

Thin-Film Crystallization of Poly(butylene terephthalate) from the Anisotropic Amorphous State

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Read Online Cite This: Macromolecules 2023, 56, 9650–9660 ACCESS Metrics & More Article Recommendations Supporting Information ABSTRACT: Crystallization of poly(butylene terephthalate) smectic nodules (PBT) thin films from the glassy state has been investigated. The thin films on the silicon substrate with a thickness of no more than 300 nm were prepared by spin-casting and were examined by lath-like grazing-incidence X-ray scattering and atomic force microscopy crystals anisotropic before and after isothermal annealing at various temperatures $(T_{s}s)$. amorphous It is found that the virgin spin-cast thin films are anisotropic Isothermal annealing amorphous, with the PBT chains preferentially lying down on the Increasing T_a substrate. The phase structure and morphology of the annealed thin films are strongly T_a -dependent. At T_a s below 80 °C, the thin PBT thin film films remain amorphous due to the restricted chain segment

mobility imposed by the one-dimensional (1D) confinement of the thin film. For T_a of 80–180 °C, isothermal annealing results in dominantly smectic nodules with a size of around 10 nm, which can be sustained regardless of extending the annealing time. When T_a is in the range of 180–200 °C, lath-like PBT crystals of α -form, which are edge-on lamellae, are observed to coexist with the smectic nodules. Further increasing T_a allows the lath-like crystals to grow substantially. However, owing to the high nucleation density, the crystals are small, showing a lateral size of just several dozens of nanometers. It is interesting to note that the 1D confinement condition could largely arrest the transformation from smectic-tocrystal over a wide temperature range, letting the smectic nodules survive at T_a below 200 °C. We further explored the interplay of smectic and crystal phases. It is unveiled that when the well-formed nodules are taken as the initial state for crystallization, the nodules can rapidly turn into nearly square-shaped crystal particles above 200 °C, which serve as the element blocks for the subsequent crystal growth. The combination of these blocks makes the lath-like crystals extend their lengths. Accordingly, we conjecture that when the PBT thin films are crystallized from the glassy state, there may exist a pathway of "glass-to-smectic-tocrystal".

■ INTRODUCTION

Owing to its excellent mechanical properties and good processability, poly(butylene terephthalate) (PBT) is a commercially important engineering plastic, which has been applied to a great variety of applications. It has been realized for a long time that, after normal processing such as injection molding and extrusion, the PBT products usually present the crystalline structure of α -form with a triclinic unit cell of P1 space group,^{1–5} of which the equilibrium melting temperature $(T_{\rm m}^{\rm o})$ is estimated to be 245 °C.⁶ Compared to poly(ethylene terephthalate) (PET), PBT possesses two more methylene units in the backbone, allowing an additional polymorphism of triclinic β -form and a reversible α - β transition when PBT is subjected to tension.¹⁻⁵ It is manifested that in the strain range of 4-20%, the external stretching can cause the methylene sequence switching from the conformation of gauche-transgauche in α -form to an all-trans conformation in β -form,³ and correspondingly, the c-axis (chain axis) is enlarged from 1.162 to 1.311 nm. For the semicrystalline PBT, two types of amorphous states, i.e., mobile and rigid, are suggested.⁷ The mobile amorphous PBT renders the glass-transition temperature (T_g^{moblie}) at 41 °C;⁷ the rigid amorphous fraction (RAF) presents its glass-transition temperature (T_g^{RAF}) depending on the crystal morphology. Recent thermal analysis indicates that the RAF of PBT would finally vanish at around 190 °C,⁸ suggesting that the T_g^{RAF} can be much higher than that of 102 °C reported previously.⁷ Intriguingly, it has also been found that stretching the amorphous PBT can lead to a mesophase,⁵ similar to that observed in PET⁹ and poly(ethylene naphthalene).¹⁰ The mesophase is proposed to be smectic, of which the layer period is rather close to the *c* parameter of

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the α -form.^{5,11} Once the temperature exceeds T_g^{moblie} of PBT, the smectic structure in the bulk state can quickly transform into α -form.

The polymorphism and glass transitions of mobile and rigid amorphous fractions endow PBT with rich crystal morphologies and complex phase transition behaviors. Despite abundant research on PBT crystallization, the mechanisms underneath have not been fully unveiled, and there exist controversial or competitive opinions and explanations regarding some similar observations. Particularly, one of the interests is that PBT presents nodular morphologies with a size of ~ 10 nm when crystallized at large undercoolings or from the glassy state. It was suggested by Androsch et al. that the PBT nodules were solely the result of extremely high homogeneous nucleation density of the α -form crystals.¹² They considered that this case was different from those of isotactic polypropylene $(i-PP)^{13,14}$ and polyamide 6 (PA 6),¹⁵ wherein the appearance of high nucleation density is coupled with the development of a mesophase. On the contrary, Konishi et al. proposed that the PBT nodules were associated with the mesophase.¹⁶ For PBT crystallization from the glassy state, they presumed that a mobile mesophase appeared first, which could be smectic, followed by crystal formation through the rapid thickening process.¹⁶ They found that the inverse nodule size (D^{-1}) was a linear function of the crystallization temperature (T_c) at below 200 °C. Following the conjectures of high-pressure crystallization of polyethylene by Keller^{17–19} and the multistage model of polymer crystallization by Strobl,²⁰⁻²² the line of $T_c \sim D^{-1}$ was assigned as the mesophase-crystalline (M-C) transition line and the extrapolated temperature of 333 $^{\circ}$ C was taken as the equilibrium M-C transition temperature.¹⁶ Moreover, Konishi et al. also suggested that in melt crystallization, PBT would go through the mesophase prior to the crystalline phase of α -form.^{23,24} However, so far, the existence of a smectic mesophase is only caught by X-ray diffraction in the samples stretched from amorphous PBT at near T_g .⁵ Although it seems reasonable to assume that PBT crystallization in the quiescent state may invoke a mesophase as an intermediate structure,^{17,20,25} it is still uncertain if the smectic mesophase truly participates in the crystallization process toward the α -form.

The present work attempts to further elucidate the correlations among glass transition, mesophase formation, and crystallization of PBT. To this end, we investigate the thinfilm crystallization of PBT from the amorphous state. Usually, polymer thin films with a thickness of less than $\sim 1 \ \mu m$ can impose a significantly one-dimensional (1D) confinement effect.²⁶⁻³⁰ Polymer crystallization of thin films on solid substrates, including commercial engineering plastics, such as PET^{31} and PA 6,³² has demonstrated that the chain orientation, segmental mobility, transporting process, and surface free energy at the interface can be influenced greatly by the 1D confinement.³³⁻³⁵ The lamellae with preferential orientations, either flat-on or edge-on, grown in polymer thin films indicate that the crystallization pathway or kinetics are different from that in bulk crystallization. 28,30,36,37 It is also reported that some preordered structure, which is hardly detected or even absent in the bulk state, can be trapped in the 1D confined space.^{38,39} For PBT thin films, we hypothesize that the 1D confinement effect may retain the mesophase once it has developed and/or slow down the transition from the metastable state to the crystal phase.

We carried out the isothermal crystallization of the thin films of amorphous PBT by bringing the spin-cast thin films from room temperature to the annealing temperature (T_a) ranging from 40 to 220 °C. To characterize the chain packing and surface morphology of PBT thin films, grazing-incidence wideand small-angle X-ray scattering (GI-WAXS and GI-SAXS) and atomic force microscopy (AFM) were mainly employed in this work. It is interesting to note that the PBT chains in the virgin spin-cast films tend to lie down on the substrate, presenting an anisotropic amorphous structure. This chain orientation can maintain up to the T_a as high as 220 °C, just below the practical melting temperature (T_m) of bulk PBT at around 230 °C.6 The nodular morphology with the smectic mesophase can be clearly detected for $80\degree C \le T_a < 180\degree C$, and surprisingly, the mesophase does not transform into the α form even when the duration of annealing is prolonged. At T_a \geq 180 °C, lath-like crystals of the α -form develop, which are the edge-on lamellae. While for T_a of 180–200 °C, edge-on lamellae coexist with the smectic phase, further increasing T_a results in solely the α -form crystals. Because of the high nucleation density, the edge-on lamellae easily impinge with each other, showing the lateral dimension much shorter than that grown from isothermal melt crystallization. Moreover, taking the nodules as the initial state, we find that the edge-on lamellae are grown based on the merging of small crystalline blocks.

EXPERIMENTAL SECTION

Materials and Sample Preparation. Commercial-grade PBT without any additives was produced by DSM (Geleen, the Netherlands). The number average molecular weight of the PBT sample is ~20 kg/mol measured by solution ¹H NMR.⁴⁰ The PBT sample possessed a polydispersity of 2.28, which was determined using gel permeation chromatography (GPC, Agilent PL-GPC50) with hexafluoroisopropanol (HFIP) as the elute and the calibration based on poly(methyl methacrylate) (PMMA) standards (Figure S1). To fabricate the PBT thin films on a flat solid surface, we selected the (100) silicon wafer without a native oxide layer as the substrate. When performing the spin-casting, we placed a drop of HFIP solution of PBT on the silicon substrate, which was spinning at a rate of 2000 rpm. By properly choosing the solution concentration, which ranged from 5 to 20 mg/mL, we could obtain the films with various thicknesses ranging from 50 to 300 nm. To remove the residual solvent, the film samples were dried in vacuum at room temperature for more than 3 h. Isothermal annealing of the film samples was conducted with a Mettler hot stage (FP-90). The virgin spin-cast film was directly inserted into the hot stage with a preset temperature of T_a (40 °C \leq $T_a \leq$ 220 °C), which could reach the target temperature in less than 5 s. After isothermally annealing at the T_a for a period of time (t_a) , the sample was quickly taken out and quenched in ice water, with a cooling rate of around 500 $^{\circ}$ C/s.

Instruments and Experiments. The surface morphologies of virgin and isothermally annealed PBT films were examined at room temperature with a Dimension Icon AFM (Bruker Nano). PeakForce tapping mode was applied using SCANASYST-AIR probes (tip radius: ~ 2 nm; spring constant: ~ 0.4 N/m; frequency: ~ 70 kHz). The PBT film thicknesses were measured by AFM scanning at the edge of the film, and the average results were used.

GI-WAXS and GI-SAXS experiments were performed with the Ganesha system (SAXSLAB, U.S.) equipped with multilayer focused Cu K α radiation as the X-ray source (Genix3D Cu ULD), using an incidence angle of 0.15°. In the Ganesha system, both the sample stage and the two-dimensional semiconductor detector (Pilatus 300 K, DECTRIS, Swiss) are set in a long vacuum chamber; moving the detector sitting on the guide rail can easily switch the measurement from wide angle to small angle (Figure S2). Thin-film samples were placed vertically when GI-WAXS and GI-SAXS were carried out, of



Figure 1. (a) GI-WAXS patterns of the virgin spin-cast PBT films on the silicon substrate with thicknesses of 50 and 200 nm. The thin-film samples were placed vertically. The x- and y-axis are perpendicular and parallel to the substrate surface, respectively. (b) 1D intensity profiles obtained from panel (a). The two amorphous halos are indexed as 1 and 2.

which the sample-to-detector distances were 50 and 1200 mm, respectively. The scattering peak positions were calibrated by LaB_6 for the wide-angle region and silver behenate for the small-angle region, respectively.

RESULTS AND DISCUSSION

Virgin State of Spin-Cast PBT Thin Films. The structure of virgin PBT thin films prepared after spin-casting followed by drying in vacuum at room temperature was characterized by GI-WAXS. The films with thicknesses in the range of 50-300 nm present the same scattering feature. Figure 1a shows two GI-WAXS patterns of the virgin PBT films with the thicknesses of 50 and 200 nm, respectively, and the corresponding 1D profiles of intensity (I) vs scattering vector ($q = 4\pi \sin \theta / \lambda$, with 2θ the scattering angle and λ the X-ray wavelength) are depicted in Figure 1b. As indexed by 1 and 2 in Figure 1, two rather broad scattering halos are observed, whereas no crystal diffraction can be detected, indicating that the virgin PBT thin films are amorphous. It is reported that to suppress the crystallization taking place during cooling and thus to obtain the fully amorphous PBT in the bulk state, one has to cool the melt at a cooling rate higher than 300-500 °C/s.¹² For the spin-casting carried out at room temperature, we presume that the fast evaporation of HFIP can cause effective cooling, leading to the sample temperature being well below the T_{σ} of PBT. In this case, PBT crystallization can be avoided when the solution becomes concentrated during the solvent evaporation. Thermodynamically, the noncrystalline PBT must be metastable, but in the thin film, it can remain for a long time at room temperature.

For amorphous PBT, usually, a single scattering halo is observed at around q of ~15.0 nm⁻¹ in the high-angle region.¹⁶ Meanwhile, it is also reported that the amorphous PBT can present two separated broad scatterings centered at q of 12.0 and 17.0 nm⁻¹, respectively,⁴¹ similar to those shown in Figure 1b. The locations of these two scatterings are in fact rather close to those of (010) and (100) diffractions of the PBT α form. The terephthalate moiety in the PBT chain has a coplanar structure of its benzene ring and the two carbonyl groups and can thus be viewed as a rod-like unit.⁴² In the PBT α -form, the 0.379 nm *d*-spacing of (100) is largely determined by the $\pi - \pi$ interaction of the conjugate terephthalate moiety in a face-to-face fashion, while the 0.513 nm d-spacing of (010) corresponds to the distance between the two adjacent chains in the transverse direction, wherein the π - π interaction is absent. As located at the positions close to (010) and (100)diffraction, the scatterings of 1 and 2 suggest that PBT chains

in the thin film are apt to align parallel to each other. However, during spin-casting, the fast solvent evaporation arrested the chain packing toward the crystalline phase, leaving a shortrange order and thus the amorphous PBT films on the silicon substrate.

It is worth noting that the scatterings of 1 and 2 are more or less concentrated in the out-of-plane direction (i.e., azimuthal angle $\Phi = 90^\circ$, see Figure 1a). To analyze the data more quantitatively, we measured the azimuthal scanning profiles of scattering 1 for the films with different thicknesses (Figure S3). The Hermans-Stein orientation distribution function f was calculated (see the Supporting Information (SI) for the details), with f = 0 corresponding to the random orientation and f = 1 corresponding to the perfect alignment of chains parallel to the substrate. For the two GI-WAXS patterns shown in Figure 1a, the f value was estimated to be about 0.3. Albeit not large, it still unambiguously indicates somewhat preferential orientation; i.e., the PBT chains tend to lie down on the substrate. Considering the terephthalate moiety as a rigid mesogen, the orientation may be caused by the shear flow induced by spin-casting. Moreover, the 1D confinement effect arising from the thin-film geometry should also help the PBT chains lie down. It is found that f decreases with increasing the film thickness. For a film with a thickness of 800 nm, the value of f was measured to be 0.14. This implies that the 1D confinement effect would gradually release as the film becomes thicker. Given the preferential chain orientation, the amorphous PBT films are anisotropic.43

The anisotropic amorphous PBT thin films with two broad separated scattering halos are interesting. We suggest that the spin-induced orientation could be one reason for this. While the rigid segments on PBT respond to the shear field of spincasting, both the parallel packing modes of terephthalate moieties with and without $\pi - \pi$ interaction would be promoted. As a result, while the correlation lengths of the parallel packing remain short, the amorphous scatterings at q of 12.0 and 17.0 nm⁻¹ get enhanced. After the PBT thin film was melted at 280 °C for 2 min and subsequently quenched into ice water, GI-WAXS revealed that the amorphous scattering at 15 nm⁻¹ became much pronounced; however, the scatterings at 12.0 and 17.0 nm⁻¹ could still be sensed (Figure S4). This outcome indicates that although melting at 280 °C could erase largely the spin-caused orientation, the 1D confinement would still conduce to the lying down of chain segments. Consequently, we consider that the 1D confinement effect is also responsible for the two separated amorphous scatterings



Figure 2. AFM images of virgin spin-cast PBT films with thicknesses of (a) 50 and (b) 200 nm on the silicon substrate.



Figure 3. Set of GI-WAXS patterns of 200 nm thick PBT films recorded at room temperature after isothermal annealing at various T_a s for 30 min. The thin-film samples were placed vertically. The *x*- and *y*-axis are perpendicular and parallel to the substrate surface, respectively. For $T_a \le 200$ °C, 1 and 2 indicate the scatterings mainly from the disordered lateral packing of the chain segments, and 3 indicates the smectic layer scattering. At above 200 °C, 1, 2, and 3 correspond to the (100), (010), and (001) diffraction of PBT α -form.

observed. For a 300 μ m thick film that we prepared by compression, the sample subjected to 280 °C melting and ice water quenching presented a single amorphous halo with the maximum at *q* of 15 nm⁻¹ (Figure S4).

We employed AFM to detect the morphologies of the spincast PBT films. At a large length scale, the virgin films appeared smooth. Figure 2 shows two zoomed-in AFM images obtained with a scan area of 512×512 nm². The root-mean-square average height deviations (R_{qs}) are ~0.5 nm, indicating that the height undulation on the surface is quite small. Some dotor worm-like entities with the size of a few to a dozen nanometers distribute irregularly on the film surface, corresponding to the noncrystalline nature of PBT. On the other hand, the preferential orientation of PBT chains cannot be reflected from the surface morphology.

Structures of Isothermally Annealed PBT Thin Films. To elucidate the structure evolution of the spin-cast films from the glassy state, isothermal annealing experiments were performed by directly bringing the amorphous PBT thin films from room temperature to various T_a s. The highest T_a applied is 220 °C, nearly 10 °C lower than the T_m normally reported for bulk PBT;⁶ and the lowest T_a of 40 °C is close to

the $T_{\rm g}^{\rm mobile}$ of PBT. It is known that polymer thin films may have the $T_{\rm g}$ either higher or lower than the bulk value, depending on the interaction between the polymer and the substrate.²⁹ Moreover, the chain mobility gradient may exist vertically across the film thickness.^{44–47} In the present study, we pay attention to the overall structure and morphology development of PBT thin films resulting from the isothermal annealing of the anisotropic glass. The possible differences among the surface, interface, and interior regions of the films caused by the variation of $T_{\rm g}$ and chain mobility were not analyzed.

Figure 3 presents some GI-WAXS results collected after the 200 nm thick films were annealed for $t_a = 30$ min at various T_a s. At a glance of Figure 3, one may notice that the main scattering feature of the virgin films remains. Namely, there exist two strong scatterings in the vicinities of 17.0 and 12.0 nm⁻¹ along the out-of-plane direction (i.e., $\Phi = 90^{\circ}$), indicating that the preferential orientation of the chain lying down does not relax even if T_a is much higher than the T_g of PBT. A close examination can reveal that the film structure becomes more ordered with increasing T_a , which will evolve

into a smectic phase first, and the crystalline α -form will develop when $T_{\rm a}$ exceeds 180 °C.

For $T_a < 180$ °C, the GI-WAXS patterns and the corresponding 1D intensity profiles shown in Figure 4 indicate



Figure 4. 1D intensity profiles based on the GI-WAXS results obtained from the 200 nm thick PBT films annealed at various $T_{a}s$ for 30 min. The vertical dashed lines indicate the crystalline diffractions of the PBT α -form.

that the thin films present amorphous halos in the high-angle region and crystalline diffractions are hardly identified. The smectic phase can be justified based on the appearance and location of the scattering at around $q = 6.4 \text{ nm}^{-1}$ (indexed as 3 in Figure 3). While it is rather faint and broad at low T_a s, scattering 3 gradually narrows and increases in intensity when $T_{\rm a}$ is elevated to higher than 60 °C. In a wide temperature range, this scattering exhibits its highest intensity at $\Phi = 0^{\circ}$ (Figure 3). One may note that it possesses the *d*-spacing of 0.98 nm, almost identical to that of (001) of the PBT α -form. However, it is worth emphasizing here that when scattering 3 is at Φ = 0°, the amorphous scatterings of 1 and 2 show their highest intensities at $\Phi = 90^\circ$. Consequently, scattering 3 of the PBT thin films with the disorder of lateral chain packing is unlikely for the (001) diffraction of α -form. The geometrical relationship of scatterings shown in the GI-WAXS patterns with T_a of 80–180 °C in fact can be attributed to a smectic Alike structure with the layer normal parallel to the substrate, namely, scattering 3 arises from the smectic layers rather than the (001) of α -form. The *d*-spacing of scattering 3 is comparable to the value of c-axis of α -form (0.98 vs 1.126) nm), suggesting that the smectic layer period is largely determined by the PBT repeating unit. Meanwhile, without the restriction of crystalline packing, the methylene sequences on the backbone may have more gauche conformations, and thus, the repeating unit looks more bended.

It is known that a smectic structure can be generated by stretching the glassy PBT in the bulk state.⁵ However, such a stretching-induced mesophase will rapidly relax to the crystalline phase upon heating to temperatures above the $T_{\rm g}^{\rm mobile}$ of PBT. For crystallization from the glassy state, Konishi et al. suggested that PBT formed first a mesomorphic phase (smectic) and then quickly transformed into α -form.¹⁶ Namely, in bulk crystallization, the mesomorphic/smectic phase could be a transient state with a very short lifetime. Surprisingly, the smectic structure developed in the spin-cast

films is quite stable. Prolonging t_a would not alter the GI-WAXS pattern. One of the possible reasons is that the 1D confinement imposed by the thin film could significantly suppress the chain mobility. Moreover, we presume that the chain segments in the vicinity of the smectic domains of parallel packed chains may experience an additional constraint and thus form an interface between smectic and amorphous, which is similar to the RAF observed in PBT bulk crystallization. This RAF-like interface could further arrest the transition from smectic to crystal.

We find that isothermal annealing at $T_a \ge 180$ °C can result remarkably in α -form crystals in the PBT thin films. As indicated by the dashed vertical lines in Figure 4, the crystal diffractions in the high-angle region start to emerge from the scattering halos at T_a of 180–200 °C; further increasing T_a could make them distinct peaks. Accordingly, the low-angle scattering of 3 becomes more pronounced and can be well recognized in the two-dimensional (2D) GI-WAXS patterns (Figure 3). For T_a s of 180–200 °C, scattering 3 shows a broad azimuthal distribution with the intensity maxima at $\Phi = 0^{\circ}$, implying that the smectic structure may still be abundant and coexist with the crystals. For T_{a} s of 210 and 220 °C, several sharp diffractions of the α -form can be identified, indicative of the sufficient crystallization of PBT. Meanwhile, scattering 3 moves its intensity maximum from $\Phi = 0^{\circ}$ to $\Phi = 33^{\circ}$ and appears as an arc in the quadrant (Figure 3), which can unambiguously be assigned as the (001) diffraction of the α form. As the angle between the *c*- and *c**-axis of the PBT α form is 33° , the location of (001) diffraction indicates that the PBT chains keep lying down on the substrate after crystallization. The PBT crystals formed in the thin films should possess rotational disorder around the chain axis (caxis), and thus, the (100) and (010) diffractions remain on the out-of-plane direction. Unexpectedly, for $T_a = 220$ °C, the (010) diffraction presents the intensity maximum close to Φ = 0° . Seemingly, a part of the crystals rotate their (010) planes to be perpendicular to the substrate during the annealing, implying that the lamellar crystals might have an orientation other than edge-on. However, the mechanism underneath is unclear at this moment.

The GI-WAXS results described above illustrate the T_a dependence of the thin-film structures of PBT. Namely, three regions may be identified: (1) $T_a < 80$ °C, the spin-cast film remains amorphous; (2) 80 °C \leq $T_{\rm a}$ < 180 °C, smectic is dominant; and (3) $T_a \ge 180 \text{ °C}$, α -form crystals are developed. When quantitatively checking the variation of peak width at around 6.4 nm^{-1} (scattering 3 in Figure 3), we can also see the three regions (Figure S5). For 80 $^{\circ}C \leq T_a < 180 ^{\circ}C$, the full width of half-height (FWHH) is 0.9 nm^{-1} , showing a trend of slightly decreasing with T_a . The 6.4 nm⁻¹ scattering is remarkably broader at $T_a < 80$ °C. On the other hand, when T_a exceeds 170 °C, the FWHH suddenly drops to below 0.8 nm⁻¹. The two discontinuous reductions of FWHH at around 80 and 180 °C indicate the enlarging of correlation lengths of the ordered chain packing, corresponding to the change from amorphous-to-smectic to smectic-to-crystalline, respectively. Worthy to remark is that the boundaries of structure change should not be sharp. As mentioned above, for T_{a} of 180–200 °C, the crystalline and smectic phases coexist together. It is also noted that, albeit rather weak, scattering 3 may extend the azimuthal distribution to Φ = 33° for T_a < 180 °C, implying some small crystalline entities embedded in the thin film. For the virgin spin-cast films and the films annealed at below 80



Figure 5. Set of AFM images of 200 nm thick PBT films recorded after isothermal annealing at various T_{s} s for 30 min.

°C, there exists a faint scattering at q of ~6.4 nm⁻¹, which may be contributed by some smectic packing in addition to the form factor of the PBT repeating unit.

Morphologies of Isothermally Annealed PBT Thin Films. Structure determination reveals that with increasing T_a from 40 to 220 °C, the PBT thin films change from amorphous to mesomorphic (smectic) and crystalline. Correspondingly, the film morphologies are also changed with T_a . Figure 5 collects some typical AFM images of the samples that were annealed at various T_a s for the isothermal time $t_a = 30$ min.

For $T_a < 80$ °C, the isothermally annealed PBT thin films look quite similar to the virgin films, i.e., tiny dot- or warm-like entities were observed. When T_a is ranged from 80 to 180 °C, the AFM results indicate that nodular particles are prevailing on the film surface (Figure 5), coincident with the development of the smectic structure. The nodules are reminiscent of that observed after cold crystallization of fully glassy PBT films.¹⁶ In the PBT bulk sample, the high density of the nodules shall be the result of high nucleation density produced upon cooling extremely fast from the melt.^{11,48} Moreover, the arrest of nodules growing to be bigger may be attributed to the ridge amorphous chains surrounding the crystalline core.⁸ As discussed above, the PBT thin films on the substrate form a smectic structure at $T_a = 80-180$ °C. In this case, we consider that the nodular morphology of PBT thin films is also similar to that found for quenched *i*-PP, which bears the mesophase of smectic.¹³ The PBT nodules become larger with increasing T_{a} , in accordance with that reported in literature studies,¹⁶ Figure 6 shows the plots of the size of nodules (D) vs T_a , showing that D gradually increases from ~6.7 nm at $T_{\rm a}$ of 80 °C to ~10.8 nm at 180 °C. The nodule size around 10 nm is quite close to that reported by Konishi, which was measured from bulk glassy PBT subjected to annealing in a wide range of T_a using SAXS.¹⁶ The nodules in the thin film are found to tend to be more and more quadrangles in shape at higher T_{at} implying more ordering of chain packing in the nodules.

At $T_a = 180$ °C, in addition to the quadrangle-like nodules, we actually can also find some anisotropic entities with lateral sizes larger than longitudinal sizes, which could be the crystalline particles. Further increasing T_a leads to a pronounced anisotropic morphology, which is lath-like with



Figure 6. Nodule size (*D*), lath width (*W*), and long period (*LP*) of PBT as functions of T_a . The black squares for nodules and triangles for lamellae represent the data measured from AFM. The red dots are *LPs* measured from GI-SAXS. Note that at $T_a = 180$ °C, some nodules become anisotropic, and thus, the short dimension shown by AFM is taken as the nodule size.

the length significantly larger than the width of the lath. According to the GI-WAXS results mentioned before, the glassy PBT thin film can adequately develop into the crystalline phase at $T_a > 180$ °C, and thus, the morphology switching from nodule to lath indicates clearly the occurrence of crystallization. Given that the PBT chains are lying down, the laths shall represent the edge-on lamellae. We find that at $T_a > 180$ °C, the laths cover throughout the film surface, and moreover, when tending to fulfill the space, they have the orientation largely random. This morphology is quite different from that of thin-film melt crystallization, wherein the flat-on lamellae or sheaf-like lamellar stacks of edge-on lamellae are frequently observed.^{26,49} While the lath length exhibits a large distribution, the lath width (*W*) is quite uniform and could be taken as a measure of the thickness of the edge-on lamellae. Compared with the nodule size *D*, *W* increases more rapidly

with increasing T_a (Figure 6), particularly when T_a exceeds 200 °C. The value of *W* is measured to be ~11.9 nm from the AFM image of $T_a = 200$ °C; however, it becomes ~18.0 nm at $T_a = 220$ °C.

We further employed GI-SAXS to investigate the film morphology. Figure 7 depicts a set of GI-SAXS patterns of the



Figure 7. Set of GI-SAXS patterns of 200 nm thick PBT films recorded after isothermal annealing at various T_a s. The thin-film samples were placed vertically. The *x*- and *y*-axis are perpendicular and parallel to the substrate surface, respectively. The arrows indicate the in-plane scattering from packing of the nodules or lamellae.

thin films annealed at various $T_{\rm a}$ s. For the PBT chains packed in the smectic structure, a faint small-angle scattering can be sensed in the area near the substrate surface, as pointed out by the arrows in the GI-SAXS pattern of $T_{\rm a} = 160$ °C in Figure 7. For $T_{\rm a} = 180$ °C, probably because the quadrangular nodules pack denser and more regular, a relatively concentrated scattering located at q around 0.55 nm⁻¹ (*d*-spacing of 11.4 nm) can be recognized. After isothermal annealing at higher $T_{\rm a}$ s, the GI-SAXS patterns clearly show the scattering peak located in the in-plane direction, characteristic of the edge-on lamellae. In accordance with the AFM observation, the position of the scattering peak moves to the smaller angle with increasing T_a . At $T_a = 220$ °C, the small-angle scattering becomes rather close to the incident beam, giving the *d*-spacing of ~15.5 nm. The GI-SAXS experiments manifest that the PBT chains with the preferential lying down orientation will eventually form the edge-on lamellae at higher T_a s. The long periods (*LPs*) of the edge-on lamellae measured from GI-SAXS are also presented in Figure 6 (the red dots), which match with the lath width *W* measured from AFM.

Growth Mechanism of Lamellae in PBT Thin Films. We disclose that isothermal annealing of the anisotropic glassy PBT thin films can result in either smectic nodules or edge-on lamellae depending on the T_a applied. It is interesting to ask how the smectic and crystal interplay when the transition from glass to crystal takes place. To unveil the transition mechanism, the change of morphologies during the isothermal annealing at the temperatures where the α -form lamellae can grow was examined. We performed isothermal annealing experiments by directly inserting the virgin PBT thin film into the hot stage with a preset T_a ($T_a \ge 200$ °C), and after a duration of t_a , the sample was quenched with ice water.

The morphologies of the isothermally annealed films were inquired at room temperature using AFM. As examples, Figure 8a,b depicts two AFM images of the PBT thin films after being annealed at $T_a = 210$ °C for $t_a = 5$ and 150 min, respectively. In both images, the lath-like edge-on lamellae are dominant, and prolonging t_a can result in longer laths. We measured the lath lengths (*Ls*) of individual lamellae and thus obtained the distribution of *L* at different t_a s. As shown by Figure 8c, the distribution of *L* shifts to the right with increasing t_a , indicating the lateral growth of the edge-on lamellae. For T_a of 200 and 220 °C, the distribution of *L* at various t_a s was also measured (Figure S6).

We calculated the mean values of $L(\bar{L})$ at different t_a s based on the distribution, which are plotted as a function of t_a in Figure 9. As mentioned above, the 1D confinement and RAFlike interface may restrain the smectic structure from relaxing to the crystalline phase. When T_a was selected to be higher than ~190 °C, which corresponds to the T_g^{RAF} for bulk PBT,⁸



Figure 8. Growth of lath-like lamellae in the 200 nm thick PBT films at $T_a = 210$ °C. (a, b) AFM images recorded at room temperature after isothermal annealing for t_a of 5 and 150 min, respectively. (c) Distribution of the length of lath-like lamellae measured for various t_a s.



Figure 9. Average length (\overline{L}) of the lath-like lamellae grown at different $T_{a}s$ as functions of annealing time (t_{a}) .

we suspect that the restriction of chain motion would be well relieved so that the isothermal annealing can trigger the crystal growth. When comparing the early stages of isothermal annealing ($t_a = 5 \text{ min}$), we find that the \overline{L} ($t_a = 5 \text{ min}$) increases drastically with increasing T_a , which jumps from ~20 nm at $T_a = 200$ °C to ~50 nm at $T_a = 220$ °C. As a result, the higher the T_a the faster the lamellar growth is. Androsch et al. have demonstrated that the isothermal crystallization rate of PBT presents a bimodal dependence of crystallization temperature (T_c).¹² At the low undercooling side wherein the heterogeneous nucleation dominates, increasing T_c leads to reduction of the crystallization rate. Therefore, the crystallization kinetics of glassy thin film is essentially different from that of isotropic melt of PBT.

For $T_a = 220$ °C, the \overline{L} keeps nearly a constant of ~50 nm when varying t_a . Such a small lateral dimension of lamellae, which is 1-2 orders of magnitude lower than that of melt crystallization, shall be ascribed to the extremely high nucleation density that is related to the initial state of anisotropic thin film glass produced by fast solvent evaporation. As the edge-on lamellae present a random orientation, the lamellae frequently collide with each other and thus the growth can be easily ceased.⁵⁰ Given the high nucleation density, the edge-on lamellae formed at T_a values of 200 and 210 °C are also tiny. Nevertheless, as the growth rate was reduced in comparison with that at 220 °C, the lamellar development can be followed. After the early stage of isothermal annealing, fairly linear growth behavior can be found (Figure 9), of which the rate increases again with increasing T_a .

As shown in Figures 8c and S6, of particular interest is that there exist many particles with a size of no more than 20 nm at $t_{\rm a}$ = 5 min. These tiny particles will no longer be detected after extending the annealing so that they might be consumed by crystal growth. Moreover, it is also found that the population of short laths decreases with increasing t_{av} implying that the shorter laths may merge together or join in the longer ones.⁵¹ When the virgin PBT thin films were immediately placed at T_{a} higher than 200 °C, the lamellae of α -form could be assumed to grow directly from the glassy state. Nevertheless, the small particles with a size of less than 20 nm observed at the early stage are seemingly related to the quadrangle-like smectic nodules, which might develop prior to crystallization. Therefore, in addition to the direct transition from glass to crystal, we conjecture that there might be an alternative pathway of "glass-to-smectic-to-crystal", wherein the smectic mesophase is taken as a transient state. To further explore the inter-relation between smectic and crystal, we designed a two-step protocol to perform the isothermal annealing. At the first step, the glassy PBT thin film was annealed at 180 °C for 30 min for the cultivation of smectic nodules, and then, the sample was shifted to 210 °C for the second step annealing. In this case, the PBT thin-film crystallization in the second step takes place with the initial state of well-formed nodules.



Figure 10. (a, b), AFM images of 200 nm thick PBT films recorded at room temperature after the second step annealing at $T_a = 210$ °C for $t_a = 30$ and 60 min, respectively. Before the second step of annealing, the films were annealed at 180 °C for $t_a = 30$ min. The right panels in (a, b) are the zoomed images of the area indexed by the dashed yellow squares in the left panels. (c) Distributions of the length of lath-like lamellae after the second step annealing of various t_a s. (d) Schematic of the lath-like lamella growth via the merging of element crystalline blocks.

The AFM results of two-step annealing experiments are depicted in Figure 10a,b, using the second step annealing of t_a = 30 and 60 min, respectively, as examples. In general, the change of morphology is similar to that shown in Figure 8, namely, the lath-like lamellae elongate with extending t_a . Figure 10c presents the distribution of lath length L after the second annealing at 210 °C for different $t_a s$, from which the average lath length \overline{L} can be measured to be ~33 and ~47 nm at $t_a =$ 30 and 60 min, respectively. Interestingly, for $t_a = 30$ min (Figure 10a), we observe that there exist many particles with size around 20 nm, which could be tightly related to the smectic nodules with size around 12 nm preformed during the first step annealing at $T_a = 180 \text{ }^\circ\text{C}$ (see Figures 5 and 6). For the smectic nodules formed at lower T_a s, experiments reveal that lengthening t_a would hardly alter the nodule size, indicating that the constrained chain segments surrounding the nodules not only hinder the smectic-to-crystal transition but also limit the growth of the smectic domain. The enlarged particle of \sim 20 nm appearing after the second step annealing at $T_a = 210$ °C could be due to the chain motion promoted at a sufficiently high temperature releasing the obstacle for crystallization.

The zoomed AFM image shown in the right panel of Figure 10a illustrates that the particles are more regular and squareshaped in comparison with quadrangle-like nodules at $T_a = 180$ °C (see Figure 5) and, moreover, several adjacent particles may align in line locally. It reflects that the PBT segments in the nodules may just partially melt at 210 °C and meanwhile quickly relax into the crystalline lattice accompanied by the adjustment of the particle orientation.

Furthermore, we can infer from Figure 10a that the squareshaped particles of \sim 20 nm could be the element block for the growth of edge-on lamellae. It is noted that the second step annealing of $t_a = 30$ min results in a large number of lath-like particles that possess a lath length of ~40 nm. Very likely, these lathes are the dimers of the element block. In Figure 10d, the schematic drawing elucidates the steps of dimer formation: (1) the quadrangle-like nodules formed at 180 °C adjust their shape and orientation at 210 °C, turning in crystal particles with more square shape, which are the element blocks and (2) two adjacent blocks with the same PBT chain orientation merge together to form a dimer. Prolonging the annealing time would largely eliminate the element blocks. As shown by Figure 10b of $t_a = 60$ min, the frequency of finding the particles of ~20 nm becomes quite low. The average lath length \overline{L} of ~47 nm at $t_a = 60$ min implies that the trimers become dominant, which could be a result of the process of a "dimer + element block". We also detect some lath-like edge-on lamellae with L obviously longer than that of the trimer (indexed by a dashed rectangle in the right panel of Figure 10b). The AFM result shows that the top surface of the long lath is not strictly smooth, and ripples appear on the lath somewhat periodically. The ripples are probably associated with the merged boundaries of the element blocks, from which we may judge the number of blocks involved in the edge-on lamella. For example, the lath indicated by the dashed rectangle in Figure 10b is composed of 5 element blocks, as schematically drawn in Figure 10d. The lathes could not grow freely along their long axis because of the crystal impingement. As shown by Figure 10c, the distribution of the lath length of the second annealing with $t_a = 150$ min is quite similar to that of $t_a = 60$ min.

The experimental results of two-step annealing confirm the transformation from nodule to lath-like crystal in the PBT thin film. Most likely, the nodules that should be the smectic particles turn easily into square-shaped crystallites and bypass the complete melting. The enhanced chain mobility at higher $T_{\rm a}$ allows the nodules to expand in both lateral and longitudinal directions, in the expanse of the amorphous PBT chains and the less stable nodules with a smaller size. When forming the square-shaped crystallites with a size larger than that of the nodules, lamellar thickening shall be involved. As a result, the small crystallites have enhanced thermodynamic stability so that they can survive during the early stage of high-temperature annealing. Later on, free energy reduction tends to eliminate the surface and interface, driving the small crystallites to combine to form larger lamellae. These two processes, thickening/chain registration occurring in the smectic-to-crystal transition and the crystalline blocks merging into lamellae, recall the multistage model of polymer crystallization proposed by Strobl.²² However, in our experiments, the nodule growth and the lamella growth are well separated into two distinct steps (i.e., the two-step annealing); thus, we could not answer if the mesophase layer could generate dynamically at the lamellar growth front. It is also worth emphasizing that for both the mesophase formation and crystallization from the glassy PBT thin film, the nucleation density is extremely high. This may reflect that the dense domains or embryos of the ordered structure exist across the virgin thin films,^{48,51} even though the films are trapped in the amorphous state overall.

CONCLUSIONS

In summary, we have investigated the phase structures and morphologies evolved from glassy PBT thin films with thicknesses less than 300 nm at different T_{a} s. It is found that after spin-casting, the PBT chains within the thin film are apt to lie down on the silicon substrate, resulting in an anisotropic amorphous structure. Isothermal annealing at T_a s ranging from 80 to 180 °C leads to smectic nodules with a size of around 10 nm. Different from that observed in bulk PBT, the smectic structure in the thin film can be retained for a long time. We presume that the one-dimensional confinement imposed by the thin-film geometry could significantly reduce the chain mobility; the RAF-like interface induced by the smectic chain packing would also prevent the transition from smectic to crystal. At above 180 °C, isothermal annealing will lead to the growth of edge-on lamellae, which are lath-like under AFM observation, as a result of enhanced chain mobility at higher temperatures. For 180 °C $\leq T_{a}$ < 200 °C, the α -form crystals can coexist with the smectic nodules. Further increasing T_a leads solely to the α -form crystal. As the lying down orientation of PBT chains did not relax, the lath-like PBT crystals detected in the thin film are edge-on lamellae. Crystallization from the anisotropic amorphous thin film demonstrates a tremendously high nucleation density. In this case, the lath-like crystals easily impinge one another, and their growth is limited, giving the lateral size just several dozens of nanometers. Using a two-step annealing protocol, we further examined the crystallization from the nodules that are largely smectic formed in the first-step annealing. It is found that the nodules would quickly transform into crystal particles with a square-like shape, which are the element blocks for further crystallization. The lath-like crystals grow via the merging of these blocks. The experimental results of PBT crystallization in

the anisotropic amorphous thin film have revealed the interrelations among the glass, smectic mesophase, and crystals, which are complex and deserve more in-depth investigation. Also, the control of edge-on lamella growth in thin films may provide guidance for the fabrication of advanced and functional materials based on PBT and other polyesters.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.3c01313.

GPC curve of the PBT sample; illustration of experimental setting for GI-WAXS/GI-SAXS; azimuthal scanning profiles of the scattering 1 of initial film with different thickness; WAXS curves of amorphous PBT films; the width analysis of the scattering at ~6.4 nm⁻¹; length distributions of lath-like lamellae grown at T_a of 200 and 220 °C for various t_a s (PDF)

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