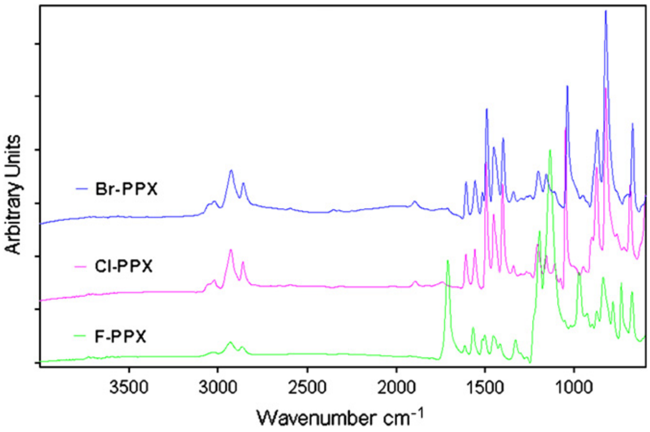

Fig. 4. IR spectra for nanostructured thin films of Br-PPX, Cl-PPX and F-PPX are shown.

We demonstrated co-deposition of two types of PPX monomers. Novel physicochemical properties can be obtained by co-deposition of two or more types of PPX monomers with different side groups. These properties can be manipulated by changing the film morphology (i.e., chiral, chevron or columnar deposition). Additionally, the topology of the nanostructured PPX can be modified by depositing the polymer on microscale lithographically patterned substrates [20]. Hence, we can optimize the physicochemical properties of the nanostructured PPX by controlling surface topology, chemistry and film morphology at the same time, and create a new generation of advanced coating material for naval and biomedical applications.

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