

A Crystalline Micelle Intermediate Links Crystallization and Melting in Crystallization-driven Self-assembly

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Article

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A Crystalline Micelle Intermediate Links Crystallization and Melting in Crystallization-driven Self-assembly

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KEYWORDS: Block copolymer, multi-step crystallization, CDSA, Entropy-enthalpy competition, real-time SAXS/WAXS

Abstract:

Crystallization-driven self-assembly (CDSA) provides a powerful strategy for constructing well-defined polymer nanostructures, yet the relationship between crystallization and melting remains poorly understood. In particular, it is unknown whether melting simply retraces the crystallization pathway or proceeds through distinct structural intermediates. Here we combine real-time small- and wide-angle X-ray scattering, transmission electron microscopy, and differential scanning calorimetry to resolve both the crystallization and melting pathways of poly(styrene)-block-poly(L-lactide) (PS-*b*-PLLA) platelet crystals. During self-seeding crystallization, residual seed crystallites first direct the epitaxial growth of crystalline cylindrical micelles, which assemble into highly ordered arrays before laterally coalescing into platelet crystals. Upon heating, the platelet crystals do not melt directly. Instead, they undergo edge fragmentation into ordered arrays of crystalline cylindrical micelles, generating a transient re-entrant ordered state before complete dissolution. Thus, crystallization and melting are linked by a common crystalline micelle intermediate but follow distinct microscopic pathways. The emergence and disappearance of this intermediate are marked by characteristic SAXS correlation peaks, while WAXS and calorimetry indicate that the intermediate exists within the PLLA melting interval, before crystallinity is completely lost. A scaling analysis of the competing interfacial and corona-stretching free energies places the platelet-to-micelle crossover at an effective PLLA-solvent interfacial tension of order 10 mN m⁻¹, providing an energetic basis for the observed restructuring. These findings reveal a reversible yet pathway-dependent hierarchical assembly mechanism in CDSA, establish crystalline micelles as the key mesoscale building blocks governing both growth and disassembly, and provide a general framework for understanding reversible nonclassical crystallization and designing adaptive crystalline polymer nanomaterials.

Introduction

Crystallization is generally regarded as the reverse of melting.^{1,2} In classical thermodynamics, these transformations connect the same equilibrium states and are therefore often assumed to follow identical microscopic pathways in opposite directions. Increasing evidence from nonclassical crystallization, however, suggests that this assumption is not always valid.³⁻⁵ Crystal growth frequently proceeds through hierarchical assembly involving transient intermediate structures rather than direct addition of individual molecules, whereas dissolution may occur through distinct restructuring pathways that do not simply retrace crystal formation.⁶⁻⁹ Such pathway-dependent behavior has been observed in a variety of inorganic, molecular, and biomolecular systems, raising fundamental questions about the microscopic reversibility of crystallization and melting.^{6,9-11} Despite these advances, reversible pathway-dependent transformations remain poorly understood in soft crystalline materials, where interfacial interactions, polymer conformational entropy, and crystallization thermodynamics are strongly coupled.^{12,13}

Crystallization-driven self-assembly (CDSA) of block copolymers provides an ideal platform for addressing these questions because crystallization and self-assembly occur simultaneously across multiple length scales.^{13,14} In CDSA, a crystallizable block forms a semicrystalline core, while the soluble corona regulates interparticle interactions, colloidal stability, and growth kinetics. This coupling enables precise control over one-dimensional fibers, two-dimensional platelets, and more complex hierarchical nanostructures through seed-mediated epitaxial growth.¹⁵⁻³⁶ Recent advances have further demonstrated transient intermediate states, hierarchical organization, and pathway-dependent assembly, establishing CDSA as a model system for studying nonclassical crystallization in polymeric materials.^{22,37-40} For example, Teng et al. demonstrated that formation of two-dimensional platelet micelles may proceed through hierarchical self-assembly involving transient intermediate structures and particle-attachment mechanisms rather than direct crystallization.⁴⁰

Although crystallization pathways in CDSA have been extensively investigated, remarkably little is known about the corresponding melting pathways.¹³ Most studies terminate after the desired crystalline morphology has been obtained, implicitly assuming that heating simply reverses the assembly process. However, this assumption has rarely been tested experimentally because directly following melting requires simultaneous structural characterization over molecular, mesoscopic, and particle length scales while preserving the solution-state morphology. As a result, it remains unknown whether crystalline micelles dissolve directly from platelet crystals, whether transient intermediates emerge during melting, or whether assembly and disassembly explore different regions of the free-energy landscape. Resolving these questions is essential for understanding reversible CDSA and for designing adaptive crystalline polymer nanostructures capable of controlled structural transformations.

Here, we combine real-time small- and wide-angle X-ray scattering, transmission electron microscopy, and differential scanning calorimetry to resolve both the crystallization and melting pathways of poly(styrene)-block-poly(L-lactide) (PS-*b*-PLLA) (Figure 1a) under self-seeding conditions.^{27,41-46} We show that crystallization proceeds through epitaxial growth of crystalline cylindrical micelles, which assemble into ordered arrays before laterally coalescing into platelet crystals (Figure 1b). Surprisingly, heating does not simply reverse platelet formation. Instead, platelet crystals fragment into the same crystalline micelle intermediate

prior to complete melting, producing a transient re-entrant ordered state. These results demonstrate that crystallization and melting are linked by a shared crystalline micelle intermediate while following distinct microscopic pathways, providing a mechanistic framework for reversible hierarchical assembly in CDSA and offering new insights into pathway-dependent nonclassical crystallization.

Results

Real-time SAXS reveals hierarchical crystallization through an ordered micelle intermediate

To elucidate the mechanism of structure formation during crystallization-driven self-assembly, the time evolution of PS-*b*-PLLA in *p*-xylene was monitored using real-time SAXS measurements following a typical “self-seeding” protocol (Figure 1c): After removing thermal history at 130°C, sample solution was quickly cooled to 20 °C, crystallize for 5 min; then, after a brief self-seeding treatment at 104 °C (5 min), sample was cooled to temperatures between 94 °C and 75 °C and crystallize for 60 min before cooled to 20 °C. Figure 1d shows the SAXS evolution during crystallization at $T_c = 94^\circ\text{C}$. Following a short induction period, a series of sharp, evenly spaced correlation peaks appears at $q \approx 0.10, 0.20, 0.30$, and 0.40 nm^{-1} , characteristic of a one-dimensional periodic structure. The intensities of these peaks continuously increase with time, and at later stages ($\sim 60 \text{ min}$), the corresponding 2D SAXS patterns (Figure 1e) exhibit diffraction spots superimposed on isotropic scattering rings, indicating the development of orientational ordering. As crystallization proceeds at higher temperatures (Figure 1d and Figure S1), the correlation peaks increase continuously in intensity while shifting slightly toward lower q , indicating progressive growth and lateral ordering of the micellar arrays. The characteristic spacing ($d = 2\pi/q_1 \approx 60\text{--}70 \text{ nm}$) remains nearly constant throughout this temperature range and is comparable to the length scale expected for interactions between neighboring PS coronas in *p*-xylene. This observation suggests that corona-mediated interactions contribute significantly to the organization of the intermediate structure. Interestingly, despite the strong correlation peaks, the high- q scattering follows an approximately q^{-2} dependence and lacks the oscillatory features characteristic of platelet form factors as indicated by the red arrow in Figure 1g. Increasing the self-seeding time from 5 to 10 min substantially reduces the crystallization rate, consistent with a lower density of surviving seed crystallites. Nevertheless, the same correlation peaks are observed without the appearance of platelet form-factor oscillations within the experimental time scale $\sim 60 \text{ min}$ (Fig. S2).

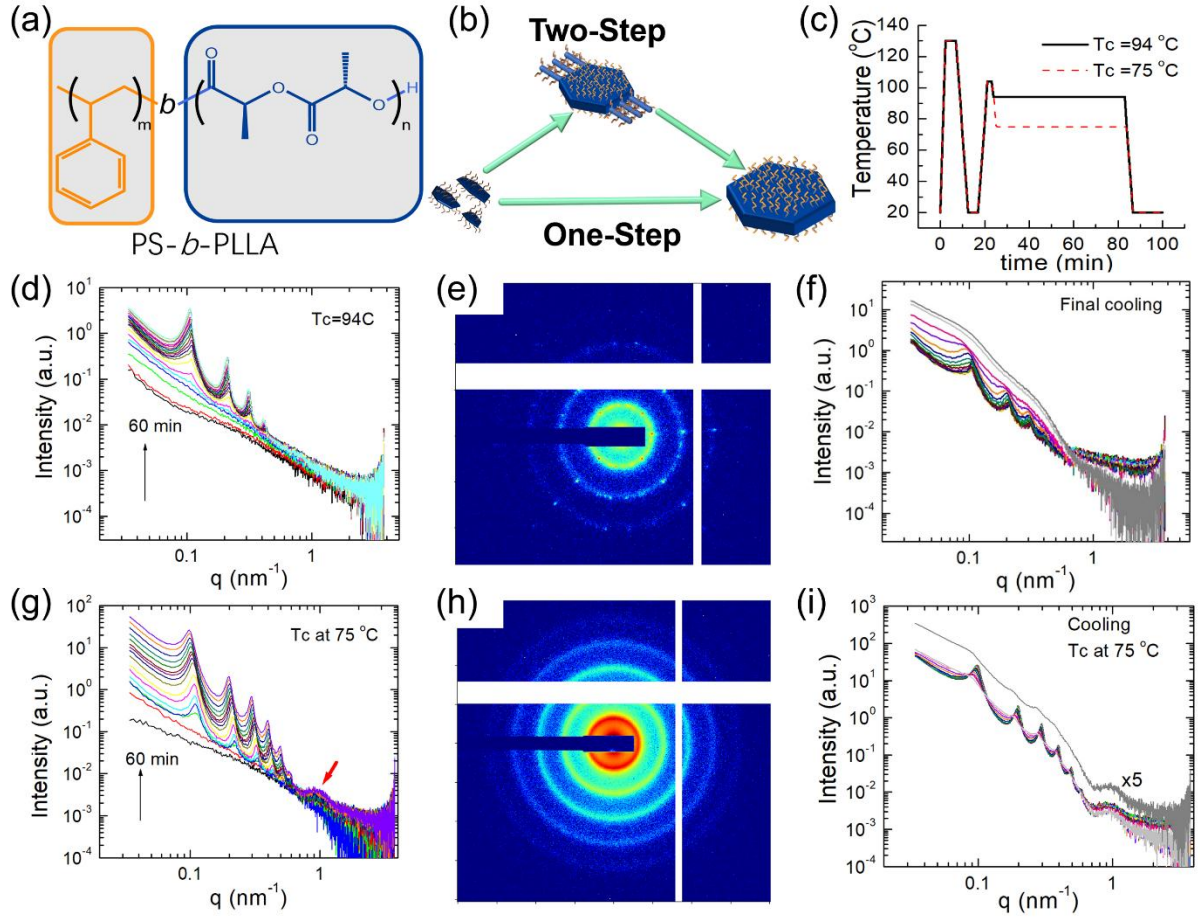


Figure 1. Hierarchical crystallization through a crystalline micelle intermediate: (a) molecular structure of PS-*b*-PLLA; (b) Two-step versus one-step growth via a metastable state; (c) thermal history of self-seeding process; (d-f) real-time SAXS profiles of crystallization, representative 2D SAXS pattern, and final cooling for T_c at 94°C , and (g-i) for T_c at 75°C . The last curve in (i) was shifted upward by a factor of 5 for clarity.

Upon lowering the crystallization temperature from 94 to 75°C , the SAXS evolution changes qualitatively (Figure 1g and Figure S1). The structural evolution becomes clearer at lower crystallization temperatures. Figure 1g shows the corresponding real-time SAXS evolution at $T_c = 75^\circ\text{C}$, where crystallization proceeds more rapidly because of the larger thermodynamic driving force. Similar to the behavior at 94°C , sharp correlation peaks emerge shortly after the temperature quench, with up to five orders of reflections visible during the early stage. In contrast to the more anisotropic patterns observed at 94°C , the 2D SAXS patterns at 75°C remain largely isotropic (Figure 1h), suggesting that although local positional correlations are present, the ordered domains are randomly oriented on the macroscopic scale. However, unlike the higher-temperature case, additional oscillatory features gradually develop in the high- q region at longer times (~ 30 min), including a pronounced minimum near $q \approx 0.7 \text{ nm}^{-1}$, characteristic of platelet form-factor scattering. These results indicate that the SAXS correlations do not arise from stacked platelet crystals but instead originate from a different ordered intermediate structure. The observed scattering behavior is consistent with aligned arrays of anisotropic cylindrical objects with finite cross-sections. As demonstrated by the TEM observations presented below and schematically illustrated in Figure 1b, these scattering

features are consistent with arrays of crystalline cylindrical micelles that grow epitaxially from the edges of residual platelet seed crystallites.

To further examine the existence of multiple growth stages, Figure S3 summarizes the time evolution of the first SAXS correlation peak intensity during crystallization at different temperatures. At lower crystallization temperatures ($T_c = 75 - 80^\circ\text{C}$), the correlation peak intensity increases rapidly after a short induction period, followed by a change in growth rate at intermediate times. At later times (≥ 30 min), a further increase in growth rate becomes apparent, resulting in a three-stage kinetic behavior. As T_c increases, both the induction period and the overall timescale of structural evolution increase substantially, consistent with a reduced crystallization driving force and slower development of mesoscale order. Near $T_c \approx 92 - 94^\circ\text{C}$, the delayed onset and weaker growth of the correlation peak suggest that the intermediate ordered state persists over extended times before the appearance of platelet features. Overall, the presence of multiple kinetic regimes and their strong temperature dependence support a hierarchical assembly pathway involving sequential structural transformations rather than direct formation of platelet crystals from solutions.

The ordered micelle arrays are metastable intermediates. Consistent with our previous observations,⁴³ the aligned micelle array correlation peaks formed during crystallization diminish markedly upon cooling to room temperature for all crystallization temperatures investigated, including samples crystallized at $T_c = 75^\circ\text{C}$ (Figure 1f, 1i and Figure S1). In contrast, the overall SAXS intensity increases during cooling, indicating continued crystal growth. The simultaneous increase in scattering intensity and disappearance of the sharp higher-order reflections demonstrates that the periodic structure responsible for the correlation peaks is not retained in the final crystalline morphology. Instead, the ordered state associated with these reflections exists only within a limited temperature window during crystallization. Upon further cooling, continued crystal growth and structural reorganization progressively disrupt the positional order of the micellar arrays, causing the characteristic SAXS correlation peaks to weaken while the overall platelet morphology is preserved. The persistence of platelet form-factor features together with the loss of the correlation peaks therefore identifies the aligned micelle arrays as a transient, metastable intermediate in the hierarchical crystallization pathway.

TEM Observations Reveal Epitaxial Growth and Coalescence of Crystalline Micelles into Platelets

To directly visualize the structures formed during crystallization-driven self-assembly, PS-*b*-PLLA solutions with polymer concentrations ranging from 0.3 to 10 mg mL⁻¹ were crystallized at 94 °C following self-seeding at 104 °C for 30 min and subsequently annealed for extended times (>12 h) before quenching to room temperature. The resulting TEM images (Figure 2 and SI) provide direct real-space evidence for the hierarchical structural evolution inferred from SAXS and reveal a strong concentration dependence of the final morphology.

At the lowest concentration (0.3 mg mL⁻¹), the samples consist predominantly of isolated, well-faceted hexagonal platelets with lateral dimensions of approximately 500–600 nm (Figure 2a). The sharp edges and uniform contrast indicate highly developed single-crystal platelets. Their dimensions closely match those reported previously for PS-*b*-PLLA platelet crystals prepared under comparable self-seeding conditions,^{43,44} confirming the reproducibility of the crystallization process. Increasing the concentration to 1 mg mL⁻¹ preserves the platelet

morphology but introduces short rod-like protrusions along the platelet perimeter (Figure 2b). These rod-like structures appear preferentially along two opposite platelet faces. The individual rod-like structures are approximately 10–15 nm wide, comparable to the platelet thickness, whereas their organization in solution exhibits a substantially larger characteristic spacing of ~60–70 nm as shown in SAXS. This distinction supports an ordered array of narrow crystalline micelles separated by solvated PS coronas. Their coexistence with well-developed platelets suggests that crystalline growth remains active at the platelet edges even after extended annealing.

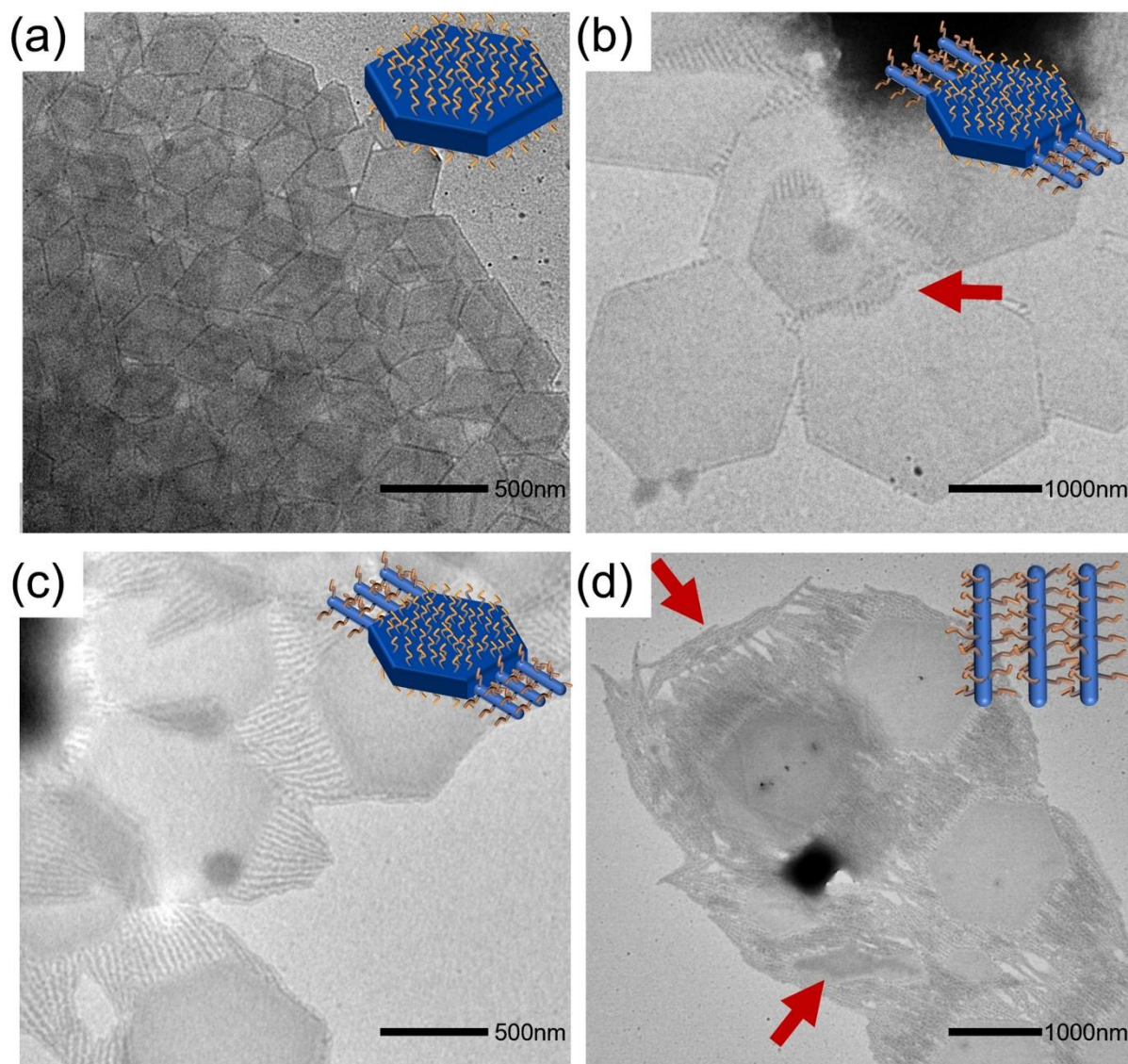


Figure 2. TEM visualization of epitaxial micelle growth and platelet coalescence. TEM images of crystals after crystallization at 94 °C for 12h. The initial polymer concentrations are (a) 0.3 mg mL⁻¹, (b) 1.0 mg mL⁻¹, (c) 5.0 mg mL⁻¹ and (d) 10 mg mL⁻¹. Scale bar is 500 nm in (a, c) and 1 μ m in (b,d).

More complex hybrid structures emerge at 5 mg mL⁻¹ (Figure 2c). In this concentration regime, platelets are surrounded by dense arrays of elongated cylindrical micelles that extend primarily from two opposite faces of the platelet. Many of these micelles remain aligned over several hundred nanometers and exhibit a high degree of positional correlation as illustrated in Figure

2b, 2c. The images suggest a structural continuity between the platelet and the surrounding micellar domains, consistent with epitaxial growth of cylindrical crystalline micelles from the platelet edges. Inam et al. studied the CDSA behavior of several PLLA-based systems and similar epitaxial relationship was observed in PDMA-*b*-PLLA platelets.²⁷ However, the preferred orientation is different, where cylindrical structures preferentially align along the (110) growth faces. In the present PS-*b*-PLLA system, the cylindrical micelles develop through epitaxial growth of PLLA from pre-existing crystalline platelet/seed surfaces, with preferential growth associated with the (200) faces. In the platelet-forming PDMA-*b*-PLLA system, the highly soluble block copolymer was proposed to remain predominantly as unimers above the PLLA crystallization temperature and to crystallize directly into 2D platelets upon cooling. This pathway differs from that observed here, where cylindrical crystalline micelles emerge through preferred epitaxial growth from pre-existing PLLA crystalline surfaces before developing into the platelet morphology. The different crystallographic relationships therefore likely reflect distinct assembly pathways rather than simply differences in corona chemistry.

At the highest concentration investigated (10 mg mL⁻¹), extended micellar sheets and interconnected networks become the dominant morphology (Figure 2d). These structures consist of densely packed cylindrical micelles exhibiting substantial local alignment and partial lateral fusion (top arrow). Small platelet-like domains are observed within the micellar matrix (bottom arrow), indicating that platelet formation can occur within these highly correlated assemblies. The concentration-dependent morphology can be rationalized by kinetic competition between the generation of crystalline micelles and their incorporation into growing platelets. Because the micelles grow epitaxially from platelet edges by addition of polymer from the surrounding solution, their growth rate is expected to increase with bulk polymer concentration. In contrast, conversion of the attached micelles into the platelet morphology requires local lateral association and structural reorganization and may therefore be less sensitive to concentration. At low concentration, micellar growth is slower than their incorporation into the platelet, so the intermediate is largely consumed during prolonged annealing. At higher concentration, the enhanced supply of polymer accelerates micellar growth sufficiently for the intermediate structures to accumulate, producing increasingly extensive micellar arrays and networks. Consequently, the probability of observing partially transformed structures increases substantially at higher concentrations, allowing the intermediate stages of crystallization to be captured directly by TEM.

The periodic spacing measured from the aligned micellar arrays (Figure 2c, 2d and Fig.S4) is approximately 42–44 nm, significantly smaller than the characteristic spacing of ~60–70 nm obtained from *in situ* SAXS measurements in Figure 1. This discrepancy is attributed to collapse of the solvent-swollen PS coronas during sample drying. In solution, the *p*-xylene-swollen PS chains maintain a larger separation between neighboring micelles, whereas drying reduces the corona volume and decreases the apparent spacing observed by TEM.

The TEM observations provide a structural basis for interpreting the SAXS correlation peaks observed during crystallization. The highly aligned micellar domains surrounding platelet crystals possess a characteristic periodicity and orientational order capable of producing the strong higher-order reflections and anisotropic SAXS patterns observed at intermediate crystallization stages. Combined with the SAXS results, these observations support a hierarchical crystallization pathway (Figure 1b) in which residual seed crystallites first promote epitaxial growth of crystalline cylindrical micelles. These micelles subsequently organize into

ordered arrays and gradually coalesce through lateral crystal growth to form the final platelet morphology. The aligned micellar structures therefore represent long-lived intermediate states that bridge the transition between seed crystallites and mature platelet crystals.

Melting proceeds through re-formation of the crystalline micelle intermediate

To investigate the reverse structural pathway, pre-formed PS-*b*-PLLA platelet crystals were heated in *p*-xylene while monitoring the structural evolution by DSC, real-time SAXS, WAXS, and TEM. Question here is whether melting proceeds through direct dissolution of the platelet crystals or *via* the same intermediate in Figure 1b in a reverse order. Figure 3a shows the well-defined hexagonal platelet crystals used in this study, with an average lateral size of approximately 600 nm and a thickness of about 10 nm. Selected-area electron diffraction confirms the single-crystalline nature of the PLLA cores and the α -form of PLLA.^{47,48} The platelet suspension (Figure 3b) forms a nematic phase at room temperature because of the high aspect ratio of the platelets, consistent with previous reports.^{43,44,46}

The thermal stability of the platelet crystals was first characterized by differential scanning calorimetry (DSC) and WAXS. As shown in Figure 3c, the DSC heating trace exhibits a single broad endothermic peak centered at 106.0 °C, with onset and completion temperatures of 98.5 and 119.3 °C, respectively, indicating that melting occurs over an extended temperature interval. Consistent with the DSC results, the real-time WAXS measurements (Figure 3d) show that the characteristic PLLA Bragg reflections persist throughout most of the heating process and disappear completely only above approximately 115 °C, indicating that PLLA crystallinity persists until the final stage of melting. Together, the DSC and WAXS results establish the thermal window over which the structural evolution of the platelet crystals occurs and provide the framework for interpreting the real-time SAXS measurements presented below.

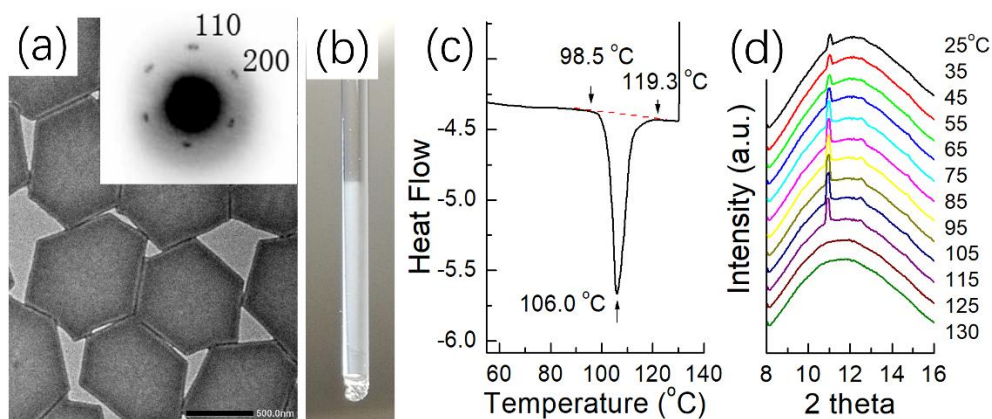


Figure 3. Thermal characterization of platelet crystals prior to melting: (a) TEM images and selected area diffraction pattern of platelet crystals; Scale bar is 1 μ m. (b) The I-N transition of 10 mg mL⁻¹ crystal suspension in a quartz capillary and (c) DSC heating scan of platelet crystals in solution. (c) DSC heating curve for platelets in *p*-xylene shows the peak melting point at 106.0 °C, the onset starting and ending temperatures are 98.5 and 119.3 °C, respectively. Heating rate 10 K min⁻¹. (d) Real-time WAXS during heating indicate the melting of crystals above 115 °C.

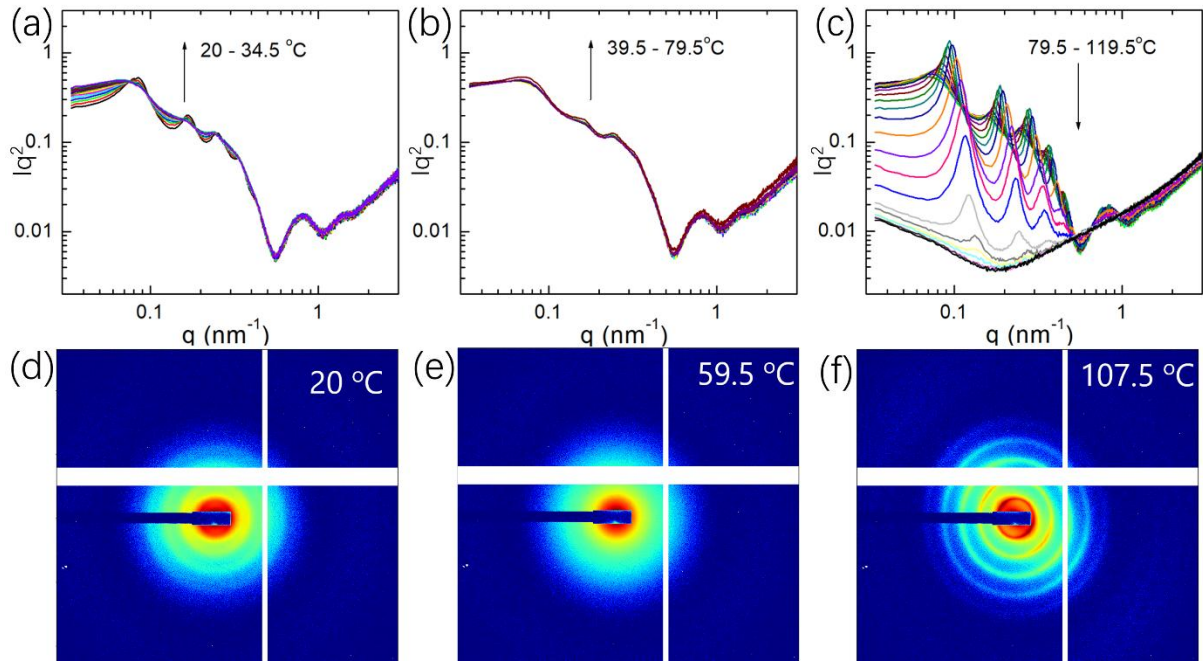


Figure 4. Re-formation of the crystalline micelle intermediate during melting: (a-c) Kratky plot of real-time SAXS profiles at different temperatures during heating reveal the different stages. (d-f) Representative 2D SAXS patterns at 20 °C for the N phase order; 59.5 °C disappearance of N phase order, and 107.5 °C the renewed anisotropic ordering before melting.

SAXS measurements of the suspension directly in the nematic (N) phase reveal a pronounced face-to-face correlation peak (Figure 4a,4d). The spacing determined from the primary peak position is $d = 2\pi/q_1 = 2\pi/0.0845\text{nm}^{-1} \approx 74.4$ nm. The 2D pattern (Figure 4d) shows slight anisotropic scattering pattern with a ring corresponding to the primary peak in Figure 4a. In our previous work, we reported an apparent enhancement of ordering during heating.⁴³ However, more detailed measurements in the present study (Figure 4a,4b) reveal a more complex evolution. Upon slight heating, the initial nematic ordering first decreases rather than increases. The corresponding Kratky plots over the temperature range of 20–35 °C clearly show a gradual reduction in the intensity of the correlation peaks with increasing temperature, whereas the oscillatory feature at higher $q \sim 0.7$ nm⁻¹ remains essentially unchanged. Since the high- q oscillation reflects the platelet form factor, its persistence indicates that the platelet morphology itself remains largely unchanged. Therefore, the decrease in correlation intensity is attributed primarily to the loss of entropy-driven nematic alignment and weakening of interparticle orientational correlations, rather than to changes in platelet size or structure.

At temperatures below 95 °C (Figure 4b, 4e), the SAXS profiles of the platelet suspensions display well-defined form-factor oscillations consistent with the hexagonal platelet geometry (Figure 3a). The 2D pattern exhibits isotropic scattering pattern (Figure 4e). As the temperature approaches 100 °C (Figure 4c), a new series of narrow correlation peaks emerges at $q_1 \approx 0.085\text{--}0.10$ nm⁻¹ and its higher harmonics ($2q_1, 3q_1$, etc.). The correlation peaks become most pronounced between 105 and 108 °C (Figure 4c), coinciding closely with the maximum of the DSC endotherm. The corresponding 2D SAXS pattern (Figure 4f) becomes more anisotropic, indicating a strong orientation dependent ordering. At temperatures above 110 °C, the intensity of the correlation peaks gradually decreases, while the platelet form-factor oscillation also weakens. By 118 °C, both the SAXS correlation peaks and the WAXS reflections disappear

completely, indicating the loss of both mesoscale ordering and PLLA crystallinity and the formation of a homogeneous solution. Notably, the original platelet correlations in N-phase vanish well before complete loss of crystallinity. The renewed correlation peaks closely resemble those observed during crystallization, suggesting the re-formation of an ordered crystalline micelle state during heating!

Real-space evidence for this intermediate is provided by the TEM observations (Figure 5, Fig.S5). To capture transient structures during melting, platelet suspensions were deposited onto preheated TEM grids and allowed to anneal during solvent evaporation. Although this procedure does not directly image the in-solution morphology, it effectively preserves the intermediate structures formed at elevated temperature. As the temperature approaches the PLLA melting region, the initially faceted platelets first develop roughened and destabilized edges, followed by progressive separation into elongated crystalline domains that remain locally aligned (Figure 5a). With further heating, these domains evolve into arrays of rod-like or cylindrical micellar structures before complete dissolution occurs (Figure 5b). The persistence of elongated ordered structures suggests that the crystalline character of PLLA is largely retained during the early stages of restructuring, indicating that fragmentation occurs before bulk melting. The resulting micrographs (Figure 5) reveal abundant rod-like crystalline domains and fragmented platelet remnants, consistent with the existence of cylindrical micellar intermediates inferred from in-situ SAXS measurements. Although drying may modify the extent of ordering and aggregation, the absence of intact platelets and the prevalence of aligned micellar structures provide qualitative support for a platelet-to-micelle fragmentation pathway during heating.

Taken together, the DSC, WAXS, SAXS, and TEM results demonstrate that melting does not proceed through direct dissolution of the platelet crystals. Instead, the platelets first undergo fragmentation into the similar crystalline cylindrical micelle intermediate observed during crystallization, followed by complete melting of the PLLA cores. The appearance of this common intermediate during both cooling and heating establishes that crystallization and melting are linked through a shared metastable state, although the microscopic pathways connecting it to the initial and final morphologies are distinct.

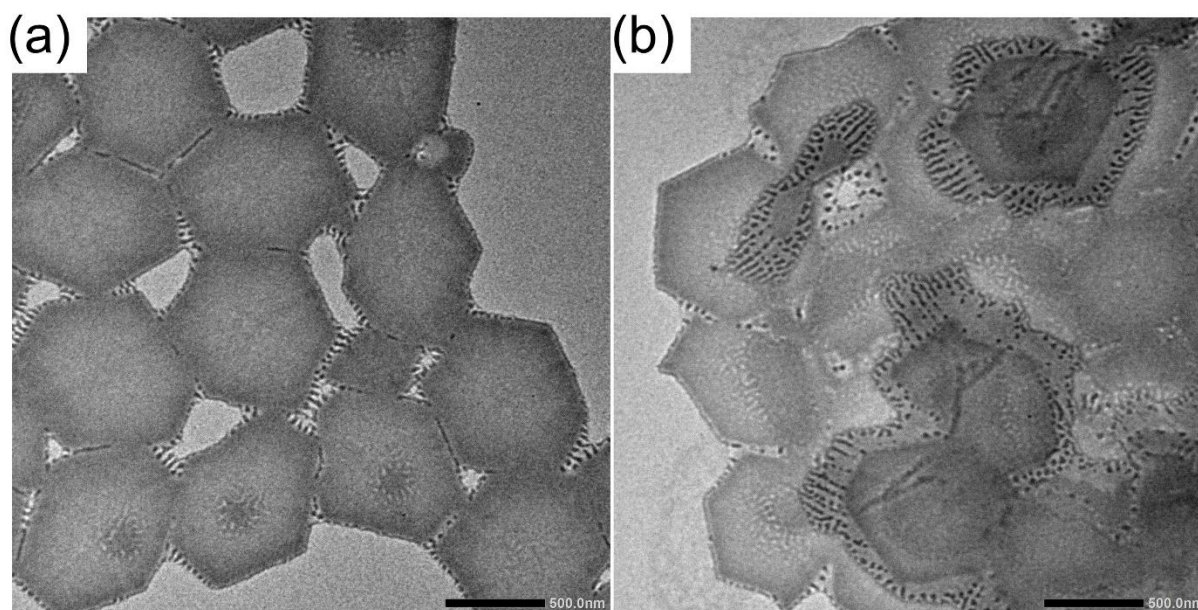


Figure 5. Hierarchical platelet fragmentation revealed by TEM: (a) TEM images of hexagonal platelets after annealing at 105 - 110 °C for 5 min; (b) Longer treatment (20 min) led to aligned micelles around platelets.

Energetic origin of the shared crystalline micelle intermediate

The coexistence of two distinct ordered regimes, i.e. a crystalline micelle array during crystallization and melting at higher temperatures, and faceted platelet crystals at lower temperatures, suggests that their relative stability is governed by a temperature-dependent energetic balance. The proposed free-energy landscape and the pathways of both crystallization and melting are illustrated schematically in Figure 6. The platelet and micelle states correspond to two local free-energy minima whose relative stability reverses with temperature. Both seeded platelet crystallization and platelet melting proceed through a crystalline-micelle intermediate, revealing a two-step transformation pathway.

To quantify this balance, we approximate the free energy per unit area (G/A) of a PS-*b*-PLLA platelet as the sum of two principal terms: (1) an interfacial contribution $G_{\text{surf}} = \gamma A$, proportional to the PLLA core-solvent interfacial tension γ ; and (2) a brush contribution $G_{\text{brush}} \sim k_B T N \sigma^{5/3} a^{4/3}$, describing the entropic penalty of stretching the PS chains tethered at a grafting density σ with polymerization degree N .⁴⁹ Using the measured molecular parameters (PLLA core thickness ≈ 10 nm, PS block 21 kDa, lateral size 600 nm), the grafting density is estimated as $\sigma \approx 0.15$ chains nm⁻². Substituting these values yields a critical interfacial tension $\gamma_c \approx 10$ mN m⁻¹ at which the brush and surface terms are comparable (Experiments and Methods).

This analysis provides a simple physical picture for the observed structural transition. At lower temperatures, the relatively high PLLA-solvent interfacial tension favors reduction of the total interfacial area, making lateral coalescence of crystalline micelles into platelet crystals energetically favorable despite the accompanying loss of brush entropy. As the temperature increases, the interfacial tension decreases while the PS coronas become increasingly mobile. When $\gamma(T) < \gamma_c$, the balance reverses, the system now lowers its free energy by fragmenting into smaller micellar units that relieve brush stretching. The resulting aligned micelle arrays therefore represent a metastable intermediate stabilized near the crossover between interfacial and entropic contributions.

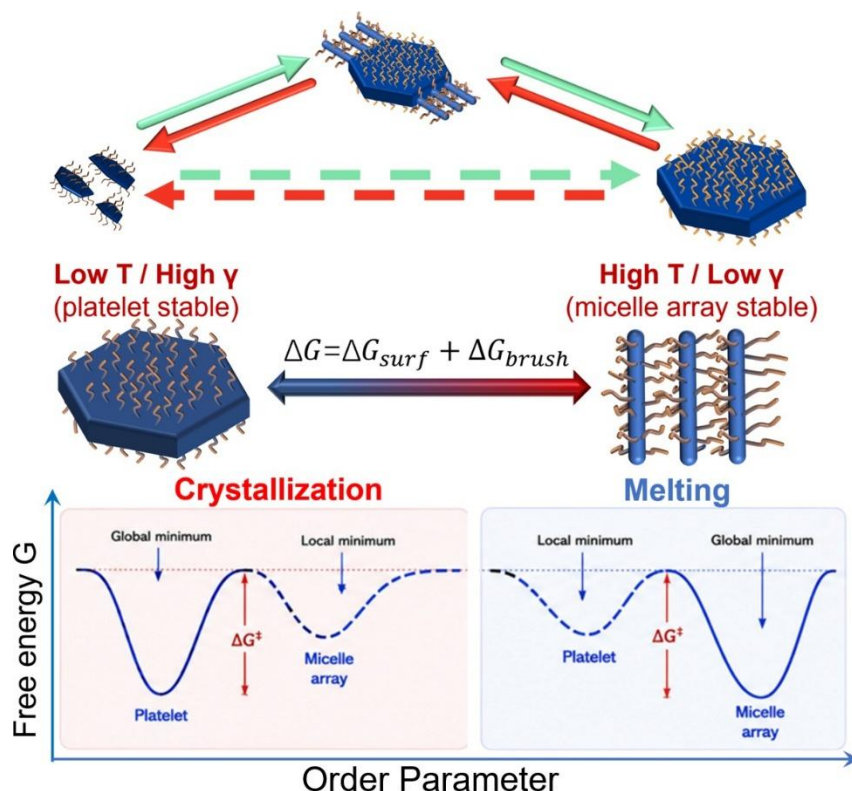


Figure 6. Schematic illustration of crystallization and melting pathways and the free-energy landscape governing the platelet to micelle transition.

Discussions

The most significant finding of this work is the identification of a shared crystalline cylindrical micelle intermediate that links crystallization and melting in PS-*b*-PLLA crystallization-driven self-assembly. During crystallization, time-resolved SAXS, WAXS, and TEM demonstrate that platelet formation does not proceed directly from dissolved polymer chains, but instead follows a hierarchical pathway: residual seed crystallites first generate epitaxially aligned crystalline cylindrical micelles that subsequently undergo lateral ordering and coalescence into faceted platelet crystals. Upon heating, however, the reverse transformation is not a simple dissolution of the platelet. Instead, the platelet first fragments from its edges into crystalline cylindrical micelles before complete melting. The observation that the same intermediate appears during both assembly and disassembly establishes a direct mechanistic connection between crystallization and melting and demonstrates that reversible morphology transitions can occur without passing directly between ordered platelets and homogeneous solution.

The energetic analysis provides a physical explanation for the emergence of this shared intermediate. The morphology transition is governed by the competition between two opposing free-energy contributions: reduction of the PLLA–solvent interfacial area favors coalescence into large platelet crystals, whereas the conformational entropy of the solvated PS corona favors fragmentation into smaller crystalline micelles. Quantitative estimation based on Milner–Witten–Cates brush theory⁴⁹ predicts that these contributions become comparable at an interfacial tension of $\sim 10 \text{ mN m}^{-1}$ at a representative restructuring temperature of approximately 100 °C. Consequently, the crystalline cylindrical micelles occupy a metastable

free-energy minimum separating the platelet and dissolved states (Figure 6): At low temperatures, the higher PLLA crystallization driving force favors lateral fusion of micelles into platelets. As temperature increases, the reduction of interfacial tension together with increased corona mobility reverses the energetic balance, destabilizing large platelets and regenerating the micellar state before complete melting. The free-energy landscape proposed in Figure 6 therefore provides a unified thermodynamic framework that explains both the crystallization and melting pathways.

An important consequence of this energetic picture is that macroscopic reversibility does not imply microscopic reversibility.⁶ Although repeated heating and cooling recover the platelet morphology, crystallization and melting reach the shared micelle intermediate through fundamentally different microscopic mechanisms. During cooling, the intermediate is generated through epitaxial crystal growth from residual seed crystallites and evolves into platelets by lateral coalescence driven by crystallization enthalpy. During heating, it is regenerated through edge-induced fragmentation of existing platelets as the balance shifts toward corona entropy and reduced interfacial energy. Crystal morphology changes before complete melting were reported in literature. For example, Osichow et al. studied crystallization and melting of ideal polyethylene nanocrystals.⁵⁰ Their results demonstrated that structural reorganization prior to complete melting can be achieved through chain rearrangement and crystal thickening/thinning, i.e. increased chain mobility changes crystal morphology.⁵⁰ In contrast, the present work reveals a fundamentally different restructuring mechanism in CDSA, where entire crystalline micellar building blocks emerge as metastable intermediates before dissolution. The shared crystalline micelle intermediate should therefore be regarded not simply as a transient precursor of platelet growth, but as a metastable structural state that is accessible from both directions through distinct kinetic pathways. The reversible platelet–micelle transition is thus governed by a pathway-dependent free-energy landscape rather than by exact microscopic reversal of crystal-growth events.

These observations broaden the conceptual framework of crystallization-driven self-assembly. Classical descriptions of CDSA generally emphasize crystal growth from dissolved polymer chains into one- or two-dimensional nanostructures through seeded epitaxial growth, whereas the resulting morphologies are frequently considered kinetically stabilized.^{13,14} Our results instead demonstrate that platelet formation itself follows an assembly-mediated crystallization pathway, in which crystalline cylindrical micelles act as mesoscale growth units that subsequently coalesce into the final platelet crystals.⁴⁰ In this sense, CDSA describes the thermodynamic driving force arising from block copolymer crystallization, whereas the microscopic structural evolution follows a nonclassical crystallization pathway mediated by hierarchical intermediate assemblies.^{3,11} The regeneration of the same crystalline micelle intermediate during melting further demonstrates that intermediate structures are not unique to crystal growth but can also govern disassembly, extending the role of hierarchical intermediates beyond conventional nonclassical crystallization.

More broadly, the energetic framework developed here should be applicable to other semicrystalline block copolymer systems in which interfacial energy competes with corona-chain entropy. Because both contributions can be systematically tuned through block architecture, molecular weight, solvent selectivity, or corona chemistry, the entropy–enthalpy crossover identified here provides a general strategy for designing reversible morphology transitions in crystalline polymer assemblies. Rather than viewing CDSA as a sequence of

kinetically trapped morphologies, the present work suggests that reversible crystallization-driven self-assembly is better understood as navigation through a free-energy landscape containing multiple metastable states connected by pathway-dependent transformations. This perspective establishes a conceptual bridge between CDSA, nonclassical crystallization, and responsive soft materials, and provides new design principles for adaptive crystalline nanostructures capable of reversible structural reconfiguration.

Conclusions

We have shown that crystallization and melting in PS-*b*-PLLA crystallization-driven self-assembly are connected by a shared crystalline micelle intermediate. During crystallization, residual seed crystallites first generate epitaxially aligned crystalline micelles that subsequently coalesce into platelet crystals, whereas heating induces hierarchical fragmentation of the platelets back into the same micellar intermediate before complete dissolution. This reversible morphological transition is governed by a temperature-dependent balance between PLLA–solvent interfacial energy and PS-corona entropy, providing a unified energetic framework for both crystallization and melting. More broadly, these results show how competition between crystal interfacial energy and corona conformational entropy can introduce metastable crystalline intermediates into block-copolymer crystallization, providing a route to redirect assembly between discrete crystals, one-dimensional crystalline objects and interconnected structures. Such pathway selection offers a general strategy for controlling hierarchical morphology in crystallizable polymer systems.

Experiments and Methods

Materials and sample preparation

The PS-*b*-PLLA was purchased from Polymer Source, Inc. and used as received. The number average molecular weight (M_n) and polydispersity were measured to be 45300 (M_n PS, 21000; M_n PLLA, 24300) and 1.1 by gel permeation chromatography (GPC), respectively. According to the producer, the PS-*b*-PLLA was prepared by living anionic polymerization in sequential addition of styrene followed by lactide monomer or by taking the OH end-functionalized polystyrene and using co-ordination polymerization process. The PS block was atactic with a $T_g = 97^\circ\text{C}$ and the PLLA block was exclusively L-form to minimize the influence of optical isomer ratio on polymer property.⁵¹ The *p*-xylene ($\rho = 0.857\text{ mg mL}^{-1}$) was obtained from Sinopharm Chemical Reagent Co., Ltd. And used as received.

Single crystals of PS-*b*-PLLA were prepared according to the self-seeding technique reported previously.^{46,52} In brief, a 0.3 mg mL^{-1} solution of PS-*b*-PLLA in *p*-xylene was first heated to 130°C for 30 min to completely dissolve, and then the solution was quenched and stored at 4°C for 36 h to generate the supersaturated solution. Next, the supersaturated solution was heated to different seeding temperatures for 30 min to form BCSCs with different sizes. Subsequently, the solutions were crystallized at 94°C in an oil bath for 12 hours. For seeding temperatures 104°C and 105°C , the resulting hexagonal single crystals had an average effective diameter $\langle D \rangle$ of 550 nm, 1000 nm, respectively, with a standard deviation of 10%. The higher self-seeding temperatures led to larger average size of the single crystals. The crystals were further collected using membrane filters with a pore size of 0.25 or $0.45\text{ }\mu\text{m}$ (Millipore Corporation). The membranes with crystals were washed three times with *p*-xylene to remove the un-crystallized molecules, then the crystals were re-dispersed in *p*-

xylene for further use. The suspensions were filled in quartz capillaries for the phase behavior and structure characterization by SAXS.

Real-time SAXS/WAXS

Small angle X-ray scattering (SAXS) experiment was performed on beamline ID02 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The X-ray energy was 12 keV, which corresponds to a wavelength of 1.0 Å. The sample-to-detector distance of 2 m was used to cover a broad q range. The data were collected by an Eiger detector placed in an evacuated flight tube. The sample solutions were loaded into a quartz capillary with a diameter of 1.5 mm and a wall thickness of 0.01 mm, the capillary was inserted in a Linkam stage. The data sets were reduced by subtracting the scattering of pure solvent as a background. Further details on beamline, q -resolution, calibration, and data reduction can be found in Ref.^{53,54} One-dimensional SAXS profiles were converted from the 2D patterns using SAXSutilities developed at ESRF. For real-time SAXS/WAXS measurements, polymer solutions of initial concentrations of 5 and 10 mg mL⁻¹ in *p*-xylene were prepared and filled in quartz capillaries and sealed with epoxy glue.

Small and wide-angle X-ray scattering (SAXS/WAXS) experiments were carried out on the biological small-angle X-ray scattering (BioSAXS) beamline (BL19U2) at the Shanghai Synchrotron Radiation Facility (SSRF). The X-ray wavelength was 1.033 Å. The distance from sample to detector was 5080 mm. Sample solutions in 1.5 mm quartz capillaries with a wall thickness of 0.01 mm for phase behavior were used directly for SAXS/WAXS measurements. One-dimensional SAXS/WAXS profiles were converted from the 2D patterns using Fit-2D program.

Transmission electronic microscopy (TEM) was performed on JEM 1400 TEM with an accelerating voltage of 120kV. The TEM was equipped with a charge-coupled device camera that was used to take micrographs. The samples were prepared by dropping about 10 µL of crystallizing solution directly onto a carbon-coated copper TEM grid before filtration and allowing the solvent to evaporate under ambient conditions.

DSC of BCSC in *p*-xylene heating scan. The thermal stability of the crystals in solution and bulk states was characterized using differential scanning calorimetry (DSC) (TA Q100). The instrument was calibrated using an indium standard prior to measurement. All experiments were performed under a nitrogen atmosphere. To evaluate the thermal stability of the single crystals in solution, the platelet crystal suspension was first concentrated to a polymer concentration of approximately 8 wt%. An aliquot of the concentrated suspension (approximately 10 mg) was then sealed in a standard aluminum DSC pan. The sample was heated from 16 °C to 130 °C at a rate of 10 K min⁻¹, and the corresponding heat-flow curve was recorded during the heating scan.

Energetic estimation of platelet-to-micelle fragmentation.

The thermodynamic balance associated with the platelet-to-micelle transition was estimated by comparing the increase in PLLA–solvent interfacial free energy upon fragmentation with the entropic gain arising from relaxation of the PS corona chains using Milner–Witten–Cates (MWC) brush scaling.⁴⁹ The platelet PLLA core was approximated as a hexagonal prism with a lateral dimension of approximately 600 nm and a thickness of 10 nm, based on TEM measurements. This geometry gives a PLLA core volume of approximately $2.34 \times 10^6 \text{ nm}^3$ and a total geometric surface area of approximately $4.9 \times 10^5 \text{ nm}^2$. The fragmented state was represented by cylindrical PLLA cores with a radius of 5 nm and a contour length of approximately 1.2 µm. Assuming conservation of PLLA core volume, one platelet corresponds to approximately 25 cylindrical micelles, with a combined PLLA–solution interfacial area of approximately $9.5 \times 10^5 \text{ nm}^2$. The increase in interfacial area upon fragmentation is therefore

$$\Delta A \approx 4.6 \times 10^{-13} \text{ m}^2,$$

and the corresponding interfacial free-energy penalty is

$$\Delta G_{\text{interface}} = \gamma \Delta A,$$

where γ is the effective PLLA-*p*-xylene interfacial tension.

The conformational free energy of the PS corona was estimated using strong-stretching Milner–Witten–Cates brush scaling,

$$F_{\text{brush}} \sim k_B T N (\sigma a^2)^{2/3},$$

where $N \approx 202$ is the degree of polymerization of the PS block, $a \approx 0.7$ nm is the statistical segment length, and σ is the effective grafting density. The PLLA core volume corresponds to approximately $N_{\text{ch}} \approx 7.5 \times 10^4$ block-copolymer chains per platelet. At a representative restructuring temperature of $T = 373\text{K}$, the effective grafting density of the platelet state is

$$\sigma_p \approx \frac{7.5 \times 10^4}{4.9 \times 10^5} \approx 0.15 \text{ chains nm}^{-2},$$

whereas redistribution of the same number of chains over the larger surface area of the cylindrical state gives

$$\sigma_m \approx \frac{7.5 \times 10^4}{9.5 \times 10^5} \approx 0.079 \text{ chains nm}^{-2}.$$

Using the same brush-scaling expression for both morphologies gives approximately

$$F_p \approx 1.8 \times 10^{-19} \text{ J chain}^{-1}$$

for the platelet state and

$$F_m \approx 1.2 \times 10^{-19} \text{ J chain}^{-1}$$

for the cylindrical-micelle state. The resulting reduction in corona stretching free energy is therefore

$$\Delta G_{\text{brush}} = N_{\text{ch}} (F_p - F_m) \approx 5 \times 10^{-15} \text{ J}.$$

The crossover condition,

$$\Delta G_{\text{interface}} = \Delta G_{\text{brush}},$$

then gives an estimated critical interfacial tension of

$$\gamma_c = \frac{\Delta G_{\text{brush}}}{\Delta A} \approx 1.1 \times 10^{-2} \text{ N m}^{-1} \approx 11 \text{ mN m}^{-1}.$$

This estimate indicates that the reduction in corona stretching associated with the higher-curvature micellar morphology can be comparable to the energetic cost of creating additional PLLA–solution interface. The calculation should, however, be regarded as semi-quantitative. In addition to using the geometrical PLLA–solution interfacial area as an effective grafting area for the PS corona, we assume that all molecular and geometrical parameters entering the estimate are temperature independent over the restructuring interval. In reality, quantities such as the effective interfacial tension, corona conformation, grafting density, solvent quality, and crystalline-core dimensions may vary with temperature, particularly close to the PLLA melting region. Moreover, in a folded-chain crystalline core, the actual distribution of PS-*b*-PLLA junctions may differ between platelet and cylindrical morphologies, and a more complete temperature-dependent curved-brush treatment would be required for a precise determination of ΔG_{brush} and γ_c . Nevertheless, the analysis establishes the relevant energetic scale and supports a picture in which platelet-to-micelle restructuring is governed by competition between PLLA interfacial energy and PS-corona conformational entropy.

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Author contributions:

H.H. and F.Z. designed the experiment, N.C., C.T. and F.Z. performed experiments and analysed data. N.C., F.Z. and H.H. wrote the manuscript. All authors discussed results.

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