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ARTICLE

Thickening-Induced Faceting Habit Change in Solution-Grown Poly(L-lactic acid) Crystals

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ABSTRACT: Morphological evolution of poly(L-lactic acid) (PLLA) crystals obtained via crystallization at T_c = 85 to 97 °C from 0.1% solutions in mixed xylene was closely followed via transmission electron microscopy. Upon stirring-enhanced nucleation after the adopted incubation scheme (t_i = 10 h at T_i = 90 °C), there emerged "*a* axis" lenticular crystals of the imperfectly packed α form, as indicated by the presence of the presumably forbidden (010) spot in the selected-area electron diffraction along the [001] zone. Subsequently observed during further growth was a gradual change from lenticular to truncated lozenge with {100} and {110} facets, driven by the outward propagation of the thickened interior (truncated lozenge in shape) within the lenticular crystal. The width of the {100} facets clearly decreased with decreasing T_c, resulting in rhombic lozenges with {110} edges at 87 °C. This change in faceting habit is interpreted in terms of the competition between primary growth (controlled by surface-nucleation) and interior thickening (controlled by the reeling-in of chains from the primary thin rim via slip diffusion on the {110} surfaces). Eliminating the stirring-enhanced nucleation procedure, we have observed direct transition from lenticular to rhombic lozenge crystals at T_c = 85 °C without interior thickening, that is, bypassing entirely the truncated lozenge stage. It is hence proposed that the lamellar thickening is intrinsically a nucleation-and-growth process, initiated by the (presumably thick) nucleus from stirring, followed by the reeling-in process of stems in the rim. The supercooling dependence of the reeling-in rate is anisotropic and decreases most significantly along [100] directions with increasing T_c. Therefore, the {100} facets of truncated lozenge develop wider at higher T_c.

Introduction

Poly(L-lactic acid) (PLLA), a biodegradable synthetic polypeptide, has been extensively studied in the past two decades in view of its potential applications in biotechnology and biodegradable commercial plastics.[1−6] However, even the most simplified case of PLLA crystallization from the dilute solution state is not fully understood in many aspects. Generally speaking, the solution crystallization behavior of PLLA shares some common features of the well-examined case of polyethylene (PE). For instance, it is known that isothermal crystallization of PLLA from dilute xylene solutions results in orthorhombic (α) crystals in the shape of either fully developed {110} lozenges or their truncated counterparts.[7−9] The fold surface energy of the α phase was estimated to be 75 mJ m^{-2},[7] slightly lower than that (ca. 90 mJ m^{-2}) of PE, implying that the PLLA chains should experience lower nucleation barrier for crystallization. This, however, is at odds with experimental observations that either large supercooling or self-seeding is needed for efficient nucleation of PLLA from dilute solutions.[7−9] In addition, crystalline forms of lenticular shape ("lenticular" crystals) or rounded crystal habit have been extensively reported in the case of long alkanes, PE, and other polymers.[10−13] In view of the similarity in crystal structure and faceting habits between PE and PLLA, one would anticipate the presence of such lenticular crystals in solution-grown PLLA crystals, which is not yet documented in the literature.

Reported here are results of our recent investigation of temperature and time dependence of growth habit for PLLA crystals grown from dilute solutions in mixed xylene (a moderate solvent) in the crystallization temperature (T_c) range of 85 to 97 °C. Upon stirring-enhanced nucleation at the end of the adopted 10 h of incubation at T_i = 90 °C, there emerged first lenticular crystals (defectively packed α phase) that subsequently evolved into truncated lozenge crystals (perfected α phase). This shape change is identified as a consequence of the competition between the development of thickened interior (truncated lozenge in shape) and the primary growth of the outer thin rim that prefers the rhombic lozenge shape. The mechanism of this interior thickening via secondary reorganization is discussed in terms of reeling-in of chains from the prior grown outer rim.

Experimental Section

Materials/Instruments. Both the PLLA sample (with nominal molecular mass of 40 to 60 kDa) and the solvent, mixed xylene (electronic grade of low ion impurity level, xylene content is >99%, the isomeric composition is unspecified but should generally correspond to[14] 40−65% of *m*-xylene and up to 20% each of *o*-xylene and *p*-xylene, and also minor content of ethylbenzene), were purchased from Sigma-Aldrich and used without further purification. Transmission electron microscopy (TEM) observations were made by use of a JEOL JEM-1400 instrument operated at 120 kV; bright-field images were obtained using a Gatan digital detector, whereas electron diffraction patterns were recorded on photographic films. Tapping-mode

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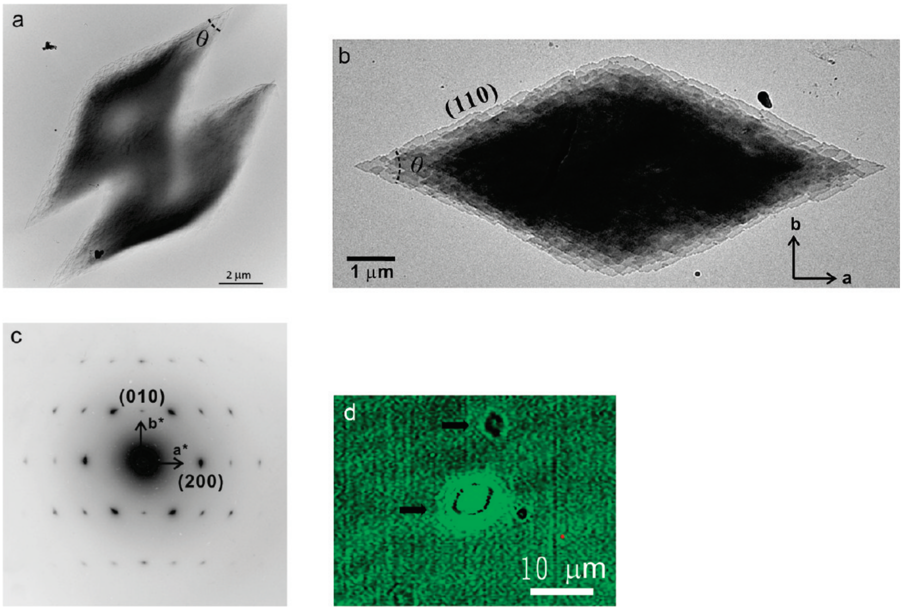

Figure 1. (a) A pair of *a* axis lenticular crystals (decorated by overlaying "over-grown" crystals) obtained immediately after stirring-induced nucleation, that is, (T_c, t_c) = (90 °C, 0 h). The lenticular crystal is characterized by geometric features of sharp acute apexes ($\theta \approx 30°$) and rounded obtuse apexes. (b) At (T_c, t_c) = (90 °C, 3 h), the angle of acute apex had increased, whereas the obtuse apex remained rounded. The arrow near the bottom obtuse apex highlights sawtooth features in development. Note also that the surface decoration has developed into stacked platelets of oriented growth. (c) Corresponding SAED pattern of the crystal in part b, where the presence of the supposedly forbidden (010) reflection implies defective packing of molecular stems within the lenticular crystal. (d) In situ OM observation of lenticular crystals formed in dilute xylene solution after 12 h of isothermal incubation at 90 °C. As the crystals were floating in the solution, the focusing was slightly off but still adequate to reveal basic lenticular features.

atomic force microscopy (AFM) observations were made by the use of either a Veeco Innova AFM with NanoDrive controller or an Omega Olympus/LX70 instrument.

Isothermal Crystal Growth. Solutions of 0.1% PLLA in xylene were prepared by 1 h of dissolution at 128 °C. Isothermal crystallization of PLLA was conducted by quenching the solution to an incubation temperature of T_i = 90 °C (i.e., transferring ca. 2 mL of the solution to a test tube already thermally equilibrated at 90 °C in an oil bath) and maintaining at this temperature. The development of aggregation/preordering can be identified as the major event in the solution after being equilibrated at T_i. Gentle stirring using a glass capillary tube was applied for 20 s to initiate crystal growth after 10 h of incubation at 90 °C (t_i = 10 h). Subsequent crystal growth at T_c = 90 °C for different periods of time, t_c, beyond the stirring-induced nucleation was followed by TEM observation. This stirring was found to increase dramatically the population of lenticular crystals; in the absence of stirring or with the immersion of a still capillary tube, there was only insignificant formation of lenticular crystals even after prolonged induction time of many hours (cf. Figure SI, Supporting Information). At the end of a given t_c, the capillary tube containing a droplet of the solution was quickly transferred into an ice-water-cooled xylene bath to terminate the crystal growth by depleting the dissolved PLLA chains via the formation of very small ("overgrown") crystals at such a high supercooling. The quenched solution contained in capillary was then immediately cast on a copper grid and dried by filter paper or was quickly evaporated on glass slide for microscopic observations. It should be noted that the chosen incubation period of t_i = 10 h bears some significance: for shorter times, stirring would not be effective in inducing nucleation; for longer times, there could be many overlaying lenticular crystals that hamper TEM observations. This implies some preordering process slowly in progress; details are not yet clear and will be the subject of future studies.

In Situ Optical Observations. To confirm the growth of lenticular crystals at 90 °C, in situ observation was performed by the use of an inverted optical microscope (OM, Motic AE31) equipped with a house-designed hot stage and a digital camera (Moticam 2300). After incubation at 90 °C for 13 h, the solution was quickly transferred to a capped quartz beaker pre-equilibrated at 90 (±0.5) °C on the hot stage of the microscope. This minimized the solvent evaporation to allow for in situ OM observations that followed immediately. The slow isothermal crystal growth can continue within the quartz beaker for hours without detectable loss of solvent and sudden change of crystal growth habit.

Temperature-Dependent Growth Habit. To delineate the temperature dependence of PLLA crystal growth behavior, T_c values different from 90 °C were adopted. At the end of the 10 h of incubation at T_i = 90 °C, the solution temperature was changed to an alternative value of T_c = 80 to 97 °C. This was achieved by drop-by-drop transferring of the PLLA solution maintained at 90 °C to an empty test tube equilibrated at the desired T_c. After the accumulation of a sufficient amount (ca. 2 mL) of PLLA solution in the test tube equilibrated at T_c, stirring was applied to initiate nucleation, followed by similar specimen preparation procedures for microscopic observations, as in the case of isothermal crystal growth.

Results and Discussion

Lenticular Crystals at 90 °C. Crystallization of PLLA from the dilute xylene solution upon quenching to 90 °C was slow: only a limited number of lenticular crystals appeared after 10 h of incubation. To induce nucleation effectively, gentle stirring for 20 s using a glass capillary was applied at the end of the incubation period. As detailed in the Experimental Section, this stirring merely results in shear-induced nucleation of lenticular crystals; side effects such as the formation of a new phase or the emergence of new morphological features are safely excluded.

After the stirring, lenticular domains (Figure 1a) started to develop in high population. The formation of lenticular crystals is preferentially observed at elevated crystallization temperatures in solution crystallization of long alkanes and PE,[15−19] for which solvent-dependent mesomorphic preordering has been proposed as the origin.[19−22] Demonstrated

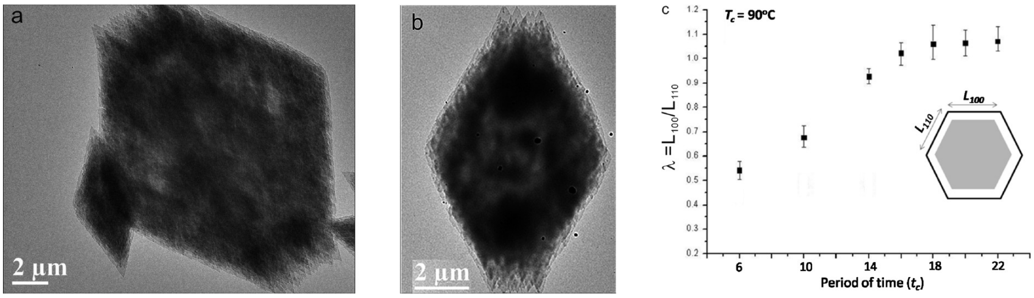

Figure 2. (a) Representative truncated-lozenge crystal with {100} facets obtained at T_c = 90 °C. (b) In the earlier stage of morphological change, the initial development of {100} facets can be arrested by quenching process. The width of {100} growth front increases subsequently with increasing t_c. Note that surface decoration effects from heavy overgrowth of oriented platelets piled on top of these newly developed truncated lozenge crystals. (c) The ratio λ between the widths of the (100) and (110) facets increases with t_c before reaching a plateau value of 1.05 for $t_c > 16$ h.

in Figure 1d is an in situ observation of lenticular crystals at 90 °C using the OM hot stage (cf. Experimental Section). This demonstrates the development of lenticular crystals in solution at 90 °C and ensures that lenticular crystals in Figure 1a,b were not formed as artifacts during solution cooling or TEM specimen preparation. It is noteworthy that individual lenticular crystals could be easily observed mainly within the period t_c = 2 to 6 h. At a shorter or longer t_c, lenticular crystals were low in population and difficult to be identified through the same cooling process.

We note in particular from Figure 1a that the central region of the PLLA lenticular domain in this early stage can be thinner than its immediate surroundings because of decoration effects but is nevertheless thicker than the outer periphery. The angle of the acute apex lies in the range of 28 to 34°, lower than that of typical rhombic lozenge crystals. The tips of the lenticular crystals are rather extended, possibly because of the diffusion-controlled growth analogous to dendritic PE single crystals.

With further isothermal growth, the habit of sharp acute apexes and rounded obtuse apexes became clearly identifiable (Figure 1b). Because the lenticular long axis lies parallel to the crystallographic *a* axis according to the [001] zone pattern (Figure 1c) of the orthorhombic phase, the crystal morphology can be categorized as "*a* axis" lenticular;[16,19,20] in addition, the angle of the acute apex in this stage has approached the lozenge value of 60°. It has been previously proposed[20] that the growth of rounded lateral faces of "*a* axis" lenticular crystal of long alkanes is a result of asymmetric step-deposition kinetics in opposite directions at the growth front. This attribution is consistent with sawtooth features near the obtuse apex of PLLA lenticular crystals (Figure 1b). Therefore, the lenticular morphology here is considered to be a kinetically favored growth habit, not necessarily a stable mode.

Immediately before the solution was rapidly quenched by dipping the capillary into a cold xylene bath for the preparation of TEM specimens, there was a significant fraction of PLLA chains remaining dissolved. Fast precipitation and crystallization of these PLLA chains during quenching at preferred sites gave rise to decorations as stacked platelets in Figure 1a,b. These "overgrown" platelets are basically in the lozenge geometry, implying rhombic lozenge habit at low temperatures. Given this habit of overgrown lozenge platelets and increased angle of acute apex, the growth and evolution of lenticular crystals of PLLA must have taken place at 90 °C in the solution. The oriented growth of stacked platelets as surface decorations in Figure 1b and the absence of such decorations in Figure 1a suggest the involvement of some type of epitaxial origin.

Lenticular-to-Lozenge Shape Change. At t_c = 6 h, 6 h after the stirring-induced nucleation, truncated-lozenge crystals of the same orthorhombic phase yet with additional, but narrow, {100} facets emerged from solution (Figure 2a,b). Beyond this point of time, truncated-lozenge crystals greater in size (as compared with that of lenticular precursors) and with rounded obtuse apexes started to prevail, whereas the number of lenticular crystals quickly decreased. Both the greater crystal size and rounded obtuse apexes suggest that the truncated lozenges were isothermally transformed from lenticular precursors.

Also characteristic of this change of growth habit is the accompanying increase in the ratio between widths of (100) and (110) facets ($\lambda \equiv L_{100}/L_{110}$), as shown in Figure 2c. This ratio may be designated as zero in the first 6 h after stir-induced nucleation (because there were only lenticular crystals), followed by a step jump to ca. 0.54 upon emergence truncated-lozenge crystals and subsequent increases with time before reaching the plateau value of ca. 1.05. In other words, at the onset of morphologic transition, truncated lozenges with narrow {100} facets were developed from the original lenticular crystals; {100} faces of these truncated lozenges subsequently grew wider before reaching the characteristic geometric ratio of $\lambda \approx 1.05$. Consistent with this scenario is the increase in the angle of acute apex during the development of PLLA lenticular crystals. In the case of long alkanes, the acute apex angle of lenticular crystals has been observed[20] to increase before appearance of the microscopic {100} sector that serves as a slow-growing substrate for {110} faces.

Thickened/Faceted Interior. With continuing isothermal treatment, the overgrowth of small lozenge crystals became less severe because most of the originally dissolved molecules had joined the crystal growth. This helps greatly in revealing a salient feature of developed truncated-lozenge crystalline monolayer. As illustrated in Figure 3, there are two distinct regions different in lamellar thickness: a thickened interior region, truncated-lozenge in shape, and a thin outer rim. Results of AFM measurements (Figure 3d) indicated a lamellar thickness range of 15 ± 1 nm for the inner truncated-lozenge and 10 ± 1 nm for the outer rim, which remained insensitive to extended isothermal crystallization time; this implies single-step thickening. As the thickness of basal lenticular monolayer was also 10 ± 1 nm (Figure 4a), this particular lamellar thickness appears to be a primary growth habit of PLLA crystals at 90 °C.

The thickened interior is not limited to the well-developed truncated-lozenge crystals: there are hints of its presence back in the lenticular stage. First, we note that the decoration via overgrowth is not limited to previously discussed platelets. As illustrated in Figure 4b, circular or semispherical domains also provided surface decoration to lenticular crystals obtained in the early stage of isothermal crystallization.

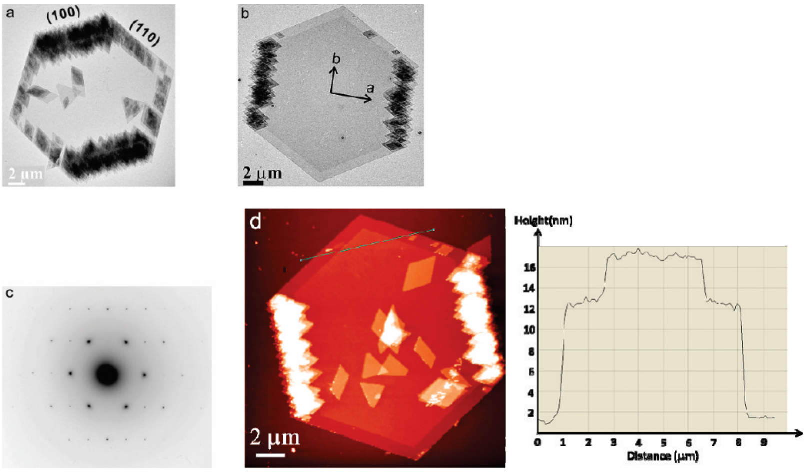

Figure 3. (a) Representative truncated-lozenge crystals upon isothermal growth at (T_c, t_c) = (90 °C, 4 h). Note the clearly developed {100} facets: the ratio between widths of {100} and {110} facets increases with increasing crystal size. (b) Truncated-lozenge crystal at (T_c, t_c) = (90 °C, 12 h). An inner thickened region with the shape of truncated-lozenge is now clearly developed. Note also the nearly equal widths of (100) and (110) facets. (c) Corresponding SAED [001] zone pattern signifies the orthorhombic phase of PLLA. (d) Representative AFM image, with height profile along the indicated cross-section shown at right. Thickness of the inner region is ca. 15 nm, whereas that of the outer skirt is ca. 10 nm.

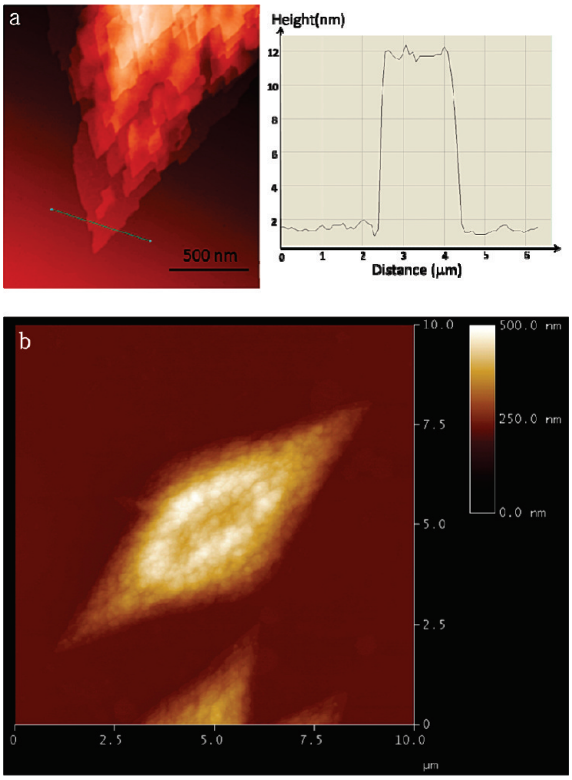

Figure 4. (a) Representative AFM image near the tip of the lenticular monolayer, with the high profile of the indicated cross-section given at the right. The lamellar thickness is ca. 10 nm for the basal monolayer, coinciding with that of the outer skirt of the fully developed truncated-lozenge crystal in Figure 3c. (b) Magnified AFM image of the lenticular crystal obtained after stirring-induced nucleation. Here the thickened region at the crystal center appears craterlike, surrounded by protruding decoration of excessively overgrown crystals because of capillary effects along the step change in height upon solvent evaporation.

Such decoration behavior has been previously observed.[23,24] It is then interesting to note that the center of the lenticular crystal, although considerably thicker than the peripheral region, is surrounded by a heavily decorated (and hence greatest in total thickness) intermediate zone. With the knowledge that the formation of overgrown crystals/precipitates is preferred near ledges of different height, one may envisage that the central region has already thickened to some extent: the heavy overgrowth decoration around the thickened central region simply results in the highest total thickness, whereas the central region became the second in total thickness. This scenario is also supported by the image shown in Figure 1a, where the thickness contrast indeed indicates that the center region is intermediate in total thickness contrast, with the peripheral region being the thinnest.

On the basis of preferential overgrowth at ledges, one may further observe that the outline of the central region is reminiscent of the shape of truncated lozenge with narrow {100} faces. From previous discussion of the evolution of dimensional ratio, the appearance of similar truncated lozenge interior was also recognized at the onset of shape change to truncated lozenge. These clues to the evolution of lenticular crystals, including the development of inner thickened region and the concomitant widening of acute apex, suggest that an outward propagation of thickened interior (truncated lozenge of greater lamellar thickness) is responsible for overriding the original lenticular appearance.

Temperature Dependence. To confirm the generality of the picture above and to explore the temperature dependence of the growth habit, a two-step process of crystal growth was adopted. After isothermal incubation at T_i = 90 °C for 10 h, the solution temperature was quickly changed to an alternative value T_c ranging from 80 to 97 °C, with the stirring action immediately applied to induce nucleation for isothermal crystallization at T_c. As demonstrated in Figure 5, there are always two distinct lamellar thicknesses within each truncated lozenge crystal. The thickness of either the thickened/faceted inner region or the outer thin rim remains temperature-independent within the range studied. In addition, the width of {100} growth faces increases with increasing T_c. This renders the truncated lozenge increasingly elongated along the crystallographic *b* axis with increasing temperature. In addition, the gap between corresponding {110} facets of thickened interior and the breadth of the outer rim decreases from ca. 0.7 to 0.3 μm as T_c decreases from 97 to 87 °C. This trend continues to $T_c \leq 85$ °C (Figure 6), where the lenticular crystal transformed directly to lozenge crystal yet still with a thickened region of truncated lozenge inside the rhombic lozenge. Unlike the molecular packing in lenticular crystals, the achieved regularity of lattice packing

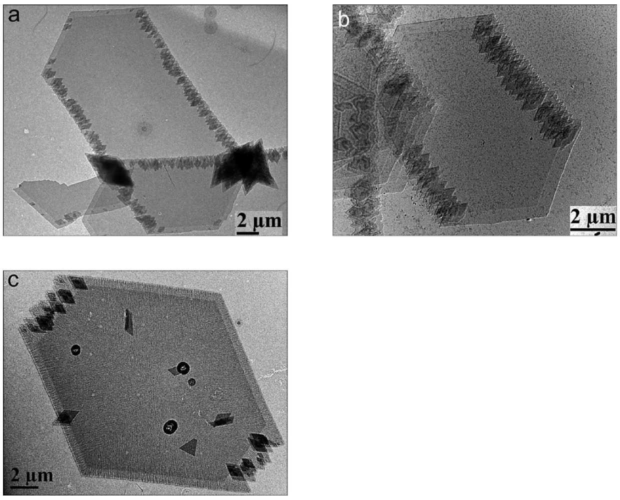

Figure 5. Truncated-lozenge crystals of PLLA upon crystallization at (T_c, t_c) = (a) (97 °C, 16 h), (b) (94 °C, 12 h), and (c) (87 °C, 14 h). Note that the width of {100} growth fronts decreases with decreasing T_c, resulting in decreased extent of truncation at lower T_c. In addition, the gap between corresponding {110} facets of thickened interior and the outer rim decreases from ca. 0.7 to 0.3 μm as T_c decreases from 97 to 87 °C.

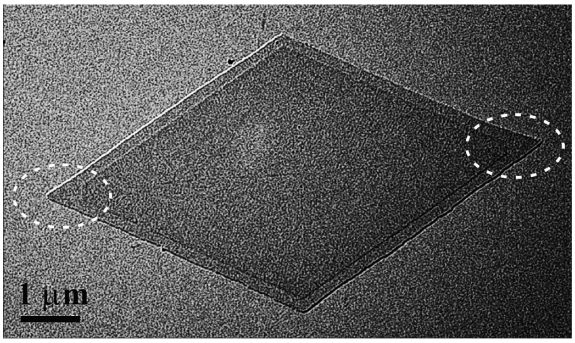

Figure 6. Representative rhombic lozenge crystal at (T_c, t_c) = (85 °C, 15 h). The inner thickened region (with very short {100} facets) is approaching a fully developed lozenge in shape. Note the further decreased breadth of the outer thin rim to ca. 0.2 μm here.

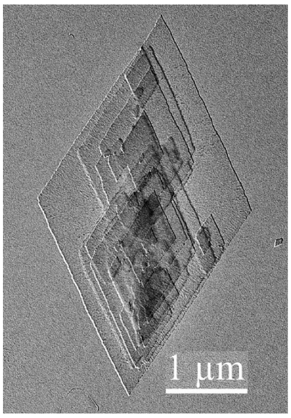

Figure 7. Without stirring-enhanced nucleation, the initial lenticular crystal (cf. Figure 1a) develops directly into lozenge crystal (without going through the truncated-lozenge stage) at (T_c, t_c) = (90 °C, 24 h). Note the absence of overgrown decoration, which is now replaced by spiral growth of overlaying lamellae.

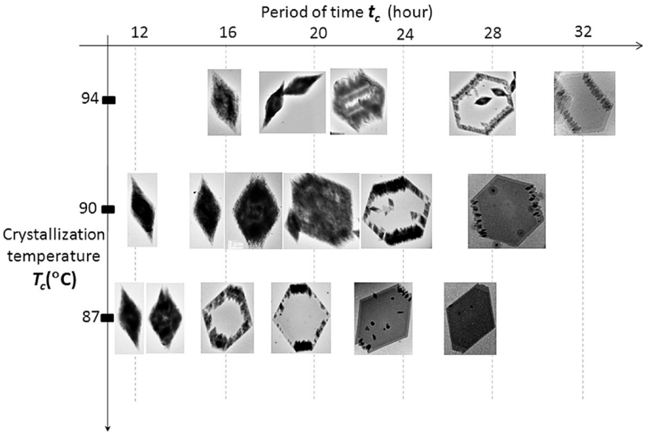

Figure 8. T_c−t_c map summarizing morphological development of solution- grown PLLA crystals. t_c is the period of time after stirring-induced nucleation, and T_c is the crystallization temperature. With decreasing T_c, the lenticular-to-truncated lozenge shape transition occurs at shorter t_c, whereas the final crystal shape approaches rhombic lozenge.

in transformed lozenge crystal appeared able to keep lozenge morphology and hinder the breakthrough of thickening process. The width of {100} facets of the thick inner region became much more narrow than that developed at a high T_c, whereas the breadth of the outer rim decreases further to ca. 0.2 μm.

Summarized in Figure 8 are our observations of morphological development of solution-grown PLLA crystals and the corresponding shape transition at different crystallization temperatures. With decreasing T_c, two main features are clearly identifiable: the lenticular-to-truncated lozenge shape transition occurs at shorter t_c, whereas the final crystal shape approaches rhombic lozenge.

Reorganization within Lenticular Crystals. For polymer crystals, it is generally accepted that lamellar reorganization takes place preferentially at the edges, defect-concentrated regions, or certain sets of crystalline planes.[25−30] In the absence of foreign seeds and self-seeding treatment, the thickened/faceted lateral features within the PLLA crystalline monolayer is rather peculiar. A hint to the origin is the observation that without stirring-enhanced nucleation, the morphological transition took place directly from lenticular to rhombic lozenge (Figure 7), bypassing entirely the intermediate stage of truncated-lozenge with thickened interior. In addition, the overgrown decoration is replaced by spiral growth of a large number of overlaying crystals, implying the presence of screw dislocations that are characteristic to isothermal growth of the single-crystal substrate. The role of the stirring action is therefore most likely to result in seeds of lamellar thickness greater than that of the subsequently developed lenticular domains where the lamellar thickness is determined by unperturbed molecular kinetics.

In the presence of the stirring-induced thick seed, reorganization takes place preferentially from the center of crystal domain probably via mechanistic steps discussed by Kovacs et al.[23,24] for melt-crystallized poly(ethylene oxide) (PEO). A closer examination of the SAED patter from a lenticular crystal (Figure 1c) indicates the presence of the presumably forbidden (010) spot as indeed absent (Figure 3c) in the subsequently evolved case of truncated-lozenge monolayer. This suggests that the molecular packing within the lenticular crystal is not fully regular, hence less restricted lattice packing and additional free volume for the slip diffusion of molecular stems.

Assuming that packing regularity or lattice restriction may result in adequate differentiation between kinetic barriers of

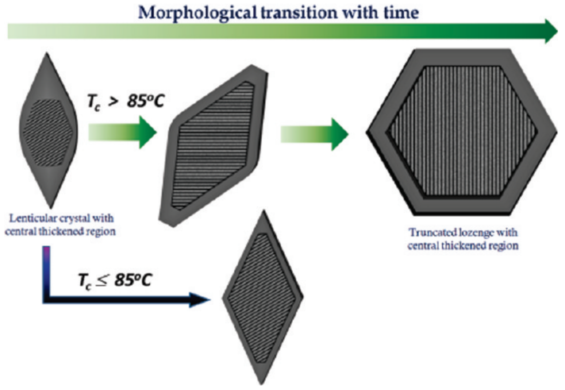

Figure 9. Schematic illustration of morphological transformation stages in terms of lateral geometry and crystal thickness. Lamellar thickening propagating from the central region leads to the appearance of {100} growth fronts and gradually changes the crystal morphology to truncated lozenge. A "reeling in" action of neighboring stems is assumed to be responsible for this thickening process. The interior thickening process is restricted upon the quick transition to rhombic lozenge crystal below 85 °C. Therefore, the thickened region with {110} and {100} facets is retained inside the lozenge domain.

slip diffusion of molecular stems along different crystallographic planes, the propagation rate of lamellar reorganization may become anisotropic, resulting in thickened interior of faceting. However, this phenomenon is rarely observed and different from the isotropic propagation of the lamellar reorganization in bulk-crystallized PEO. In view of the emergence of an additional {100} sector, this secondary reorganization probably involves not only the slip diffusion along molecular chain but also the translation motion of molecular stems.

Thickening-Driven Transition of Growth Habit. At each T_c, the presence of the outer rim (ca. 10 nm in thickness and submicrometer in breadth normal to {110}) is persistent during further growth in size, which implies quasi-steady competition between interior thickening and primary growth of the thin rim. Some reeling-in process of molecular stems is presumably involved in the propagation of inner thicker region. This thicker region is bounded with {100} and {110} facets, which implies that the reeling-in of molecular stems is still a nucleation-controlled process with anisotropic supercooling dependence. Therefore, with decreasing T_c, the rate of interior thickening is able to increase because of increasing nucleation efficiency, although the molecular motions become slightly slower. A faster propagation of the inner thickened region causes the narrowing of the {100} facets of the thickened interior and the decreasing breadth of the outer rim with decreasing T_c (cf. Figures 5 and 6). With increasing T_c, the reeling-in rate along [100] directions decreases more strongly (because of the larger separation between {100} planes) than that along [110] directions; this leads to the widening of {100} facets as the primary growth habit of the outer rim remains unchanged. In support of this interpretation, a closer look at the two {100} facets of outer rim indicates the presence of sawtooth-like edges, which comprise indeed an array of short, slow-growing {110} facets.

Schematically summarized in Figure 9 are stages of morphological transformation in terms of lateral geometry and crystal thickening. It is tentatively proposed that lamellar thickening started from the nuclear region propagates by quickly reeling-in PLLA stems from the surrounding thin region. This nucleation-controlled reeling-in process is anisotropic (i.e., relatively slow in both [100] and [110] directions) and propagates continuously outward, resulting in the lenticular-to-truncated lozenge shape transition at $T_c > 85$ °C. At $T_c \leq 85$ °C, the more strongly increased primary growth of the outer rim allows for more complete development of the rhombic shape.

Conclusions

For solution crystallization of PLLA, we have observed the initial development of metastable lenticular crystals as a kinetically favored process in the mixed xylene solvent. The subsequent lenticular-to-truncated lozenge shape transition at $T_c \geq 87$ °C is attributed to the outward propagation of thickened interior through secondary reorganization initiated from the stirring-induced seed that eventually overrides the original lenticular morphology. For $T_c \leq 85$ °C, direct lenticular-to-rhombic shape transition was observed, but the feature of thickened interior remained present; the more complete development of the rhombic shape is attributed to the more strongly increased rate of primary rim growth in this lowered T_c range. The observed morphological transition is interpreted as a result of competition between primary growth of the outer thin rim and interior thickening. The width of {100} facets of the truncated lozenge crystals increases with increasing T_c; this anisotropic supercooling dependence implies a certain nucleation-controlled mechanism for the interior thickening process.

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Supporting Information Available: Quiescent development of lenticular crystals in 0.1% solutions of mixed xylene as examined via TEM. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Leenslag, J. W.; Pennings, A. J.; Bos, R. R. M.; Rozema, F. R.; Boering, G. *Biomaterials* **1987**, *8*, 311.
(2) Vanionpaa, S.; Rokkamen, P.; Tormala, P. *Prog. Polym. Sci.* **1989**, *14*, 679.
(3) Vert, M.; Li, S.; Garreau, H. *Macromol. Symp.* **1995**, *98*, 633.
(4) Ikada, Y.; Shikinami, Y.; Hara, Y.; Tagawa, M.; Fukuda, E. *J. Biomed. Mater. Res.* **1996**, *30*, 553.
(5) Ikada, Y.; Tsuji, H. *Macromol. Rapid Commun.* **2000**, *21*, 117.
(6) Drumright, R. E.; Gruber, P. R.; Henton, D. E. *Adv. Mater.* **2000**, *12*, 1841.
(7) Kalb, B.; Pennings, A. J. *Polymer* **1980**, *21*, 607.
(8) Miyata, T.; Masuko, T. *Polymer* **1997**, *38*, 4003.
(9) Cartier, L.; Okihara, T.; Lotz, B. *Macromolecules* **1997**, *30*, 6313.
(10) Keith, H. D. *J. Appl. Phys.* **1964**, *35*, 3115.
(11) Khoury, F. *Faraday Discuss. Chem. Soc.* **1979**, *68*, 404.
(12) Cheng, S. Z. D.; Chen, J. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 311.
(13) Toda, A. *Faraday Discuss.* **1993**, *95*, 129.
(14) Fishbein, L. *Sci. Total Environ.* **1985**, *43*, 165.
(15) Organ, S. J.; Keller, A. *J. Mater. Sci.* **1985**, *20*, 1571.
(16) Toda, A. *Polymer* **1991**, *32*, 771.
(17) Briber, R. M.; Khoury, F. *J. Polym. Sci., Polym. Phys. Ed.* **1993**, *31*, 1253.
(18) Toda, A.; Arita, T.; Hikosaka, M. *Polymer* **2001**, *42*, 2223.
(19) Ungar, G.; Putra, E. G. R.; de Silva, D. S. M.; Shcherbina, M. A.; Waddon, A. J. *Adv. Polym. Sci.* **2005**, *180*, 45.
(20) Ungar, G.; Putra, E. G. R. *Macromolecules* **2001**, *34*, 5180.
(21) Pechhold, W. *Kolloid Z. Z. Polym.* **1967**, *216*, 235.
(22) Heck, B.; Strobl, G.; Grasruck, M. *Eur. Phys. J. E* **2003**, *11*, 117.
(23) Kovacs, A. J.; Gonthier, A.; Straupe, C. *J. Polym. Sci., Polym. Symp.* **1975**, *50*, 283.

(24) Kovacs, A. J.; Straupe, C. *J. Cryst. Growth* **1980**, *48*, 210.
(25) Blackadder, D. A.; Schleinitz, H. M. *Polymer* **1966**, *7*, 603.
(26) Statton, W. O. *J. Appl. Phys.* **1967**, *38*, 4149.
(27) Reiter, G.; Sommer, J.-U. *Phys. Rev. Lett.* **1998**, *80*, 3771.
(28) Reiter, G.; Castelein, G.; Sommer, J.-U. *Phys. Rev. Lett.* **2000**, *86*, 5918.
(29) Loos, J.; Tian, M. *Polymer* **2006**, *47*, 5574.
(30) Roe, R.-J.; Gieniewski, C.; Vadimsky, R. G. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 1653.