Lamellar orientation of polyamide 6 thin film crystallization on solid substrates

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ABSTRACT

We studied the lamellar orientation of polyamide 6 (PA6) thin films with the thickness ranged from ~5 μm to ~20 nm on different solid substrates. The lamellar morphology was observed using atomic force microscopy and transmission electron microscopy, and the lamellar orientation was characterized using two-dimensional (2D) grazing incidence wide-angle X-ray diffraction (GI-WAXD) and selected area electron diffraction (SAED). The 2D GI-WAXD results indicate that in the films thicker than ~50 nm PA6 lamellae of the α-form are preferentially edge-on with the ab-planes (b is the chain axis) parallel to the substrate. Decrease of film thickness leads to higher order of the orientation. This edge-on orientation is insensitive to the surface properties of the substrates changed from hydrophilic to hydrophobic, suggesting that the low energy hydrogen bonded sheets of PA6 are prone to lying down in the film. For the films on the hydrophilic substrate with thickness less than ~50 nm, the edge-on orientation remains. On the other hand, on a more hydrophobic substrate, flat-on lamellae can be detected by SAED when the film thickness is reduced to be less than 50 nm. An unexpected result is that in the ~30 nm-thick thin films the strong confinement effect can result in flat-on lamellae of PA6's γ-form, although the crystallization temperature applied did not favor the γ-form formation. We consider that in comparison with that of the α-form lamellae with a lath-like shape, the growth of more symmetrical lamellae of the γ-form with large lateral dimensions can reduce more the free energy of the very thin film.

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1. Introduction

Polymer thin films on solid substrates have received extensive attention because of their important applications in the fields of adhesion, coating, liquid crystal display, optoelectronics, etc. [1,2]. For semicrystalline polymer thin films, in order to tune and enhance the performance such as mechanical and optoelectronic properties [3–6], control of crystal morphology becomes critical. It is known that reduction of film thickness can lead polymer thin film crystallization to deviate from bulk crystallization in many aspects. Particularly, when the film is thin enough, folded chain lamellae therein can exhibit preferential orientation rather than isotropic distribution [7,8]. Depending on the crystallization condition applied for the thin film crystallization, lamellae can be either edge-on with the lamellar basal surface normal parallel to the substrate or at the other extreme flat-on with the basal surface normal perpendicular to the substrate. From a geometric point of view, polymer thin film is subjected to a one-dimensional (1D) confinement in space. Therefore, the preferential lamellar orientation is considered to be a result of the confinement effect which has significant influences on crystallization kinetics and also thermodynamics of the crystalline thin film. In many researches of polymer thin film crystallization, the question of what control the lamellar orientation has been a main concern [8].

It has been realized that many factors can affect the orientation of lamellae formed in thin films on solid substrates. Among them, film thickness, crystallization temperature, and surface chemistry of substrate are the most important ones, which can interplay with each other making the situation complex [8]. The film thickness is associated with the degree of 1D confinement. In general, with reducing the film thickness, lamellae gradually lose the isotropic...
orientation and become edge-on dominant. Further decreasing the film thickness can shift the preferential lamellar orientation from edge-on to flat-on. For the film with the thickness approaching the radius of gyration of polymer chains, flat-on lamellae are usually observed. This film thickness dependence of lamellar orientation is widely encountered in many polymer systems [9–28]. For example, Schönherret al. have found that for poly(ethylene oxide) thin films on the oxidized silicon substrate lamellae are oriented edge-on when the films are thicker than 1 μm, while in the films thinner than 300 nm lamellae are preferentially flat-on [9]. For the edge-on lamellae formed in relatively thicker films, one reason is that the nucleation process produces edge-on nuclei at the free surface of films on solid substrates [19,25]. Considering that the free energy of lamellar lateral surface is much smaller than that of the fold surface, formation of the edge-on lamellae with their lateral surface exposed to the air will have a lower nucleation barrier. However, in thinner films (e.g., less than ~100 nm), the edge-on lamellae with one lateral dimension restricted by the film thickness will create far more side surface in comparison with the flat-on lamellae. As a result, the flat-on orientation becomes thermodynamically favorable. Intuitively, the increased 1D confinement due to the reduction of film thickness will greatly impede the lamellae rotation. Within a thinner film, to maximize the crystallinity, growth of flat-on lamellae with large lateral dimensions has its own preponderance.

It is also found that increase of crystallization temperature (Tc) has an effect similar to reducing film thickness. Namely, the higher the Tc, the more the flat-on lamellae form in thin films [19,20]. Chan et al. have found that in poly(bisphenol A hexane ether) films the edge-on lamellae develop at the temperatures close to the bulk glass transition temperature (Tg), while the flat-on lamellae predominantly form at temperatures near the melting temperature (Tm) [19]. To understand the temperature dependence of lamellar orientation, Chan and co-workers suggest that different segmental mobility and glass transition at different positions in the film play an important role.

For polymer thin films on solid substrates, surface chemistry of the substrate determines the substrate/polymer interface interaction, which can in turn affect the lamellar orientation. For example, a transition from edge-on to flat-on with decreasing film thickness can be observed for polyethylene on the silicon (111) wafer [21]. However, on aluminum coated silicon or polynimide surface, only edge-on lamellae can be seen. The different surface free energy is considered to be the main reason. The substrate surface property dependence of lamellar orientation can be also observed for other polymers [22,23]. Monte Carlo simulation by Ma et al. suggests that edge-on lamellae develop on the repulsive substrate (slippery wall), while flat-on lamellae exist mainly in the thin film on the adhesive substrate (sticky wall) [24]. On the contrary, on the basis of molecular dynamic simulation of crystallization in n-aliphatic thin films, Yamamoto et al. consider that the strong attraction between alkane backbone and substrate enforces the chain lying down and thus is in favor of the growth of edge-on lamella [23]. Although the surface effect is important for the thin film crystallization, how it influences the lamellar orientation is not fully revealed so far.

In the present work, we study the lamellar orientation in polycaproactam (PA6) thin films on solid substrates. The two main crystal structures of PA6 are the α- and γ-form, respectively [29,30]. The stable α-form of PA6 is monoclinic with the unit cell parameters a = 0.956 nm, b = 1.72 nm (chain axis), c = 0.801 nm, and β = 121° [30], and in some cases, the γ-form is called as pseudo-hexagonal [31,32]. In the γ-form, hydrogen bonds link the twisted parallel chains on (001) planes. Belonging to the aliphatic polyamide (PA) family, PA6 is an important engineering thermoplastic, which is also widely used as film materials due to its excellent mechanical properties, ductile and low-frictional properties, low permeability to gases and hydrocarbons, and resistance to wear and abrasion. To further enhance the performance, PA6 has been blended with other materials such as rubber particles and clay sheets which act as the filler [33–37], and the property of PA6/filler interface plays a key role for the final products. Previous researches indicate the edge-on orientation of PA6 lamellae near or at interface. For instance, Muratoglu et al. studied crystallization of PA6 thin film sandwiched between two thin rubber layers. Their diffraction result shows that the (002) hydrogen bonded planes are parallel to the interface, corresponding to the edge-on orientation of lamellae in the thin film [34,35]. In nanocomposites of PA6/montmorillonite (MMT), crystallization of the γ-form PA6 is promoted [36]. It is found that the γ-form lamellae are edge-on with respect to the MMT platelets, and the hydrogen bonded sheet may be either standing up or lying down [36,37].

In our previous work [121], we used PA6 thin films on solid substrates as a simplified system, we intend to elucidate the lamellar orientation varying with film thickness and also the substrate effect on PA6 thin film crystallization. We anticipate that the work will not only gain more useful information for the control of desired morphology in PA6 films but also widen our understanding of polymer thin film crystallization. The PA6 thin films with thicknesses ranged from ~5 μm to ~20 nm on solid substrates with different surface chemistry were prepared by spin-coating. Orientation of the PA6 lamellae in the thin films was characterized mainly by means of two-dimensional (2D) grazing incidence wide-angle X-ray diffraction (GI-WAXD) and selected area electron diffraction (SAED). The experimental results indicate that the PA6 films thicker than ~50 nm are composed of lamellae with preferential orientation of edge-on, regardless of the substrate changed from hydrophilic to hydrophobic. For the very thin films with thickness smaller than ~50 nm, while edge-on lamellae are still dominant on the hydrophilic substrate, flat-on lamellae can be frequently observed on a more hydrophobic substrate. The flat-on lamellae can possess the γ-form of PA6, which is unexpected.

2. Experimental section

2.1. Materials and sample preparation

A commercial PA6 resin (Akulon F130) from DSM without any additives was used. The sample possesses a number average molecular weight of approximately 20 kg/mol and a melt viscosity of 1070 P.s at 260 °C. In order to investigate the surface chemistry effect on the lamellar orientation of PA6 thin films, the surface of silicon wafer was modified. To clean the surface and to further introduce hydroxyl group to the oxide surface, as-received silicon wafers were first treated with UV/ozone, resulting in the hydrophilic substrate which is denoted as Si(OH) below. The hydrophilic silicon wafer, which contains octyl chains tethered on the top surface [denoted as Si(OCTS)], was obtained by immersing the Si(OH) wafer with a 300 nm-thick oxide layer into the solution of n-octyltrichlorosilane (OTCS)/toluene (10 mM) at 80 °C for 20 min. To obtain a silicon wafer substrate with the hydrophobicity in between Si(OH) and Si(OCTS), the silicon wafer covered by a thin layer of carbon [denoted as Si(C)] was prepared by carbon evaporation in vacuum. The contact angles for Si(OH), Si(C), and Si(OCTS) were measured to
be 10°, 80°, and 110°, respectively. To further prepare the thin film sample suitable for transmission electron microscopy (TEM) and SAED experiment, we also deposited a carbon thin layer on the freshly cleaved mica surface, resulting in the substrate denoted as Mica(C).

The PA6 thin films on different substrates were obtained by spin-coating the solution of PA6 in trifluoroethanol (TFE) with the concentration ranged from 0.1 to 10 wt%. TFE is toxic, and thus special care of the experiment should be aware. By properly selecting the solution concentration and spin rate, we could obtain the film with the desired thickness ranged from ~20 nm to ~5 μm. To remove the residual solvent and adsorbed moisture, the film samples were vacuum-dried for at least 24 h at 80 °C. Crystallization of PA6 thin films was carried out in a glove box full filled with dry nitrogen gas. The film sample was first melted at 260 °C for 5 min followed by cooling to a selected Tc. The samples were then isothermally held at the Tc for 12 h followed by cooling to room temperature.

2.2. Instrument and methods

For the films thinner than 300 nm, the thickness was measured by ellipsometer (UVISEL FUV, HORIBA, with the wavelength of 632.8 nm and the angle of incidence of 70°) and simulated by Lorenz dispersion model. The thickness of films thicker than 300 nm was estimated by surface profilometer (Alpha-Step IQ, DEKTAK3, Veeco Instruments Inc.).

Top surface morphology of PA6 thin films on solid substrates was acquired with atomic force microscopy (AFM, Nanoscope IIIA, Digital Instruments) at room temperature. Tapping mode was applied throughout this study using VeecoNanoProbe™ probes (model number: RTESP14, tip radius: ~8 nm, force: ~40 N/m, frequency: ~300 kHz). To properly reflect local stiffness variations on the film, moderate tapping was used (the ratio of the amplitude set point to the free oscillation amplitude was of ~0.6). The AFM height and phase images were collected simultaneously.

2D GI-WAXD was employed to characterize the crystalline structure and lamellar orientation of the PA6 thin films. The experiments were carried out at beamline BL14B1 of Shanghai Synchrotron Radiation Facility (SSRF) and 1W1A beamline of Beijing Synchrotron Radiation Facility. BL14B1 is a beamline based on bending magnet, and a Si (111) double crystal monochromator was employed to monochromatize the beam with a wavelength of 1.2398 Å. The size of the focus spot is about 0.5 mm and the end station is equipped with a Huber 5021 diffractometer. S7Nal scintillation detector was used for data collection. To check the crystallization behavior of the pure PA6 used in this study, we also examined the bulk sample by powder WAXD. Thermal 1D WAXD experiments were performed on a Philips X’Pert Pro diffractometer equipped with an Xcelerator detector and a temperature control unit (Paar Physica TCU 100) in the reflection mode. A 3 kW ceramic tube was used as the X-ray source (Cu Kα).

TEM and SAED experiments were performed on Tecnai G2 T20 with an accelerating voltage of 120 kV. The TEM samples were obtained by floating the PA6 thin films attached to the carbon layer on the mica surface [Mica(C)] onto the deionized water surface, followed by transferring to TEM copper grids. For SAED experiment, the diameter of selected area was 1.1 μm, if not explicitly stated. The d-spacings of SAED were calibrated using a TiCl3 standard.

3. Results

Crystal structure and crystallization behavior of PA6 have been well studied [29,30,38]. For the pure PA6 sample without additives used in this work, we identified that its melting and crystallization behavior were in accordance with that reported in literature. After cooling from melt state to room temperature, the sample possesses a crystallinity of ~40% and its Tm is of ~220 °C. Fig. 1 presents a set of 1D WAXD patterns taken at various temperatures upon cooling the PA6 bulk sample from isotropic melt. It can be seen that when the temperature reaches 215 °C, the scattering pattern becomes different from the typical amorphous halo. Two scattering maxima at 2θ of ~20.0° and ~23.4° emerge and gradually develop with decreasing temperature, which look quite similar to that observed at above 180 °C upon heating of PA6 and may be associated with the α-form [29]. Further cooling results in the α-form PA6. At room temperature, the two diffraction peaks at 2θ of 20.3° and 23.7° can be attributed to the (200) and (002)/(202) diffraction, respectively. We also performed small-angle X-ray scattering to detect the long period of the lamellar structure of the PA6 used. It was found that crystallization at a Tc around 150 °C resulted in lamellar crystals of PA6 with a long period of ~15 nm.

The present work will focus on the lamellar orientation of PA6 thin films. To prepare the crystalline PA6 thin films with different thicknesses on different substrates, the melt samples were cooled to a preset Tc for isothermal crystallization. Note that PA6 crystallization is rather fast. Therefore, the PA thin film crystallization might already start during cooling process before the preset Tc was reached. Nevertheless, to ensure the thin films to reach the maximum crystallinity, we isothermally held the sample at the Tc for a prolonged time of 12 h. In most of our experiments, the Tc was set at 150 °C.

3.1. Morphology of PA6 thin films

We employed AFM to detect the morphology of PA6 thin films after crystallization. Fig. 2a–c shows AFM height images of PA6 films on the hydrophilic Si(OH) substrate, of which the thickness is ranged from several hundreds to ~50 nm. As expected, typical spherulites can be observed in the relatively thick films. Shown in Fig. 2a is the PA6 film with a thickness of 220 nm, which is composed of spherulites with clear boundaries. As the thickness is
much smaller than the lateral dimension of the spherulites (>10 μm), the spherulites shall be more 2D-like. Decreasing film thickness to below ~100 nm causes significant change of the morphology. Sheaf-like structures are clearly observed in Fig. 2b and c of the films on Si(OH) with the thickness of 80 and 50 nm, respectively, resembling the baby spherulites formed in the early stage of PA6 crystallization [39]. The lamellae coming from one sheaf can be quite long and curved, penetrating into neighboring domains. In this case, the sheaf-like aggregates can fill the space.

The morphology of PA6 films on Si(C) and Si(OTCS) is found to be similar to that on Si(OH). Namely, with decreasing the film thickness from a several hundreds to ~50 nm the morphology changes from spherulite to sheaf-like aggregate. Some typical AFM images of PA6 on Si(OTCS) are presented in Fig. 2d–f. For the hydrophobic substrates such as Si(OTCS), dewetting of the PA6 thin film could take place during isothermal melting at 260 °C, which affects the film morphology formed after crystallization. Fig. 2f shows an AFM height image obtained from a 50 nm-thick film on Si(OTCS) at room temperature. In the lower left part of the image, many tiny droplets without crystalline feature can be seen, which shall be resulted from the dewetting. Because of the confinement effect, such droplets containing no heterogenous nucleus are hard to crystallize even at a large undercooling [40]. Taking the droplets as an indicative, we found that dewetting occurred obviously when the film thickness became thinner than 50 and 100 nm for the films on Si(C) and Si(OTCS), respectively.

The morphology of PA6 films thinner than ~50 nm became more complex compared to that of relatively thicker films, as shown by Fig. 3 of the films on Si(OH). On one hand, the sheaf-like structure, which can be taken as the indicative of edge-on lamellae, is partially remained. Moreover, the overall morphology also looks like a “net” made of microfibrils, wherein many “holes” can be observed. On the other hand, Fig. 3b suggests that some area of the film may be covered by lamellar stack, which may contain some lamellae with flat-on orientation.

### 3.2. Overall lamellar orientation characterized by GI-WAXD

The imaging technique of AFM catches the top surface morphology of PA6 thin films, however, it cannot tell directly the information of chain packing in lamellae. To further identify the overall crystal orientation within thin films, we performed GI-WAXD measurements. The incident angle was of ~0.2°, slightly larger than the critical angle of 0.18°, and thus the information on average structures over the entire film was obtained.

Fig. 4 presents the GI-WAXD patterns obtained from the thin films on Si(OH), Si(C), and Si(OTCS), of which the film thicknesses is ranged from ~5 μm to ~50 nm. It is clear that PA6 forms the α-form in the thin films, as the (200), (002), and (202) reflection of α-form PA6 can be well recognized. Moreover, the intensity maximum of the (002) reflection appears on the out-of-plane direction (azimuthal angle Φ = 90°, see Fig. 4a), indicating that the c*-axis is preferentially oriented along the substrate normal. Meanwhile, the (200) and (202) diffraction are located in the quadrant. The angles between the (200) and (002) diffraction and between (002) and (202) diffraction are of 68° and 49°, respectively, matching well with the theoretical values calculated based on the lattice
parameters of α-form. Therefore, it is confirmed that on average the ab-plane (b is the chain axis) is parallel to the substrate surface. Combining the morphology observed by AFM, we consider that the PA6 lamellar crystals within the thin films possess the a- and b-axis rotationally disordered around the c*-axis that is perpendicular to the substrate. This result indicates that within a wide range of film thickness the edge-on orientation is prevailing. Even the film with a thickness of ~5 nm does not exhibit the fully isotropic orientation of lamellae. For the ~80 nm thick film on Si(OTCS), the diffraction intensity is weak, which may be because that the film dewetting on the hydrophobic substrate occurred at high temperatures resulted in the low crystallinity of PA6.

The diffraction intensities of GI-WAXD patterns shown in Fig. 4 were not normalized with the film thickness. Apparently, the (002) diffraction looks narrower with reducing the film thickness. To analyze the data more quantitatively, we measured the azimuthal scanning profiles of (002) diffraction. As an example, Fig. 5a shows the profiles of the PA6 films on Si(C) which exhibit the maximum intensity located at Φ = 90°. Except the ~2 μm-thick film with the azimuthal distribution relatively broad, the films with thickness lower than 500 nm in fact give the azimuthal scanning profiles quite similar, indicating a similar degree of lamellar orientation. Based on the azimuthal scanning profiles, we further calculated the Hermans-Stein orientation distribution function (f_{002}):

\[ f_{002} = \frac{3}{2} < \cos^2 \phi_{002} > - 1 \]

Fig. 4. GI-WAXD patterns of PA6 films on different substrates after isothermal crystallization at 150 °C. (a–d): Si(OH); (e–h): Si(C); (i–l): Si(OTCS). The film thicknesses are indicated under the GI-WAXD patterns.

Fig. 5. (a) Azimuthal scanning profiles of (002) diffraction of the PA6 films on Si(C). (b) Lamellar orientation distribution function f_{002} of the PA6 films on different substrates as the function of film thickness.
thickness of ~30 nm the PA6 lamellae are still dominantly edge-on, orientation is little affected by varying from the PA6 lamellae with their lying-down on Mica(C), the (200) diffraction in Fig. 7a should come done prior to the lamellae, \( f_{002} = 0 \). For the perfect edge-on and flat-on orientation, \( f_{002} = 1 \) and \(-0.5\), respectively. Note that the (202) diffraction possesses the \( d\)-spacing very close to that of (002) diffraction, which shows the azimuthal distribution peaked at \( \phi \approx 40^\circ \) in Fig. 5a. Therefore, deconvolution of azimuthal scanning profile was done prior to the \( f_{002} \) calculation. Given in Fig. 5b are the plots of \( f_{002} \) as the function of film thickness for PA6 on different substrates. Reducing the film thickness from ~5 to ~0.5 \( \mu m \) causes the value of \( f_{002} \) increasing from ~0.3 to ~0.75. Afterward, \( f_{002} \) remains nearly a constant.

As mentioned, when the PA6 films on Si(C) and Si(OTCS) were thin enough, dewetting at high temperatures would cause low crystallinity. In this case, their GI-WAXD patterns with high quality were hard to be detected in our experiments. For the very thin film of PA6 on Si(OH), Fig. 6 of GI-WAXD indicates clearly that even at a thickness of ~30 nm the PA6 lamellae are still dominantly edge-on, with \( ab \)-plane parallel to the hydrophilic substrate. Moreover, this orientation is little affected by varying \( T_c \). The values of \( f_{002} \) for the films crystallized at 150 and 210 \( ^\circ C \) are of 0.75 and 0.71, respectively.

3.3. Local lamellar orientation characterized by SAED

We also employed SAED method to examine the films with the thickness down to nearly 20 nm. The PA6 films adhered to the silicon wafer were very hard to be removed. Therefore, the thin film samples used in SAED experiments were prepared on the mica substrate covered by a thin layer of carbon, i.e., the Mica(C) substrate. AFM experiments indicated that the morphology of PA6 thin films on Mica(C) looked similar to that on the silicon wafer substrates. For the films with thickness ranged from 100 to 50 nm, SAED experiments often showed only a pair of diffraction arcs of (200) when the incident electron beam was perpendicular to the film, which is exemplified by Fig. 7a of an SAED pattern obtained from an ~80 nm-thick film. As the (002) diffraction is absent, the SAED result indicates that the PA6 lamellae are largely edge-on. If assuming that the PA6 chain or the \( b \)-axis of \( \alpha \)-form crystal is still lying-down on Mica(C), the (200) diffraction in Fig. 7a should come from the PA6 lamellae with their \( a \)-axis tilting ~22\(^\circ \) away from the substrate. Instead of a continuous ring, the diffraction arcs observed implies that in the selected area the PA6 lamellae have a preferential orientation of the \( b \)-axis, which should be associated with the sheaf-like morphology. When the films were tilted, in addition to the split of the (200) arc, the diffusive and weak (002) or (202) diffraction can be observed [35]. Fig. 7b presents an SAED pattern recorded after the film was tilted 30\(^\circ \). The two pairs of arcs indexed in Fig. 7b are ~112\(^\circ \) apart from each other, and thus can be the (200) and (002) diffraction from a same crystal, suggesting that in the selected area there are some lamellae inclined to be flat-on. Occasionally, the (200) and (002) arcs could be observed simultaneously from the ~50 nm-thick PA6 film without tilting, particularly when a larger selected area was examined. Nevertheless, the (002) arcs are always much weaker than the (200) arcs, implying that the content of flat-on lamellae should be quite low.

When the film thickness was reduced to ~30 nm or smaller, we found that the coexistence of (200) and (002)/(202) arcs in a same SAED pattern could be encountered more frequently than in the case of thicker films, implying that the more lamellae intend to be flat-on. Fig. 8a gives the SAED pattern obtained from a ~30 nm-thick film, wherein the (200), (002), and (202) (very weak) diffraction can be identified, indicating that the \( b \)-axis is parallel to the incident electron beam. Interestingly, we also observed another type of SAED pattern with an apparently six-fold symmetry from the very thin film, which appeared more often with increasing \( T_c \) to 190 \( ^\circ C \), as shown in Fig. 8b taken from a ~30 nm-thick film. It is worthy to note that the diffraction is almost identical to that obtained from a solution grown single crystal of PA6 reported by Geil [41]. Considering the zone direction of [001], the diffractions of 0.41, 0.40, and 0.24 \( nm \) can be indexed as (001), (200) and (202) diffraction of the \( \gamma \)-form PA6 [30]. As a result, the ~30 nm-thick film in fact contains the flat-on lamellae of the \( \gamma \)-form which is sometime called pseudohexagonal phase [31,32].

4. Discussion

According to the experimental results aforementioned, for the PA6 films thicker than 50 nm, the lamellar orientation is dominantly edge-on, which looks insensitive to the surface chemistry of substrates. In disregard of what substrate is used in this study, decrease of the film thickness enhances the edge-on orientation. The orientation distribution function \( f_{002} \) reaches a value of ~0.75 when the films become thinner than ~0.5 \( \mu m \) (see Fig. 5b), and moreover, the SAED pattern of flat-on lamellae is scarce to be observed. For the PA6 films thinner than 50 nm, the edge-on orientation is maintained on the hydrophilic substrate of Si(OH). On the other hand, the very thin films (~50 nm) on Mica(C), which is a substrate more hydrophobic, can render the flat-on orientation more frequently. Also, the perfect flat-on lamellae with the \( \gamma \)-form is observed, as evidenced by the SAED result.

The overall edge-on orientation of PA6 lamellae in the films thicker than 50 nm is directly measured from 2D GI-WAXD, indicating that the \( ab \)-plane of \( \alpha \)-form lamellae is parallel to the substrate surface. For the \( \alpha \)-form PA6, the hydrogen bonded sheet is formed due to the hydrogen bonding interaction between the anti-parallel chains, and both the hydrogen bond direction and the chain

![Fig. 6. GI-WAXD patterns of ~30 nm-thick PA6 films on Si(OH) after crystallization at (a) 150 and (b) 210 \( ^\circ C \).](image-url)
folds of lamellae are along the $a$-axis. Aliphatic PAs such as nylon 66 usually grow the lath-like $\alpha$-form single crystal, with the [010] direction parallel to the length of the lath [42]. The edge-on PA6 lamellae observed in the thin films also suggest the lath-like morphology. Our AFM and also small-angle X-ray scattering result confirmed that the lamellar thickness of PA6 is very small. Fig. 9 presents the height and phase image taken simultaneously by AFM from a PA6 film with a thickness of ~80 nm, showing parallel packed edge-on lamellae. The AFM phase imaging can distinguish to a certain extent the viscoelastic difference between the crystalline and amorphous regions. This allows us to estimate the thickness of crystalline core (the bright line shown in the phase image of Fig. 9b) of PA6 lamellae which is around 6 nm, close to that reported for nylonns in literature [38,43]. While the $c^*$-axis is perpendicular to the substrate, the maximum dimension along the [001] of the PA6 lamella is limited by the film thickness, e.g., ~80 nm. On the other hand, with the $b$-axis (chain axis) lying down on the substrate, the lamellar dimension along the [100] direction is pretty large, which can reach several micrometers. In this case, the aspect ratio of length to width of the PA6 lamella is quite large. For example, as shown in Fig. 2b, assuming the width of edge-on lamellae is of the film thickness (~80 nm), the aspect ratio is ~50 when the lamellar length is of ~4 $\mu$m. As a result, the PA6 lamella shall be lath-like (or ribbon-like).

While the average structure over the entire film was measured, the lamellar orientation in a particular position of the PA6 film was not detected by our GI-WAXD experiment. For example, whether the very bottom part of the film consists of flat-on or edge-on lamellae or both cannot be inferred from the GI-WAXD pattern. Nevertheless, for the films thicker than 50 nm, the overall edge-on lamellar orientation is reliable. For polymer thin film crystallization, the edge-on lamellar orientation is usually attributed to the nucleation occurred at the free surface [19,25]. It is considered that the surface energy of lateral surface is much less than that of fold surface. Therefore, the nucleation of polymer chains at or near the melt/air interface will let the nuclei with the lateral surface exposed to air, resulting in the growth of edge-on lamellae in thin films. For $\alpha$-form PA6, the lath-like lamella can be viewed as an assembly of hydrogen bonded sheets stacked together through van der Waals interaction. Following the argument given Philips et al. [44], we consider that the hydrogen bonded sheet surface, i.e., the (001) plane of PA6's $\alpha$-form shall possesses the lowest surface free energy. When it exposed to air to control the nucleation, the particular lamellar orientation of $c^*$-axis perpendicular to the substrate can be produced. While the possibility of forming flat-on lamellae at the film bottom cannot be precluded, the growth of edge-on lamellae initiated at the top free surface should be predominate. For many crystalline polymers, the isotropic lamellar orientation is often observed when the film thickness exceeds ~1 $\mu$m; but at below 100 nm, flat-on lamellae appear to be abundant. However, in a quite wide range of film thickness (0.05~5 $\mu$m) the orientation of PA6 lamellae is always edge-on dominant. For the relatively thick film (e.g., 5 $\mu$m), the temperature at or near the free surface may be lowered first during cooling, which can lead to the nucleation happened earlier and thus may be in favor of growing more edge-on lamellae. Meanwhile, we should note that such a thick film possesses $f_{002}$ of around 0.3, much lower than the thinner films. This suggests that the growth of lamellae inside the film without preferential orientation should occur during the crystallization process.

We find that the edge-on orientation of films thicker than 50 nm is in fact not sensitive to the surface properties of substrates. In this study, three silicon wafer substrates with different surface chemistry, i.e., Si(OH), Si(C), and Si(OTCS), respectively, are used, of which the hydrophobicity is increased in sequence. Initially, we expected that the conformation and/or orientation of the PA6 chains located at the different film/substrate interface would be different, and thus the lamellar orientation would be affected accordingly. However, as shown in Figs. 2 and 4, on different substrates, not only the PA6 crystal morphology but also the GI-WAXD patterns are largely similar for the films with a similar thickness. Consequently, we consider that, in addition to the effect of nucleation at free surface, the prevailing edge-on orientation might be also associated with some sort of preferential orientation of PA6 chains on the substrate.

It is reported that aliphatic PA chains of nylon 66, 610 and 612 adsorbed onto the inert and hydrophilic substrate are oriented rather parallel to the surface plane [45,46]. Muratoğlu et al. studied the crystallization of PA6 thin films sandwiched between two rubber layers [35]. They find that the relatively thin PA6 films (~0.5 $\mu$m) possess clearly the edge-on orientation of lamellae, which can be attributed to that the low-energy hydrogen-bonded sheet is preferentially align parallel to the interface to minimize the interfacial free energy. Our observation coincides with those results.

The effect of surface chemistry of substrate appears when the PA6 films becomes thinner than 50 nm, when the case of Si(OH) is compared with that of Mica(C). On the hydrophilic substrate of
Si(OH), even with the thickness less than 50 nm, the Pa6 films mostly consist of the edge-on lamellae with c'-axis perpendicular to the substrate, although the lamellae with possible flat-on orientation can be found under AFM (see Fig. 3b). It is conceivable that the interaction between the hydroxyl group on Si(OH) and the carbonyl group of Pa6 can help the chain lying down, which should be the reason to account for the edge-on orientation. One may consider that this substrate/chain interaction may let the Pa6's hydrogen bonded sheets to stand up. If it is the case, the bc-plane rather than the ab-plane of Pa6's α-form will be parallel to the substrate, which is not observed experimentally. We consider that the anisotropic growth of lath-like Pa6 lamellae plays a role here. Lovinger has elucidated that for positive sphericalities of even—even nylons the a-axis is parallel to the spherulite radius, and thus the chains fold into the melt along the crystal growth direction [47]. Similar to that case, the lath-like α-form lamella of Pa6 grows fastest along the [100]. While the vertical dimension is restricted by the film thickness, to reduce the free energy as quick as possible and also to maximize the crystallinity, the fastest growth direction should be chosen in-plane of the film, which will give the perpendicular c'-axis of the final lamellae.

For the films on Si(OH), we found that the growth of edge-on lamellae is little affected by varying Tc. As shown in Fig. 6b, isothermal crystallization of a ~30 nm-thick film at 210 °C followed by cooling to room temperature does not alter the edge-on orientation. We also examined the films on Si(OH) with the thickness of 150 nm crystallized at 190 and 210 °C (data not shown here). GI-WAXD pattern similar to Fig. 4b were obtained, of which the f002 was calculated to be 0.71. For thin film crystallization, it is suggested that the elevation of Tc will favor to the flat-on lamellar growth [19,20]. Here, for Pa6 on the hydrophilic substrate, lamellar orientation is dominantly edge-on even when the sample was crystallized at a temperature quite close to the its Tm. It is worth mentioning that after cooling the Pa6 melt to 210 °C the bulk sample only gives the scattering of the α'-structure [48] as shown in Fig. 1. We also found that for the bulk sample the α'-structure remained unchanged even if the isothermal time at 210 °C was prolonged to 12 h. The α-form Pa6 would appear after the sample was brought to room temperature. The thin films at 210 °C may also just possess the α'-structure. However, the chain packing of Pa6 in α'-structure does not affect the final lamellar orientation of edge-on. We presume that at below the Tm of Pa6 the preferential alignment of chains or hydrogen bonded sheets parallel to the substrate surface is already established. Consequently, the growth of edge-on lamellae is favored regardless of either the α'- or the α-form are formed initially.

It is quite interesting to note that the very thin film of Pa6 on Mica(C) can grow flat-on lamellae. As SAED method only provides the local information, the overall lamellar orientation of the thin film is hard to be evaluated. Nevertheless, the existence of flat-on lamellae is confirmed. Seemingly, on Mica(C) which is more hydrophobic than Si(OH), the lamellar orientation behavior of Pa6 follows more the general trend found in other semicrystalline polymers, namely, with reducing the film thickness the lamellar orientation will shift to be flat-on eventually. Growth of the edge-on lath-like lamellae with a very larger aspect ratio will introduce more side surfaces, resulting in an increased free energy of crystalline thin films. Therefore, when crystallization occurs in very thin films, flat-on lamellae with a reduced aspect ratio will become thermodynamically favorable. Our observation indicates that the strong 1D confinement imposed by the rather small thickness indeed can cause the appearance of flat-on lamellae on Mica(C) (see Fig. 8).

For the flat-on lamellae observed, of particular interest is that not only the α-form Pa6 exists but also the γ-form Pa6 is detected in the very thin films. Moreover, more γ-form lamellae with more perfect diffraction can be found with increasing Tc. TEM experiments revealed that the α- and γ-form crystal of Pa6 rendered different morphologies. The TEM image of Fig. 10a shows the morphology of an area where the α-form diffraction can be obtained, which looks quite similar to that shown in Fig. 3b. The flat-on lamellae are partially stacked with each other. However, for the area that gives the γ-form diffraction, the film usually looks uniform with some dark lines (Fig. 10b and c). As many of the dark lines are parallel to each other (see Fig. 10b), we presume that they correspond to the cracks in the thin film which were formed during cooling due to the thermal shrinkage. As the thin film sample was not shadowed with heavy metals, the cracks shown as dark lines may be due to under- or over-focus when the TEM picture was taken. Note that some dark lines can be ~60° apart from each other (Fig. 10c). This implies that the cracks occur parallel to the (001) plane of the γ-form, considering the hydrogen-bonded sheets are stacked one by one via van der Walls interaction along the c-axis.

The appearance of the γ-form Pa6 is unexpected, since the metastable γ-form is usually formed after rapid cooling to low temperatures or through rapid crystallization during melt spinning or drawing. For the Pa6 sample used in this study, we used 1D WAXD to monitor the isothermal crystallization of bulk melt at Tc ranged from 150 to 190 °C and found that only the α-form developed with time. Therefore, the γ-form single crystal in very thin films shall be attributed to the confinement effect, although the detailed mechanism is not fully understood at this moment. Possibly, this may be again related to the tendency of reducing free energy of crystalline thin films. Compared with the α-form lamellae which are lath-like, the single crystal of γ-form Pa6 can be rhombohedral with the acute angle of 60° as shown by Geil [41]. Therefore, once the Pa6 chains in the very thin films intend to grow flat-on lamella, forming the γ-form single crystal, which is more symmetry in shape compared with that of the α-form, can further cut down the area of lamellar side surface, leading to further lowering the surface free energy. On the other hand, it is reported that for the Pa6/clay nanocomposites the addition of clay platelets may decrease the chain mobility, which can promote the

![Fig. 10](image-url) . TEM images of a ~30 nm thick film crystallized on Mica(C). (a) and (b, c) correspond to areas that can give the α- and γ-form diffraction, respectively.
crystallization into the γ-form [33] and some lamellae possess flat-on orientation at the interface [37]. Here, we consider that confinement of PA6 chains in the films on Mica(C) with the thickness of 30 nm or less may also restrict the chain motion and thus result in the γ-form coexisted with the α-form, although the Tc applied favors the α-form crystallization.

5. Conclusion

We have examined the morphology and crystal orientation of PA6 thin films with the thickness ranged from ~5 μm to ~20 nm on different substrates after melt crystallization. With decreasing the film thickness, the PA6 morphology changes from 2D spherical to sheet-like. In the films thinner than ~50 nm, both the “net” of microfibris and stack of lamellae can be observed. Our GI-WAXD results indicate clearly that for the films thicker than ~50 nm the PA6 lamellae with the α-form are preferentially edge-on with the c*-axis perpendicular to the substrate. Even in the ~5 μm thick film the edge-on orientation is dominant. Reduction of film thickness leads to higher order of the orientation. This edge-on orientation observed from the films with thickness larger than 50 nm is in fact insensitive to the hydrophobicity of substrates. For the films with thickness less than ~50 nm on the hydrophilic substrate Si(OH), edge-on lamellae are still preferred. However, for the films on the more hydrophobic surface of Mica(C), reducing the film thickness to below 50 nm can result in more flat-on lamellae. An unexpected result is that flat-on lamellae of the γ-form can also be observed in the very thin film on Mica(C). As the crystallization condition applied does not favor the γ-form formation in bulk, the appearance of flat-on γ-form lamellae should be attributed to the strong confinement effect imposing on the very thin film of PA6. While in most cases that PA6 lamellae on a surface or at an interface of PA6/filler are preferentially edge-on, the flat-on orientation found in the particular circumstance is interesting, and shall be useful in PA6 applications.

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