Additive Growth and Crystallization of Polymer Films

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Supporting Information

ABSTRACT: We demonstrated a polymeric thin film fabrication process in which molecular-scale crystallization proceeds with additive film growth, by employing an innovative vapor-assisted deposition process termed matrix-assisted pulsed laser evaporation (MAPLE). In comparison to solution-casting commonly adopted for the deposition of polymer thin films, this physical vapor deposition (PVD) methodology can prolong the time scale of film formation and allow for the manipulation of temperature during deposition. For the deposition of molecular and atomic systems, such a PVD manner has been demonstrated to facilitate molecular ordering and delicately manipulate crystalline morphology during film growth. Here, using MAPLE, we deposited thin films of a model polymer, poly(ethylene oxide) (PEO), atop a temperature-controlled substrate with an average growth rate of less than 10 nm/h. The mechanism of deposition is sequential addition of nanoscale liquid droplets. We discovered that the deposition process leads to the formation of two-dimensional (2D) PEO crystals, composed of monolamellar crystals laterally grown from larger nucleus droplets. The 2D crystalline coverage and crystal thickness of the films can be manipulated with two processing parameters, deposition time, and temperature.

INTRODUCTION

Semicrystalline polymer thin films have been extensively investigated as an enabling material for many technologies, including advanced barrier coatings,1 pressure/imaging sensors,2,3 electronic memories,4,5 and energy devices.6,7 In all applications, control of the crystalline morphology is of paramount importance due to the observed correlations between structure and performance.1,4,6,7 Typically, polymer thin films are prepared by casting from solution. However, while deposition is facile and economically appealing, the short processing time combined with rapid vitrification limits morphological development of the crystalline domains in polymer thin films.7−9 To circumvent this issue, efforts to control and improve crystalline morphology in polymer thin films, e.g., active layers in organic electronics, have aimed to prolong the time scale of vitrification or enhance molecular mobility during or subsequent to film deposition.8−12 The success of these strategies suggests that it would be beneficial to have a processing route in which slow film growth and crystallization can occur simultaneously.

Recently, there has been a considerable effort to exploit the unique advantages of matrix-assisted pulsed laser evaporation (MAPLE) for the growth of polymer thin films.13−18 In the MAPLE process, a pulsed laser ablates a target consisting of a frozen dilute solution of the desired polymer. The frozen matrix solution serves as a sacrificial matrix to transport the polymer into the gas phase. Contrary to direct laser ablation, MAPLE provides a gentle and nondestructive means for polymer film deposition.14 Control of various process parameters has been shown to tune film morphology. For instance, MAPLE has been shown to control preferential crystal orientation and the extent of crystallinity in thin polymer films by adjusting the matrix formulation17 and substrate temperature,18 respectively.

Conceptually, the film growth in MAPLE proceeds by the additive deposition of nanometer-sized droplets comprising the target polymer.20,21 With tunable laser pulse rates and target polymer concentration, the average film growth rate throughout the substrate can be controlled to <1 nm/s, thus enabling the slow growth of polymer films in a manner recently advocated for organic electronics.19 There are some experimental and simulation reports that investigated the nature of ablation process in MAPLE22,23 and the size distribution of polymer droplets as a function of process parameters.21,24 How the mechanism of MAPLE, i.e., the deposition of nanoscale polymer droplets, influences the morphology of semicrystalline polymer films has not been investigated. We note that this
effect could be significant, as nanoscale confinement strongly influences polymer crystallization.\textsuperscript{1,25–32} To achieve such a study requires ultraslow MAPLE deposition to allow for the capture of the early stages of film growth and crystalline morphology.

Here, we employ atomic force microscopy (AFM) to investigate the early stages of film growth and crystallization of a semicrystalline polymer film deposited by MAPLE at slow growth rates. The study is undertaken using poly(ethylene oxide) (PEO), a model polymer, in which crystallization in thin-film geometry has been thoroughly investigated.\textsuperscript{1,25–29,33}

The average film growth rate was extremely slow, $\sim 6\,\text{nm/h}$, to promote the simultaneous occurrence of film formation and crystallization. We investigated the influence of growth time and deposition temperature on the crystalline film morphology of PEO deposited atop as-received silicon wafers (AR-Si). We found that the film morphology strongly depends on these process parameters. We anticipate that our findings will inform the future use of MAPLE as a processing tool to deposit thin films of semicrystalline polymers in which control of the morphology is desired.

\section*{RESULTS AND DISCUSSION}

First, to investigate the nature of the PEO film growth during processing, we deposited PEO atop n-octadecyltrichlorosilane-coated silicon wafers (OTS-Si) with low surface energy (15.2 mJ/m$^2$). We found that the deposition of PEO atop hydrophobic surfaces leads to the formation of individual nonwetting droplets; we have thus been able to quantify their size distribution. Deposition of PEO at 25 °C ($T_{\text{sub}} = 25$ °C) resulted in the formation of droplets with radii ranging from $\sim 10$ nm to $\sim 10\,\mu\text{m}$ as shown via optical microscopy and AFM in Figure 1a. Figure 1b is a histogram plot of the droplet size distribution for 2 h of deposition ($t_{\text{dep}} = 2\,\text{h}$) with an average growth rate of $\sim 6\,\text{nm/h}$ (see Methods for details). The distribution shows that the dominant droplet size is $\sim 40$ nm and that the number density of droplets rapidly decreases with radii $>55$ nm. Irrespective of droplet size, the height-to-radius ratio ($h/R$) remained constant at $\sim 0.5$ as shown in Figure 1c, providing evidence that the deposited PEO is mobile on the substrate surface despite the fact that the substrate temperature is held significantly below the bulk crystallization point of 42.5 °C (see DSC measurements in Methods for details).

Under identical deposition conditions, \textit{i.e.}, the same growth rate and $T_{\text{sub}}$, we next deposited PEO onto AR-Si substrates. Figure 2a shows a film with $t_{\text{dep}} = 1\,\text{h}$ atop AR-Si, in which a primary nucleus droplet is surrounded by numerous smaller liquid droplets. All primary nucleus droplets exhibited a $\sim 10$ nm-thick platelet-like base (see Figure 2a inset) which we refer to as the monolamellar crystal (MLC). The AFM amplitude
error image of a primary nucleus droplet (Figure 2b) reveals a spiral-growth morphology. Furthermore, the conformation of liquid droplets atop AR-Si differed from those atop OTS-Si. The liquid droplets observed in Figure 2a were 2−4 nm in height irrespective of their lateral size. This height is comparable to the Rg of PEO with Mn = 4600 g/mol, suggesting that the liquid droplets on AR-Si were composed of a monolayer of PEO due to attractive interactions with the substrate.34

When increasing tdep to 2 h, the primary nuclei developed more pronounced fingerlike crystal patterns as shown in Figure 2c. Grown from the base of the primary nuclei, the fingerlike MLCs exhibited a thickness of ∼10 nm. The liquid regions surrounding the crystalline islands also transformed from an ensemble of discrete droplets to a continuous film, thus forming a monolayer-thick (2.7 ± 0.4 nm) liquid layer. Figure 2d shows the AFM phase image of region R1 in Figure 2c. The spiral morphology of the primary nucleus, the finger-like MLCs, as well as the liquid monolayer are all clearly depicted. In addition, liquid droplets were observed on the surface of the MLCs.

The unique film morphology on AR-Si is a consequence of the deposition mechanism, that is, the additive assembly of a size-distribution of liquid nanodroplets. Smaller droplets are unable to crystallize by themselves due to low nucleation probability,26 instead, they adsorb to the substrate to form a liquid layer. In contrast, larger droplets undergo crystallization when deposit onto low-temperature substrates, which we denote as primary nucleation. Henceforth, crystal growth of the fingerlike primary MLCs proceeds from the primary nuclei along the substrate, facilitated by the presence of the nearby liquid layer. Unlike crystallization of spin-cast films, in which molecular ordering is achieved during rapid solidification of the entire film, here molecular ordering is achieved within nanoconfined regions over the long time scales of film growth. The fingerlike morphology is due to the limited diffusion of PEO to the crystal growth front at large undercoolings, as predicted by the diffusion-limited aggregation (DLA) model.27,35

Film growth in which molecular-scale crystallization occurs prior to the deposition of more material provides a unique means to tune crystal nucleation and growth, hence giving the resulting morphology, as previously demonstrated for metallic or molecular films.26,34 To investigate the relationship between tdep and the extent of crystalline surface coverage, we conducted two sequential MAPLE depositions with 2 h intervals on the same AR-Si substrate at 25 °C with an intervening thermal annealing step at 35 °C for 3 h after the first 2 h deposition interval. The film morphology is illustrated in Figure 3a. Thickening of crystal boundaries occurs during thermal annealing,23,33 and therefore, can serve as a marker in distinguishing crystals formed in the first from the second MAPLE deposition. Among the four crystalline islands, denoted N1−N4 in Figure 3a, only N1 was deposited in the
first stage as indicated by the presence of the elevated edge on the fingerlike patterns. These elevated edges of N1 had continuing primary MLCs, which had no elevations at the growth front (see Figure 3b). This unique morphology clearly indicates that the island N1 was formed during the first deposition interval. The continuing fingerlike patterns grown from the elevated edges of N1 and the additional islands, N2–N4, were formed during the second deposition interval. The results demonstrate that the extent of crystalline surface coverage in MAPLE-deposited films can be controlled at a molecular scale with deposition time, thus providing an unprecedented approach to control polymer crystal growth in films.

In an effort to reach to full coverage of the substrate with crystalline PEO, we further increased the deposition time and investigated the morphological evolution of the crystalline islands. Figure 3c illustrates the film morphology with $t_{dep} = 6$ h. The crystalline structures grew more compact with increasing $t_{dep}$. Notably, under these deposition conditions the crystalline surface coverage did not increase with increasing $t_{dep}$ as predicted by DLA. Instead, the growth of the crystalline domains was hindered after $t_{dep} \sim 4$ h. To understand this, we investigated the evolution of the thickness profile of the primary MLCs (see Methods for details), as a function of $t_{dep}$ from 2 to 12 h (Figure 3d). Remarkably, the primary MLCs in the samples with $t_{dep} \leq 6$ and 12 h were submersed in a liquid layer of thickness $\sim$8 and $\sim$15 nm each, as depicted in the schematic in Figure 3d. This indicates that the liquid layer acted more as a hindrance than a source for further crystal growth. The increasing thickness of the primary MLCs at the growth front with increasing $t_{dep}$ can be explained by the continuous coverage of a liquid PEO overlayer during deposition. This addition of the PEO atop the MLC can serve as the source of secondary crystallization, nucleated by the crystalline face, along the periphery of the MLC. Evidence of secondary crystallization is shown in Figure 3, parts e and f.

The hindrance of crystallization after $t_{dep} > \sim 4$ h can be explained by suggesting that the mobility of the liquid layer decreases with increasing thickness. To test this assumption and enhance the extent of the crystalline surface coverage, we employed two different temperature protocols. In the first method, MAPLE was performed for 2 h at 25 °C. Subsequently, the sample was heated in situ to 50 °C and MAPLE proceeded for an additional 4 h at the same growth rate followed by a cooling step to room temperature. Two types of morphologies were observed. Figure 4a illustrates the first type of morphology. Clearly, in comparison to Figure 3c (same $t_{dep}$ and growth rate), the crystalline morphology is more compact and the extent of crystalline surface coverage is significantly greater. Here, most of the trenches between the islands were filled. The islands are composed of $\sim$25 nm-thick MLCs and surrounding $\sim$10 nm-thick dendrites. Figure 4b illustrates the second type of morphology. Again, in comparison to deposition at 25 °C, the extent of crystalline coverage has dramatically increased as revealed by AFM analysis and corroborated by the X-ray diffraction data shown in Figure S1 (Supporting Information). However, contrary to the first type, the second type of crystalline islands consists of uniform $\sim$10 nm-thick MLC fingers.

The morphological difference in Figure 4, parts a and b, is due to the deposition interval in which primary nucleation occurred. In Figure 4a, primary nucleation occurred in the first 2 h of deposition at 25 °C. During the following 4 h of deposition, the increased substrate temperature would facilitate the polymer chain dynamics in the liquid layer to enable the continuation of crystal growth, resulting in more compact structures of the islands. Crystal growth in the trenches of islands like region R4 in Figure 4a is diffusion-limited (DL) due to the high density of surface nucleation sites. On the contrary, crystal growth at the outermost growth fronts like R5 in Figure 4a is nucleation-limited (NL), resulting in the formation of thinner dendrites during the cooling interval.

In Figure 4b, primary nucleation occurred after MAPLE during the cooling interval, a result due to the dramatically reduced probability of primary nucleation at the increased substrate temperature. Under these conditions, prior to cooling, a liquid PEO layer of $\sim 3R_0$ in thickness is produced. Upon cooling, crystallization would proceed from larger liquid droplets. The inset in Figure 4b, a magnification of R6, shows the crystal growth from a primary nucleus. On the basis of the thickness of the MLC, we estimate that crystallization occurred at $\sim$25 °C.

To confirm the inhibition of primary nucleation at 50 °C, we performed MAPLE deposition for 2 h at 50 °C followed by cooling to room temperature; thus, eliminating the possibility of primary nucleation from liquid PEO layer during the deposition. With the exception of a small portion of crystalline islands, which are assumed to be grown from deposited}

Figure 4. (a, b) Samples were made with two sequential MAPLE depositions onto AR-Si: the MAPLE 1st was conducted with $t_{dep} = 2$ h and $T_{sub} = 25$ °C, followed by MAPLE 2nd with $t_{dep} = 4$ h and $T_{sub} = 50$ °C. The samples were cooled to room temperature after deposition. (a) AFM height image showing the morphology of a type 1 crystalline island that formed with a primary nucleation in MAPLE 1st step. (b) AFM height image showing the morphology of a type 1 crystalline island that formed with a primary nucleation step. The inset image magnifies the region R6. (c) AFM height image showing the morphology of a sample made with $t_{dep} = 2$ h at 50 °C followed by a cooling to room temperature.
heterogeneous nuclei, the major crystalline morphology in the film consisted of uniform ∼10 nm-thick MLC dendrites as illustrated in Figure 4c. The results illustrate that by simply adjusting the deposition temperature it is possible to control when nucleation occurs, and hence, the morphology in a manner not previously demonstrated for polymers.

Lastly, to check the chemical identity and crystalline structure of MAPLE-deposited PEO films, we performed Fourier transform infrared spectroscopy (FTIR) and grazing-incidence X-ray diffraction (GIXD) on these films. Figure 5a compares the FTIR spectra of MAPLE-deposited films (black line) with the starting materials, a raw PEO (red) and a DMSO solvent (blue). In the spectra of the MAPLE-deposited film the characteristic DMSO peaks are not noticeable, indicating that the film is free of DMSO. In comparison of raw and MAPLE-deposited PEO, we identified the same strong stretches in the spectra of both films, i.e., the primary alcohols (peak P6 in Figure 5a), aliphatic ethers (P5), and saturated methylene groups (P1−P4, P7),38,39 with the exception of a slight feature at ∼1200 cm⁻¹. Next, to probe the crystalline structure of PEO films deposited via MAPLE at 25 °C for 6 h, we employed GIXD; the two-dimensional GIXD pattern is shown in Figure 5b. The pattern reveals two strong reflections, located at q = 1.36 and 1.66 Å⁻¹, corresponding to the (120) reflection and the overlapping reflections of the (112), (032), (132), and (212) planes of the monoclinic PEO crystal structure, respectively.40,41 Figure 5c plots the scattering intensity as a function of scattering vector (q), where the crystalline peaks of the usual monoclinic form of PEO are clearly depicted. Figure 5d shows the azimuthal distribution of the (120) reflection; that the intensity is strongly centered at 90° suggests that PEO lamellae adopt a preferential flat-on lamellar orientation in which the c-axis of monoclinic PEO is normal to the substrate.40,41 While the azimuthal distributions suggest that the films are preferentially oriented, we do see isotropic scattering along q = 1.36 and 1.66 Å⁻¹; this can be attributed to the large primary nuclei centered at each of crystalline islands and the nonpreferentially oriented secondary crystals that grow atop the dendritic arms at long growth times (see Figure 3e). These results are in agreement with the crystalline morphology observed using AFM. The FTIR and GIXD results confirm that the target PEO was nondestructively deposited onto the substrate, free of matrix solvent, and crystallized into the usual monoclinic form of PEO.

**CONCLUSIONS**

We have investigated the early stage morphology of crystalline polymer films evaporatively deposited via MAPLE. The formation of 2-dimensional dendritic crystals was rendered by the deposition of a size-distribution of polymer nanodroplets, among which only larger droplets can undergo primary nucleation at the deposited location, while other smaller droplets form dendritic monolamellar crystals or a liquid layer. We showed that crystalline coverage and crystal thickness of the films can be manipulated with two processing parameters, deposition time or substrate temperature, which is unique to
MAPLE. We anticipate that the approach will enable dominant chain orientation when molecular-scale deposition is performed on the appropriate substrate.\textsuperscript{30–32} Furthermore, the ability to exploit MAPLE for codeposition as well as multilayer film deposition will open the possibility to engineer structures in thin film polymeric-based devices in ways that are difficult by other means.

**METHODS**

**Materials.** Poly(ethylene oxide) (PEO) with number-averaged molecular weight of 4600 g/mol and polydispersity of 1.1 was obtained from Aldrich Company. Differential scanning calorimetry (DSC) was conducted with a TA Q.2000 to investigate the melting and crystallization temperature of raw PEO in bulk (see DSC Measurements in Methods). Dimethyl sulfoxide (DMSO) (ACS reagent, \( \geq 99.9\% \)) was obtained from Sigma-Aldrich Company and used as the matrix solvent. Silicon wafers (p-type, (100)) freshly purchased from UniversityWasser Inc. were used as as-received substrates (AR-Si) after being blown with nitrogen gas. For the preparation of n-octadecyltrichlorosilane-coated substrates (OTS-Si), UV-ozone cleaned silicon wafers were immersed in an OTS/deionized water/trichloroethylene solution for 1 h. After the coating, the substrates were rinsed and sonicated in toluene to remove multicoated OTS layers, resulting in a monolayer of OTS on the silicon substrate. The surface energies of both substrates were calculated according to (Ref. 12) using the measured contact angles of deionized water and glycerol droplets on the substrates. The calculated surface energies for AR-Si and OTS-Si are 66.7 and 15.2 mJ/m\(^2\), respectively.

**MAPLE Deposition.** For the preparation of MAPLE target solution, PEO was fully dissolved in DMSO at a concentration of 1 mg/mL with heating around 70 °C. The premade solution was preheated to 60–65 °C and loaded into an aluminum target cup; the cup was then rapidly cooled in a liquid nitrogen bath until the solution became completely frozen. The substrates (AR-Si or OTS-Si), which were attached to a custom-made electric heater, and the target cup were then installed inside the vacuum chamber at a distance of \(-6\) cm apart. The chamber was immediately pumped down by a turbo pump, and the KrF laser (LightMachinery PulseMaster 844, \( \lambda = 248 \text{ nm} \), pulse duration \( = 20 \text{ ns} \)) was operated with a repetition rate of 5 Hz and a fluence of 0.09 mJ/cm\(^2\) (15 mm\(^2\) spot area) at the vacuum level. The beam was aligned above the sample at an angle of \(-0.2^\circ\) relative to the substrate's normal. Scattered intensity was collected with a two-dimensional CCD detector, positioned 108.4 mm from the sample. All GIXD images have been background subtracted.

**Differential Scanning Calorimetry (DSC) Measurements.** Differential scanning calorimetry (DSC) of the target PEO (\( M_\text{w} = 4600 \text{ g/mol} \)) was conducted with a TA Q.2000 to investigate the melting and crystallization temperature of raw PEO in bulk (data are not shown). Two melting peaks were observed at 56.3 and 60.0 °C, and a crystallization temperature at 42.5 °C. The DSC thermogram of ~2–10 mg of PEO was measured after erasing thermal history at 80 °C for 20 min. The cooling and heating cycles were recorded with a rate of 2 °C/min in order.

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