




Article

Modulating Polymer Ultrathin Film Crystalline Fraction and Orientation with Nanoscale Curvature

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Abstract: We investigated the effect of nanoscale curvature on the structure of thermally equilibrated poly-3-hexylthiophene (P3HT) ultrathin films. The curvature-induced effects were investigated with synchrotron grazing incidence X-ray diffraction (GIXRD) and atomic force microscopy (AFM). Our results demonstrate that nanoscale curvature reduces the polymer crystalline fraction and the crystal length. The first effect is strongest for the lowest curvature and results in a decrease in the out-of-plane thickness of the polymer crystals. On the other hand, the crystal in-plane length decreases with the increase in substrate curvature. Finally, the semi-quantitative analysis of crystal anisotropy shows a marked dependence on the substrate curvature characterized by a minimum at curvatures between 0.00851 nm^{-1} and 0.0140 nm^{-1} . The results are discussed in terms of a curvature-dependent polymer fraction, which fills the interstices between neighboring particles and cannot crystallize due to extreme space confinement. This fraction, whose thickness is highest at the lowest curvatures, inhibits the crystal nucleation and the out-of-plane crystal growth. Moreover, because of the adhesion to the curved portion of the substrates, crystals adopt a random orientation. By increasing the substrate curvature, the amorphous fraction is reduced, leading to polymer films with higher crystallinity. Finally, when the thickness of the film exceeds the particle diameter, the curvature no longer affects the crystal orientation, which, similarly to the flat case, is predominantly edge on.

Keywords: nanostructure; interfacial interactions; nanostructured substrates; strain



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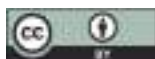
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1. Introduction

Poly-thiophenes are a class of organic semiconductors that have attracted great interest due to their solubility, easy processability, and environmental stability, which are useful for electronic devices [1,2]. In particular, among the thiophenes, poly-3-hexylthiophene (P3HT) has attracted great interest thanks to its electrical and optical properties [3,4]. It also tends to crystallize, with polymer chains that self-organize into an ordered structure [1,3]. Understanding the crystallization process and controlling the crystals' dimension are important to improve the performance of devices [3] since a strong correlation occurs between the performance of the device and the solid-state nanostructure [5]. It is known that the crystallization is driven by π - π interactions perpendicular to thiophene rings, leading to anisotropic aggregates forming [6]. Moreover, when the polymer is confined in a thin film, these π -stacking interactions can develop either along the substrate plane or along the direction perpendicular to it. The two preferred lamellar orientations of P3HT thin films are indicated as edge-on orientation, in which the lamellar stacking direction is perpendicular to the substrate surface, while π -stacking interactions are oriented along the substrate plane, and for face-on orientation, the lamellar stacking direction is

along the substrate plane [6,7]. In particular, while the edge-on orientation seems to be energetically favored, as it is obtained in close-to-equilibrium conditions, the face-on is a kinetically trapped orientation [7]. Indeed, when the P3HT film is deposited on surfaces, the fast solvent evaporation leads to a kinetically trapped morphology, where the edge-on and face-on orientations coexist. This thermodynamic and kinetic limitation leads to films with low crystallinity. Therefore, a post-deposition process must be performed to enhance the ordered structure [8,9]. Thermal annealing is a common method used to improve the crystalline quality by tuning molecular orientations and enhancing structural order [10]. Indeed, the heat treatment provides the P3HT enough energy to reorganize itself, moving from a structure characterized by a random orientation, in which both the lamellar orientations coexist together with a large amorphous fraction, to an ordered structure where the edge-on orientation is favored in view of its higher thermodynamic stability [3,11–16].

One of the most effective techniques to record both the P3HT crystal structure and orientation is X-ray diffraction as, in the case of edge-on predominant orientation, the 2D diffraction pattern shows an out-of-plane signal corresponding to the (100) polymer chain folding Bragg peak. This peak is generally accompanied by an additional signal related to the π -stacking, corresponding to (020) Bragg peak, along the substrate plane [3,14]. Moreover, it is essential to consider that the cooling rate also affects the structural order. In particular, it was observed that slow cooling can increase the density of π -stacked ordered structures upon annealing at the polymer melting temperature [17]. Therefore, slow and controlled cooling improves the crystalline quality with strong crystal orientation [18]. Finally, the crystallization of polymer thin films is believed to be initiated by heterogeneous nucleation at the polymer/substrate interface, where the amorphous regions are consumed, resulting in a smooth film characterized by strongly oriented crystallites [14,19]. Therefore, the crystalline structure and orientation are affected by the polymer molecular properties, surface nature, and polymer/substrate interactions [20–22]. It is in this perspective that, by preparing nanostructured substrates consisting of monodisperse silica particle monolayers with diameters comparable to the P3HT crystal sizes, we demonstrated that the substrate-induced nanoscale deformation, together with the surface energy balance, drives the crystallization of P3HT ultrathin films [23]. Furthermore, we observed that the substrate curvature already affects the orientation of fast-forming unannealed P3HT lamellae [24]. In the present work, we investigate the role played by the substrate nano-curvature on the crystal nucleation and growth of annealed P3HT films. We will show that the substrate nano-curvature affects not only the crystal orientation and size but also the overall crystalline fraction of the film.

2. Materials and Methods

2.1. Chemicals

Regio-regular P3HT with Mw: 54,000 and polydispersity 2.3, CHCl_3 , NH_4OH , and H_2O_2 were purchased from Sigma-Aldrich (Milan, Italy) and used as received. Aqueous suspension of silica particles (5% *w/v*) with nominal diameters of 50 ± 10 , 143 ± 4 , 235 ± 10 , 304 ± 20 , and 403 ± 10 nm was purchased from Microparticles GmbH, Berlin (Germany), and used as received.

2.2. Substrate Preparation

Hydrophilic substrates were obtained by treating silicon wafer (100) with a piranha basic solution (H_2O , NH_4OH , and H_2O_2 , ratio 5:1:1) at 60 °C for 10 min [25].

Nano-curved substrates were obtained by spin-coating the colloidal dispersion of silica particles on piranha-cleaned flat silicon wafers. The spin-coating parameters were adjusted to ensure uniform hexagonally packed arrays with a specific curvature equal to the inverse of particle radii [24], thus ranging from 0.0049 nm^{-1} to 0.0400 nm^{-1} . The so-obtained curved substrates were annealed at 90 °C for 10 min to remove the residual water and then made highly hydrophilic with basic piranha solution treatment.

A 5 mg/mL P3HT chloroform solution was spin-coated at 4000 rpm for 30 s, leading to films with a thickness of 67.5 ± 6.8 nm, regardless of substrate curvature, as measured by profilometry and UV–Vis characterization [24].

Finally, the polymeric films were thermally annealed in vacuum at 250 °C, P3HT melting temperature [26] for 30 min, then slowly cooled at 3 °C/min to room temperature.

2.3. Morphological Characterization

Morphological characterization was performed using a Nanoscope IIIA-MultiMode atomic force microscope (AFM) Digital Instruments (Santa Barbara, CA, USA) used in tapping mode. Images were recorded using Tap 300 G silicon probes from Budget sensors (Wetzlar, Germany), with a nominal resonance frequency of 300 kHz. The statistical analysis of the P3HT lamella length was obtained with an open-source program coded with MATLAB (R2023b), FiberApp (downloaded via Github) [27]. This program allows for the tracing of the lamellae in AFM images to determine their coordinate and, therefore, the lamellae length distribution.

2.4. Structural Characterization

The structural characterization was performed at the ID10 beamline of the European Synchrotron Radiation Facility (ESRF), Grenoble (France), using grazing incidence X-ray diffraction (GIXRD). A $22 \text{ keV} \pm 3.1 \text{ eV}$ X-ray beam was employed to record the GIXRD pattern, with an incident beam angle of 0.064 degrees, i.e., 80% of the total reflection at the critical angle. A Pilatus 300 k 2D detector collected the diffracted beam pattern at 389.7 mm from the sample. Samples were placed inside a sample holder covered by a Kapton dome and filled with helium.

A geometrical correction was performed on each diffraction pattern, followed by the conversion from the pixel matrix to scattering vector, q , to extract the 1D profiles by line cutting along the desired directions.

The obtained peaks were then fitted with a Lorentzian equation.

3. Results

Reference topographic images of the flat silicon substrate and of the as-deposited particle monolayers are reported in the Supporting Information (Figure S1). The deposition protocol allowed for obtaining hexagonally close-packed silica particle monolayers with micron-scale homogeneity (Figure S2).

We have already demonstrated that the spin-coated P3HT thin films homogeneously cover the surfaces without altering the particle monolayer arrangement, and the rapid solvent evaporation leads to the formation of an out-of-equilibrium crystalline structure with low crystallinity [9,24]. In order to increase the crystalline fraction, P3HT films on substrates with different curvature were subjected to thermal annealing and then characterized by synchrotron radiation grazing incidence X-ray diffraction (GIXRD), recording the 2D diffraction patterns in Figure 1 for films on both flat and nano-curved substrates.

The 2D pattern of the flat substrate (Figure 1a) shows the peculiar signature of the edge-on orientation of the P3HT lamellae, with high-intensity signals along the q_z direction, corresponding to the out-of-plane lamellar stacking (100) Bragg peak at approximately 0.45 \AA^{-1} and the higher-order peaks, namely (200) and (300). Vice versa, the π -stacking generates an in-plane (020) Bragg peak along the q_{xy} direction at approximately 1.70 \AA^{-1} . After thermal annealing, the crystalline fraction increased, with a predominance of edge-on lamellar orientation, consistent with previous literature reports [28].

The 2D patterns recorded on nano-curved substrates (Figure 1b–f) show different behavior, with a ring of uniform intensity at about 0.45 \AA^{-1} and a broad halo at 1.70 \AA^{-1} , corresponding, respectively, to (100) and (020) Bragg peaks. We have already observed similar results for the non-equilibrated films [24]. In that case, the ring was related to the variation in the lamellae orientation with respect to an ideal baseline of the flat substrate.

In other words, lamellae adhere to the particle surface with both edge-on and face-on orientations; therefore, the orientation with respect to the sample baseline is random [24].

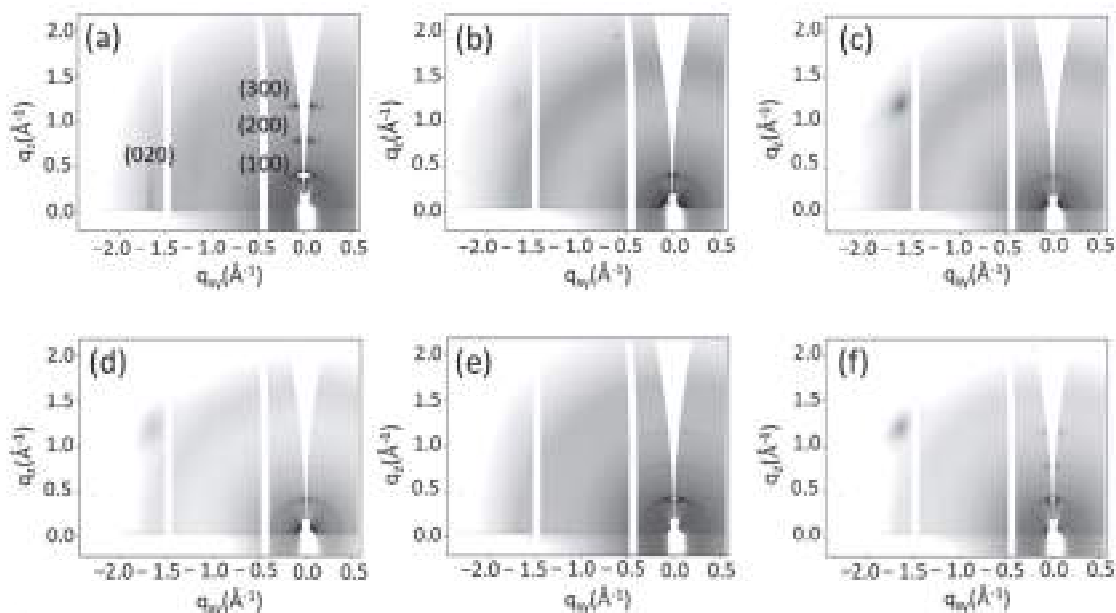


Figure 1. 2D GIXRD patterns of P3HT after thermal annealing on flat substrates (a) and on substrates having different curvature: 0.00492 nm⁻¹ (b), 0.00658 nm⁻¹ (c), 0.00851 nm⁻¹ (d), 0.0140 nm⁻¹ (e) and 0.0400 nm⁻¹ (f). The spot in the left top part of some patterns is a Si reflection, which is recorded in case of non-perfectly homogeneous substrate coverage by particles and polymer.

Similarly, thermal annealing favors the edge-on lamellae orientation with respect to the curved portion of the substrates, but to the ideal baseline, the lamellae adopt different orientations, recording, also after the annealing, a narrow ring with uniform intensity. However, with the increase in surface curvature, two more weak signals appear (Figure 1e,f) along the q_z direction, corresponding to the higher-order peaks (200) and (300) (Figure 2a), as observed for flat substrates (Figure 1a).

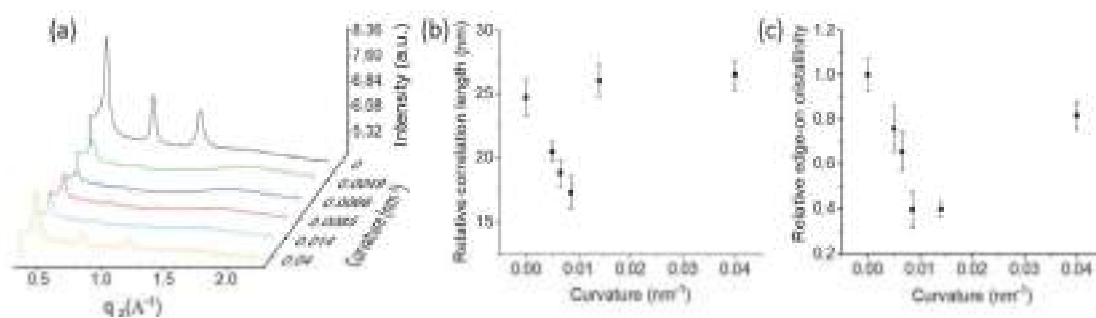


Figure 2. 1D profiles were extracted from 2D patterns along the q_z direction for different surface curvature (a). Semi-quantitative information was obtained by performing a Lorentzian fit of the (100) Bragg peak, and in particular, the relative correlation length (b) and the relative edge-on crystallinity (c) were determined.

Semi-quantitative information can be obtained by fitting 1D profiles extracted from the 2D patterns along q_z (Figure 2a). The results show that the (100) Bragg peak position is unaffected by the curvature, with a lamellar spacing d₁₀₀ ≈ 14.7 Å, regardless of the substrate curvatures. This proves that the nano-curvature does not affect the P3HT crystalline structure. Similar interplanar distances after thermal annealing have already been reported in the literature [29,30].

From the width at half height (FWHM, w) of the diffraction peak, the out-of-plane relative correlation length (Figure 2b), i.e., the average crystalline size, $2\pi/w$ can be determined. However, the experimental apparatus did not account for instrumental broadening as the 170 μm broad detector pixels are unsuitable for high-resolution diffraction measurements. Therefore, the observed peak variation can only be considered as a general indication of the crystalline size variation with curvature and thermal annealing. It should be mentioned that the relative correlation length recorded here on flat substrates is consistent with previously reported P3HT out-of-plane crystal thicknesses [31–33].

The increase in surface curvature results in an expansion in the full width at half maximum (FWHM) of the diffraction peak (Figure 2b), with a threshold curvature value of 0.0085 nm^{-1} . A further increase in curvature leads to a decrease in the peak width.

In order to investigate the orientation distribution of lamellae, we determined the relative variation in the edge-on crystallinity with the curvature from the (100) intensity signal along q_z . The (100) peak intensity on the flat substrate was used as a normalization factor. The results, reported in Figure 2c, show a decrease in the edge-on crystallinity, enhanced by the substrate nano-curvature up to 0.014 nm^{-1} , while the orientational randomization is less marked for the 0.04 nm^{-1} nano-curvature, which shows, similarly to the reference flat substrate, predominant edge-on orientation.

Further information about polymer crystallization can be obtained from the morphological characterization performed with atomic force microscopy (AFM). The AFM-phase images, reported in Figure 3, show a homogeneous distribution of polymeric lamellae on both curved portions and interstices between particles. However, the substrate curvature significantly influences the length distribution, as determined by tracing the lamellae following the procedure described above.

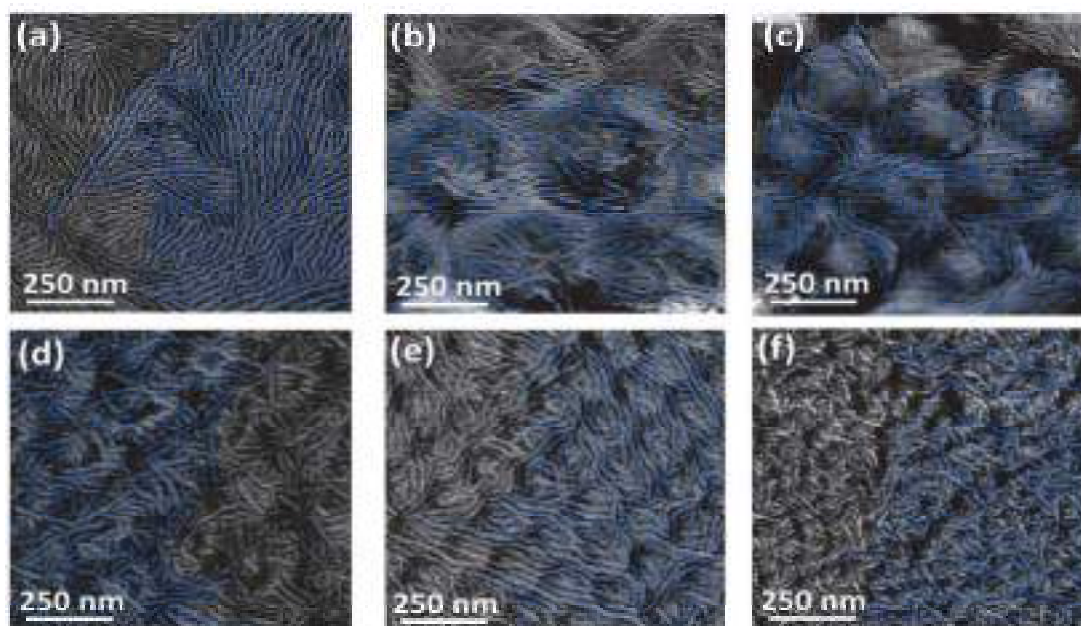


Figure 3. $1 \times 1 \mu\text{m}^2$ AFM phase images of annealed P3HT films on a flat substrate (a) and on substrates having different curvatures: 0.00492 nm^{-1} (b), 0.00658 nm^{-1} (c), 0.00851 nm^{-1} (d), 0.0140 nm^{-1} (e) and 0.0400 nm^{-1} (f). The blue traces mark the exemplificative lamellar tracing for each image, used to determine the lamellae length distribution.

In this case, the average lamellar length decreases as the substrate curvature increases until 0.0085 nm^{-1} , beyond which further increases in curvature do not produce significant variations. This is evident from the histogram distribution of the traced length (Figure 4), showing a progressive reduction in the highest lamellar lengths with curvature up to 0.0085 nm^{-1} .