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Effects of Solution Status on Single-Crystal Growth Habit of Poly(L-lactide)

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ABSTRACT: Crystal nucleation in a quiescent 0.3 wt % poly(L-lactide) (PLLA)/*p*-xylene solution is sluggish at 90 °C. Instead of straightforward crystallization, there is a sigmoid decrease in solution viscosity, reflecting reduced hydrodynamic volume (V_H), and therefore the collapse of dissolved PLLA chains during this incubation stage. With enhanced nucleation via gentle stirring, *kinetically favored* "*a*-axis" lenticular crystals start to emerge; the acute apex angle of these lenticular crystals decreases with the collapse of PLLA coils, indicating an altered preference in the step deposition of molecular stems on the growth front. In subsequent growth of transformed truncated lozenge crystals, the decreased V_H results in suppressed crystal growth and a higher L_{100}/L_{110} ratio between (100) and (110) facet widths, implying *decreased driving force* toward crystallization or *increased barriers* of surface nucleation, both are consistent with the notion of collapsed chains of lowered free energy via preordering in the solution state. We conclude that these preordered chains in the solution state are responsible for (1) easier nucleation upon shear, (2) the formation of lenticular crystals with modified growth habit, and (3) significantly suppressed surface nucleation in the later development of truncated lozenge crystals. The preordered coils are more responsive to stirring-induced nucleation yet of suppressed surface nucleation at the crystal growth front; this bears relevance and provides better insights to the precursor concept recently proposed in the literature.

Introduction

Facets of solution-grown polymer single crystals reflect the slowest growth directions. As surface nucleation is the critical step for polymer crystal growth, crystallographic planes with the highest energy barrier for surface nucleation generally correspond to the facets of single crystal. Hence only the factors capable of altering the thermodynamic status of chains in the solution are influential to the nucleation barriers and consequently the growth habit. For crystallization of polymer chains from the solution state, changes in temperature, concentration and solvent quality are known to alter the growth habit.[1−4] In the case of long *n*-alkanes,[3,5] self-poisoning may become significant with decreasing chain length, resulting in different temperature-dependence of growth habit as compared to that of polyethylene (PE).

Similar to PE, poly(L-lactide) (PLLA) also crystallizes into an orthorhombic (α) phase with the growth habit of either fully developed {110} lozenge or the truncated shapes.[6−8] However, although with a lower fold surface energy ($\sigma_e \approx 75$ mJ m^{-2}) as compared to PE ($\sigma_e \approx 90$ mJ m^{-2}),[6] the nucleation of PLLA α crystals is rather sluggish in dilute xylene solutions at crystallization temperatures (T_c) above 90 °C, in dramatic contrast to the efficient development of PE crystals under similar conditions. Consequently, shear- induced nucleation after long-term (t_i = 10 h) incubation at 90 °C was adopted in a previous study of the growth habit of PLLA α crystals from dilute solutions of mixed xylene at 90 °C.[9] In the presence of shear-induced seeds, the crystallization of PLLA was observed to start with the formation of lenticular crystals, followed by morphological transformation to the favored truncated lozenge shape via lamellar reorganization from the central seed. However, the molecular origin for this incubation period to be crucial to the effectiveness of the subsequent shear-enhanced nucleation process remains unclear.[9]

Reported here are results of our recent exploration focusing on changes of coil structure in the solution state during the incubation period. It is observed that, while the solution remains clear and without discernible precipitations, there is a spontaneous, sigmoid change in the inherent viscosity (η_{inh}) of the 0.3 wt % PLLA/*p*-xylene solution during quiescent incubation at 90 °C, indicating a change in PLLA coil size in solution. After shear-induced nucleation (via short-term gentle solution stirring), clear differences in number of nuclei and crystal growth habit/rate can be observed with the change in the molecular status of PLLA coils in solution. These are interpreted in terms of increased effectiveness of flow-induced nucleation and decreased rate of surface nucleation or even stem spreading for collapsed PLLA coils. Relevance of the present observations of swollen and especially collapsed coils to the mesomorphic precursor picture of polymer crystallization proposed by different research groups[10−13] is addressed.

Experimental Section

Materials/Instruments. Both the PLLA sample (with nominal molecular mass of 40 to 60 kDa) and the solvent, *p*- and *o*-xylene, 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 (BFI) were obtained using a Gatan digital detector.

Isothermal Crystal Growth. Solutions of 0.3 wt % PLLA in *p*- or *o*-xylene were prepared by 1-h dissolution at 128 °C, followed by quenching the solution to an incubation temperature 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).

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Preordering of dissolved PLLA chains during the incubation period (t_i) up to 10 h was monitored via dilute solution viscometry. Gentle stirring by using a glass capillary tube was applied for 20 s to enhance nucleation after incubation at 90 °C for various t_i. The applied stirring was very slow and gentle; it took about one second for the capillary to go through one circle within the test tube. In this case, this applied shear rate is considered merely able to cause nucleation, and other effect should be much less significant. Subsequent crystal growth at $T_c = 90$ °C for different crystallization time (t_c) beyond the shear-induced nucleation was followed via TEM observations. Choosing 90 °C as the temperature in this study was because the gentle stirring had much minor or no effect on nucleation at higher temperatures. At lower temperatures, the solution crystallization can take place spontaneously, and the initiation of solution crystallization cannot be controlled by applied stirring.

This stirring was found to significantly increase 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 incubation.[11] 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 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 the filter paper placed underneath) for microscopic observations.

Dilute Solution Viscometry. To follow the viscosity change of dilute PLLA solutions during incubation at 90 °C, an Ubbelohde capillary viscometer (Cannon 0C−C739) was used. The 0.3 wt % PLLA solutions (0.283 g/dL at room temperature) in *p*- or *o*-xylene were prepared by 1-h dissolution at 128 °C and then transferred to preheated test tubes in a silicon oil bath (Firstek B801) kept at 90 (±0.5) °C for various periods of quiescent incubation. At the end of the incubation period, the solution was transferred to the capillary viscometer in the same silicon oil bath. Flux times for the meniscus to pass between two markers of the viscometer in the case of *p*- and *o*-xylene blanks were respectively 137.5 and 157.0 s; in the case of 0.3 wt % PLLA solutions, the flux times were longer (up to ca. 180 s). Deviations of measured flux times in repeated runs were all within ±1 s.

Results

Molecular States of PLLA/Xylene Solutions. In spite of the fairly deep supercooling ($\Delta T \equiv T_d° - T_c \approx 38$ °C, with dissolution temperature $T_d° \approx 128$ °C), dilute PLLA/*p*-xylene solutions crystallize only very reluctantly at 90 °C, requiring days of incubation. On the other hand, the solution viscosity decreases spontaneously during incubation at 90 °C as shown in Figure 1. The sigmoid change in inherent viscosity (η_{inh}) from 0.52 dL/g (with relative viscosity $\eta_{rel} \approx 1.\ 13$) to 0.14 dL/g (with $\eta_{rel} \approx 1.03$) in the period of $t_i = 4-6$ h signifies a dramatic collapse of coil size. In the case of *o*-xylene, a better solvent for PLLA, η_{INH} ($\approx$0.66 dL/g, with $\eta_{rel} \approx 1.17$) is t_i-insensitive. Different thermodynamic states of PLLA chains in solution may thus be reached by the choice of solvent (*p*- vs *o*-xylene) or t_i, allowing for the exploration of their subsequent effects on crystal growth that can be controllably initiated via shear-induced nucleation. A more direct measure on the change of coil size in the solution at 90 °C might be made via dynamic light scattering (DLS). However, the high-temperature measurements require[14] a tailor-designed DLS instrument equipped with a high-boiling index-matching solvent, which is not yet available within our accessibility.

Crystallization of Collapsed PLLA Coils in *p*-Xylene. Given in Figure 2 are BFI of crystals formed from collapsed PLLA chains in *p*-xylene ($t_i = 10$ h) at various crystallization times ($t_c = 20$ min to 14 h) after shear-induced nucleation. The morphological evolution starts with the emergence of lenticular crystals (Figure 2a) that are fully covered with overgrowth and have developed an acute apex angle of ca. 45°. On the basis of this acute angle, the {230} instead of {110} faces are more reasonable to be considered as the growth fronts in this beginning stage of crystal growth. The lenticular crystals subsequently transform to truncated lozenges around $t_c = 90$ min (Figure 2b−d). The newly transformed truncated lozenges (Figure 2c) still exhibit rounded obtuse apexes, but with the overgrowth concentrated only around the domain periphery. In view of the decreased overgrowth, a large fraction of PLLA chains originally dissolved in the solution must have crystallized at this prolonged $t_c = 90$ min. With further increases in t_c, both the domain size and the width ratio (L_{100}/L_{110}) between {100} and {110} facets continue to increase. At $t_c = 14$ h (Figure 2d), stabilized morphology of truncated lozenge with sharp obtuse apexes and sawteeth-like {100} edges is developed. The final L_{100}/L_{110} ratio generally lies in the range of 0.9 to 1.2, indicating comparable growth rates along ⟨100⟩ and ⟨110⟩ directions.

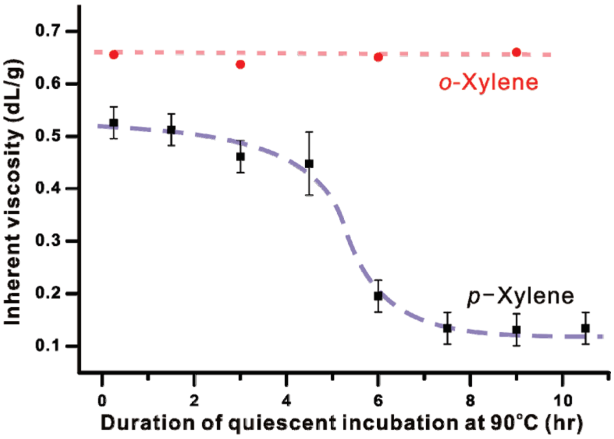

Figure 1. Changes in η_{inh} of 0.3 wt % PLLA solutions during incubation at 90 °C. The higher and t_i-independent η_{inh} value (0.66 dL g^{-1}) of the *o*-xylene solution indicates highly swollen PLLA coils in *o*-xylene. The slightly lower initial η_{inh} value (ca. 0.52 dL g^{-1}) and the strong drop during $t_i = 4$ to 6 h indicate that *p*-xylene is a moderate solvent at 90 °C, but there is collapse of chain dimension due to kinetically delayed intrachain aggregation. Stabilized η_{inh} at ca. 1.4 mL g^{-1} without discernible crystallization for $t_i \geq 7$ h suggests quasi-equilibrated preordering.

The observed morphological evolution from lenticular to truncated lozenge crystals in the present case of 0.3 wt % PLLA/*p*-xylene solution is basically similar to that reported previously[9] in the case of 0.1 wt % PLLA solution in mixed xylene (rich in *m*-xylene). It has been shown therein that this shape change is a result of lamellar reorganization propagated from the shear-induced central seed (see also the thickened interior of the truncated lozenge crystal in Figure 2d), whereas subsequent growth in size and further development of the {100} facets of the truncated lozenge crystals are rationalized to be surface nucleation-controlled.

Crystallization of Swollen PLLA Coils in *p*-Xylene. Shown in Figure 3 are morphological features of crystals formed from swollen PLLA chains ($t_i = 15$ min) up to $t_c = 14$ h. Lenticular crystals larger in size and wider in the acute apex angle ($\theta \approx 60°$) are already present at $t_c = 30$ min (Figure 3a). Fairly well-defined {110} facets (Figure 3b,c) are developed earlier than the case of lenticular crystals (cf. Figure 2a,b) formed from collapsed coils whereas overgrowth is much less extensive and concentrated mainly around domain boundaries.

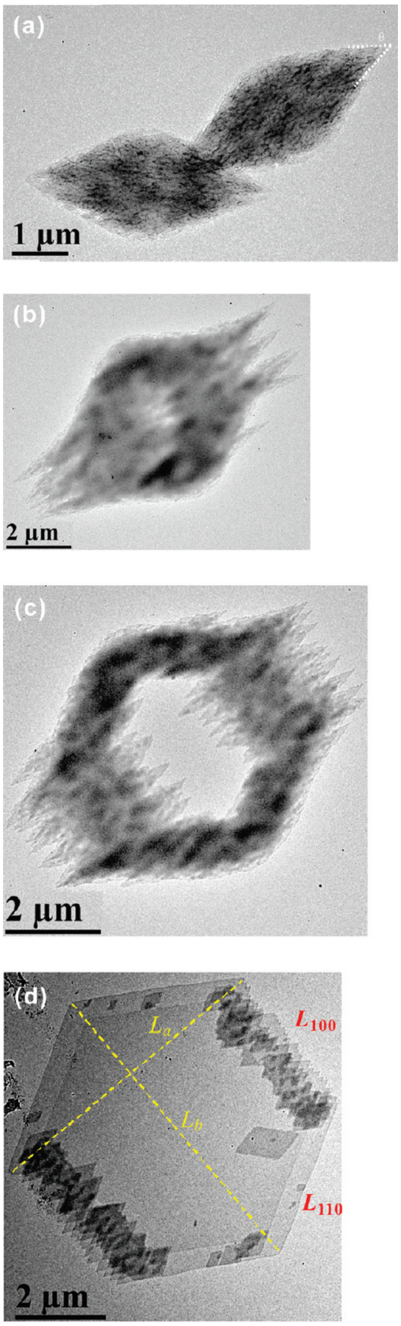

Figure 2. Representative bright field images of PLLA crystals grown (with t_i = 10 h) from 0.3 wt % PLLA/*p*-xylene solutions at (a) t_c = 20 min, (b) 45 min, (c) 90 min, and (d) 14 h, demonstrating morphological evolution from lenticular to truncated lozenge shapes. Note that lenticular crystals in part a bear acute apex angle $\theta \approx 45°$ and are fully covered with overgrown crystals precipitated during specimen preparation. The truncated lozenge crystal in part d is characterized by its thickened interior, the thinner outer rim, and a sawtooth-like {100} edge (composed of {110} fine facets). Truncated lozenge dimensions along *a*- and *b*-axes are denoted as L_a and L_b, respectively.

All these observations indicate higher growth rates in general and particularly in the ⟨100⟩ direction as compared to the case of crystals formed from collapsed coils in Figure 2. Demonstrated in Figure 3d is a fully grown (at t_c = 14 h) truncated lozenge crystal of sharp obtuse apexes and sawteeth-like {100} facets, with clear features of spiral growth from screw dislocations. Both the large domain size and the decreased width ratio $L_{100}/L_{110} \approx 0.7$ are consistent with increased growth rates, which will be further discussed below.

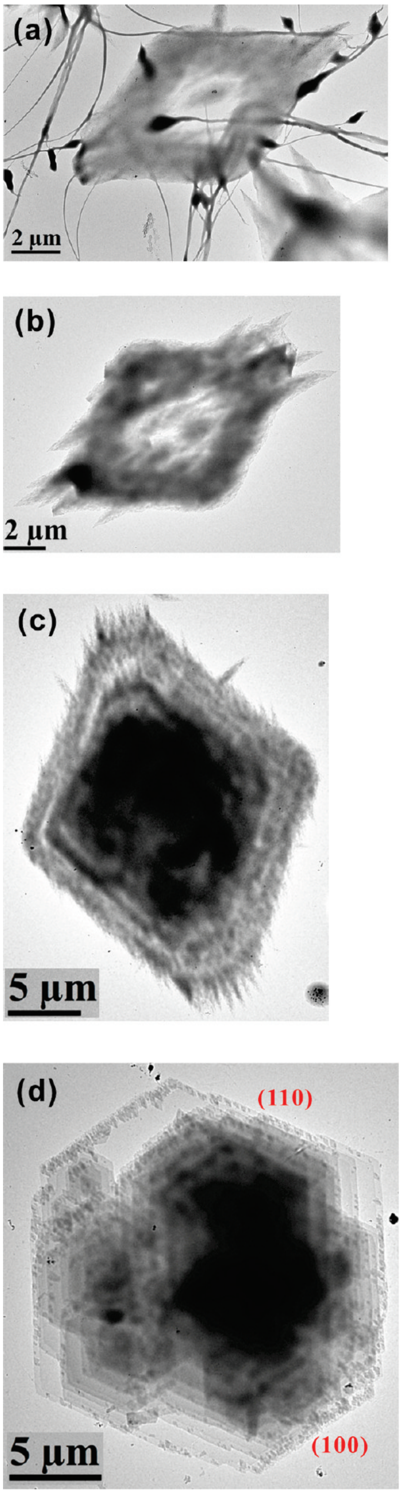

Figure 3. Representative bright field images of PLLA crystals grown (with t_i = 15 min) from 0.3 wt % PLLA/*p*-xylene solutions at (a) t_c = 30 min, (b) 45 min, (c) 3 h, and (d) 14 h. Compared to Figure 2, there are similar features of morphological transformation, but with delicate differences. The overgrowth in part a is limited to the domain periphery even at this early stage of crystallization. Furthermore, the {100} facets in parts c and d are relatively short, whereas the larger domain size causes the emergence of new features of spiral growth in part d.

Compared in Table 1 are crystal growth habits of swollen vs collapsed coils in *p*-xylene from extensive observations of crystal morphology at various combinations of t_i and t_c. First, the lenticular crystals possess different angles of acute apexes, reflecting altered growth habit of lenticular crystals

Table 1. Summary of Crystal Growth Habits in Dilute PLLA/*p*-Xylene Solutions at 90 °C upon Shear-Induced Nucleation at either Swollen or Collapsed State

	swollen state ($t_i \leq 3$ h)	preordered state ($t_i \geq 7$ h)
acute apex angle of lenticular crystals	ca. 60°	ca. 45°
overgrowth on collected lenticular crystals	along domain periphery	throughout domain
truncated lozenge dimensions at t_c = 14 h	L_a = 26.2 μm	L_a = 6.5 μm
	L_b = 28.6 μm	L_b = 7.5 μm
truncated lozenge facet ratio L_{100}/L_{110}	0.69−0.72	0.9−1.2
number of nuclei induced by stirring	small	large
growth rate	high	low

due to the collapse of molecular coils. For the later transformed truncated lozenge, the L_{100}/L_{110} ratio is known to increase with increasing T_c (or decreasing ΔT) in the solution crystallization of PE and PLLA.[3,9] Thus, this ratio can serve as an index of an increased nucleation difficulty, or lower driving force of crystallization. This L_{100}/L_{110} ratio clearly increases as the crystallization of collapsed coil dominates the growth of truncated lozenge. With lowered growth rate and increased overgrowth, the collapsed PLLA coils must bear lowered driving force toward crystallization as compared to swollen chains. This implies partial ordering within the collapsed coils. On the other hand, in view of the large number of lenticular crystals initiated, the shear-induced nucleation process appears more effective with collapsed chains.

Crystallization of Swollen PLLA Coils in *o*-Xylene. The use of a better solvent, *o*-xylene, results in significantly decreased driving force (i.e., supersaturation) toward crystallization as well as further expanded (and t_i-independent) PLLA coil size (Figure 1). In shear-initiated crystallization from the 0.3 wt % PLLA/*o*-xylene solution after extended incubation (t_i = 10 h), crystal growth is slow and morphological transformation from lenticular to truncated lozenge is much delayed. Shown in Figure 4a is a representative truncated lozenge crystal, which is small in size in view of the prolonged t_c of 24 h; the comparatively wide {100} facets ($L_{100}/L_{110} \approx 1.4$) suggests particularly suppressed growth rate along the *a*-axis.

Given in Figure 4b for comparison purposes is a truncated lozenge crystal obtained at t_c = 24 h with a short incubation period of t_i = 15 min. Note that the shear-induced nucleation is much less effective in this case, hence the more extensive overgrowth. The crystal size is larger than that in the long incubation case (Figure 4b), bringing in features of spiral growth. The apparently higher growth rate may also be attributed to the higher concentration of PLLA chains in solution due to lower population of shear-induced nuclei. In support to this attribution is the observation that the width ratio L_{100}/L_{110} (≈ 1.4) also remains the same. Summarized in Table 2 are observed effects of t_i on the crystallization behavior of 0.3 wt % PLLA/*o*-xylene solutions. Molecular origin of increased effectiveness in shear-induced nucleation upon extended incubation (which results in no apparent changes in η_{inh}) is not fully understood but will nevertheless be addressed in a later paragraph along with similar effects of extended incubation in *p*-xylene (with concomitantly suppressed η_{inh}).

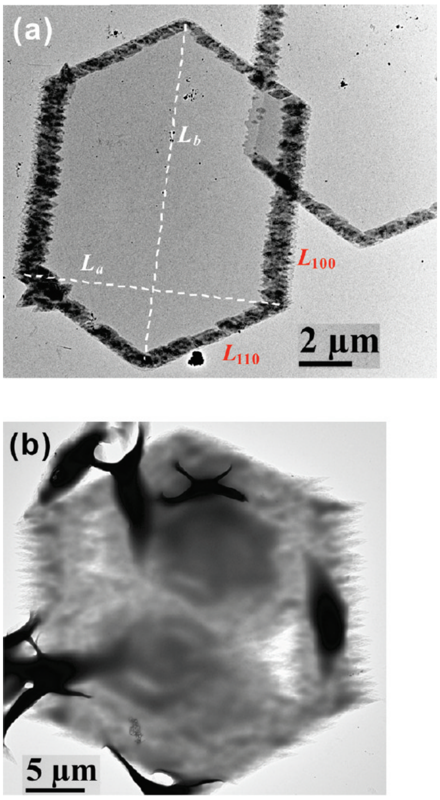

Figure 4. Representative BFI of PLLA crystals grown from 0.3 wt % PLLA/*o*-xylene solutions at t_c = 24 h with (a) t_i = 10 h and (b) 15 min. Both crystals exhibit similar width ratio L_{100}/L_{110} (~1.4). Truncated lozenge crystals in part a exhibit relatively minor overgrowth on the domain edges. In comparison, truncated lozenge crystals in part b grow faster, whereas overgrowth is much more extensive as a consequence of fewer nucleuses induced by stirring.

Table 2. Summary of Crystal Growth Habits in Dilute *o*-Xylene Solutions at 90 °C

	t_i = 15 min	t_i = 10 h
truncated lozenge dimensions at t_c = 24 h	L_a = 21.8 μm	L_a = 9.8 μm
	L_b = 31.3 μm	L_b = 14.5 μm
truncated lozenge facet ratio L_{100}/L_{110}	1.4	1.4
number of nuclei induced by stirring	small	large
growth rate	high	low

Discussion

Growth Habits of Swollen Coils in *o*- vs *p*-Xylene. For PLLA crystal grown from dilute *o*-xylene solutions, the growth rate is generally low, which can understandably be attributed to the low surface nucleation rate due to lowered driving force of crystallization of PLLA chains in a more favorable solvent. The low surface nucleation rate also results in a high width ratio ($L_{100}/L_{110} \approx 1.4$), which further assures the relationship between this width ratio and crystallization tendency. This width ratio L_{100}/L_{110} is independent of incubation period, as the degree of molecular swollenness remains unchanged in *o*-xylene solution. In contrast, for dilute *p*-xylene solutions, PLLA crystallization from swollen coils appears faster in growth rates with lower width ratio ($L_{100}/L_{110} \approx 0.7$) as compared to that from collapsed coils. In the following paragraphs, possible explanations are provided on the basis of our morphological observations.

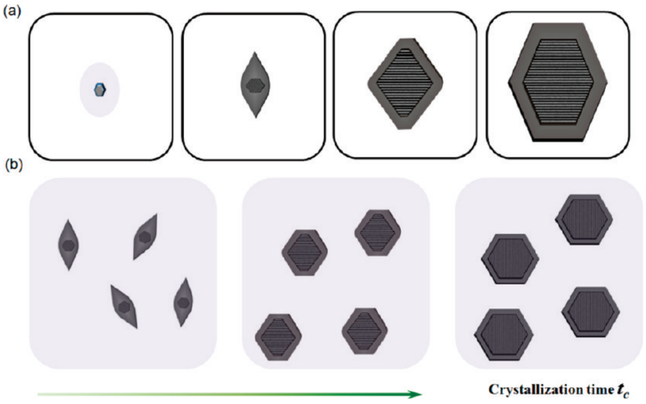

Figure 5. Schematic illustration of different morphological features in crystallization from dilute PLLA/*p*-xylene solutions of (a) swollen coils and (b) collapsed coils. Gray shades stand for solution matrix with partially ordered nanodomains. Two crystallization routes have been observed.

Origin of Chain Collapse in *p*-Xylene at 90 °C. The induction period ($t_i \approx 4$ h) required for the start of the sigmoid decrease of η_{inh} at 90 °C implies that the collapse of PLLA chains in *p*-xylene involves a certain nucleation-like process. Hence it is likely related to the aggregation of PLLA segments into locally ordered nanodomains resembling embryos of crystalline nuclei as an alternative way for the system to reach a more stable state; it could be a fringed micelle-like packing of chain segments that spatially brought together by Brownian motion. This preordering behavior is envisaged to entrap molecular segments in a thermodynamically metastable state (i.e., a local free energy minimum) and to result in a higher energy barrier for following crystal growth. In addition, the locally ordered nanodomains may serve as intrachain physical cross-links (which prevents the nearby segments along the chain from drifting apart), thereby significantly increase the chance of forming further aggregates of molecular segments. This results in an autoacceleration effect consistent with the sigmoid decrease in η_{inh} of PLLA/*p*-xylene solutions during the incubation period. Accordingly, the applied shear flow is able to orient these nanodomains and cause the efficient nucleation observed. On the other hand, these nanodomains also act as physical cross-links to restrict the stem deposition of molecular coils at the growth front during crystal growth, resulting in suppressed surface nucleation. Moreover, the growth of lenticular crystals induced by solution stirring, instead of the subsequently evolved form of truncated lozenges, also reflects a hampered growth process. The curved obtuse apexes indicate asymmetry propagation process on the growth front, which reveals the difficulty of stem deposition.[15]

Growth Habits of Swollen vs Collapsed Coils in *p*-Xylene. To rationalize the observed crystallization routes in PLLA/*p*-xylene solutions, we propose two qualitative models schematically shown in Figure 5. For $t_i \leq 3$ h (Figure 5a), the shear-induced nucleation procedure is assumed to result in a limited number of nuclei with surrounding chains in the preordered state. At this stage, a large fraction of PLLA chains in the solution still remain in swollen state. The crystallization starts from these preordered chains in collapsed form around the nuclei, yielding lenticular crystals of narrower (ca. 45°) acute apexes and imperfect stem packing, hence the supposedly forbidden (010) reflection.[9] After complete consumption of the surrounding preordered chains, further growth proceeds via surface nucleation of swollen coils, developing into {110} facets of wider (ca. 60°) acute apexes.

At longer incubation time ($t_i \geq 7$ h), the development of preordered chains prevails in the solution, which appears helpful for the stirring action to induce a large number of nuclei. In the further growing process, the attachment of chains in the preordered state dominates the growth of lenticular crystals and hence results in decreased growth rate and acute apex angle. As the lamellar reorganization leads to morphological transformation, the subsequent crystal growth of truncated lozenge proceeds via surface nucleation of stems from preordered chains that are partially stabilized in the local nanodomain. Accordingly, the growth rates at different growth fronts are decreased, resulting in modified growth habit of increased width ratio $L_{100}/L_{110} \approx 1.05 \pm 0.15$.

Relevance to the Precursor Concept. Detailed structure of the preordered chains remains to be explored. It is very tempting to relate the collapsed coils to the bundle picture theoretically proposed by Allegra et al.[10] and supported by molecular dynamics simulation results of Muthukumar et al.[11] or the mesophase precursor proposed by Strobl et al.[12] at the growth front based on experimental observations in melt crystallized polymers. There is also a somewhat similar picture of entanglement-limited nanograins which emerge, grow, and coalesce during cold crystallization as supported by scattering and microscopic evidence.[13] In all these models, the nanoscaled precursors are suggested to be the units of crystal development. This consideration, however, is inconsistent with crystallographic evidence that molecular stems "read" only the directly contacting substrate surface.[16] This apparent inconsistency is one of the basic issues in polymer physics remains to be resolved for better understanding of the ordering processes in polymers. As a resolution to this conflict, the present observations suggest the presence of nanodomains even in dilute solutions can still allow the occurrence of molecular addition and recognition process on growth surface, but in a hampered way, provided with decreased crystal growth rate that has been observed. This means that, with a swollen part of the chain attached to the growth front through the recognition process, the rest of the coil may follow albeit in a restricted manner due to the presence of nanodomains. This confirms that the kinetically favored growth path is indeed swollen coils without intrachain aggregation in dilute solutions. For collapsed chains comprising nanodomains, the molecular recognition most probably starts with the swollen part of the chain and may take longer time for the participation of the whole molecule. It thus implies the feasibility of readjustment of preordered molecular segments at the growth front to allow for continuous homoepitaxial attachment as a viable (albeit kinetically hindered) route.

Formation of nanodomains in the solution is conceived as a way to explain the delayed crystal growth, and enhanced sensitivity toward stirring-induced nucleation after the drop of solution viscosity. An attempt to obtain more direct experimental evidence for the presence of nanodomains in the solution state via small-angle X-ray scattering did not succeed due to overshadowing effects of the strong scattering from the solvent. Different strategies (such as small-angle neutron scattering) are to be adopted in the near future.

Concluding Remarks

This research explored the crystallization routes under various solution statuses of PLLA in the dilute *o*- and *p*-xylene solution. The crystal growth in the *o*-xylene solution has illustrated that, while the solution viscosity is unchanged, the shape of final truncated lozenge is independent of the incubation period. Furthermore, compared to the *p*-xylene solution, better solvent quality provided by *o*-xylene resulted in a higher width ratio L_{100}/L_{110}, accompanied by higher solution viscosity and V_H. Nevertheless in *p*-xylene solution, a spontaneous decrease in V_H is able to cause the increase of L_{100}/L_{110} width ratio. The decreased V_H has been linked to the collapse of molecular coil, and thus a preordering state in the solution. We conclude that the preordered chains in the collapsed form are responsible for (1) easier nucleation upon shear, (2) the formation of lenticular crystals with modified growth habit, and (3) significantly suppressed efficiency of surface nucleation in the final development of truncated lozenge crystals. These are all consistent with the notion that this preordered state is thermodynamically metastable, and cause the kinetic hindrance to surface nucleation-controlled crystal growth. In addition, the preordered chains are more liable to sheared-induced nucleation; molecular origin of this observation awaits further studies.

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(14) The typical design of DLS instruments (suitable for temperatures up to ca. 60 °C) adopts a quartz vessel with toluene as the solvent since its refractive index is close to quartz. The sample tube containing the sample solution is put in the center of the index solvent vessel. Thermostat water is circulated outside the vessel for temperature control. A higher temperature causes convective flow of the index-matching solvent and even air bubbles when the boiling point is approached. Both the convective flow and the air bubbles would scatter light, interfering with light scattered from the polymer. To avoid these interferences, a specially designed DLS instrument with a high-boiling index-matching solvent is needed.
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