



Feature Article

Origins of periodic bands in polymer spherulites



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ABSTRACT

Historically, in the past 60 years, continuous spiral twisting of polymer lamellae, assumed as tens of thousands of single crystal plates simultaneously radiating from a common center of spherulites, had been interpreted as a plausible mechanism for common optical ring-banding behavior in polymer spherulites. Furthermore, chain folding and congestion of such folds, unique only in polymer crystals, had been advocated as a cause for lamellae surface stresses, which were believed to contribute to continuous spiral twisting and ring bands in spherulites. With progress of powerful advanced instrumentation and newer discoveries of diversified patterns (e.g., birefringent vs. non-birefringent; circular vs. hexagonal; concentric vs. helicoidal, etc.) of ring bands in increasing numbers of polymers under different environment, more and more work reported behavior that contradicted interpretations based on such idealized models. Debates have gone on perpetually, with fully clarified settlement seeming to be still far away.

This feature article reviews and surveys evidence accumulated in past years by numerous investigators to point out that polymer spherulites are made of complex hierarchical polycrystals with multiple branches during primary and secondary growth that are supported by clear experimental observations; thus, assumption of single-crystal lamellae plates undergoing continuous spiral from center to periphery of spherulite may need critical assessment for validity. Secondly, numerous investigators since 100 years ago have amply reported (even far before discoveries of ring bands in polymer spherulites) that many small-molecule compounds, apparently without chain-folding induced surface stresses, could display exactly same orderly ring-band patterns in their crystals as those in polymer spherulites. The facts suggest that chain folding and stresses caused by congestion of folds in lamellae, may not be a necessary condition or responsible factor for ring bands in spherulites. Thirdly, crystal lamellae, being in either polymers or small-molecule compounds, do twist or scroll in responding to various external stresses; however, critical experimental evidence for matching between the twist pitches and optical inter-ring spacing, for some unknown reasons, has been lacking in past 60 years. Fourthly, it takes synchronized twists of tens of thousands lamellae that all have to be identically shaped single crystals in order to build orderly ring bands in a spherulites as viewed in optical graphs. This synchronizing identity of all single crystals might be a dauntingly impossible task for polymer crystals in spherulites by considering that even simple water molecules cannot pack into two snowflakes that are alike (though the basic hexagonal prisms may look similar in appearance but it is very unlikely for two larger complex snow crystals to be identical in appearance). Finally, conventional analyses were usually based on characterization on the top-surfaces of thin films (several micrometers, with top surfaces etched or unetched) of crystallized polymers; or alternatively, polymers were cast to ultra-thin films (nanometers) for viewing on the morphology of single crystals.

This article points out with demonstrated cases that etching with improper solvents may

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cause artificial morphology deformation owing to external stresses, or even chemical alterations, of crystals in spherulites to be characterized leading to erroneous interpretations. Banding patterns are generated from the crystal arrays of spherulites in the entire thickness optical path. However, the top-surface crystals in polymer films usually account for only a minor fraction of the whole thickness of polymer samples, and the assembly of top-surface crystals may differ from that of the interior crystals. Thus, analyses based only on the top surfaces of thin polymer films, a common approach taken by most investigators in past 60 years, might yield results that were not in full agreement with truth of entire spherulites. Additionally, observations on nanometer ultra-thin film samples or thin-solution cast single crystals, though allowing development of morphology approaching single-crystal lamellae, may yield morphologies that are far different from those in true ring-banded spherulites. Although lamellae scrolling and twisting may be proven in single crystals of some polymers owing to chain-fold induced stresses or other external forces, extrapolation of possible correlations of scroll/twist in single-crystalline lamellae to the ring-banded patterns in polycrystalline spherulites is still not yet established.

Major keys of cracking the mysteries are thus that steps must be put forward in alternative directions. One should also know the constraints of analyses based on results derived from single crystals, which are far different from the complex branched crystals in actual polymer spherulites. Lamellae twist (or bend, scroll, dislocation, etc.) and periodic ring bands are two facts in many spherulites; yet, they have to be dealt in entirely different perspectives for probing the origins. By surveying recent studies oriented in alternative approaches in comparison with conventional studies in the literature, this work demonstrates a new horizon of probing the origins of periodic banding behavior in polymer spherulites. This article is just an initiative. It takes courage to raise skepticism on unsettled interpretations – and strong evidence accumulated based on novel approaches – to steer in right directions.

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1. Introduction

Crystals are characterized by several natural habits: aggregation into spheres (if not confined by pressure or boundaries); irregular twist or bend; periodic helices. These habits are commonly associated with single crystals grown from molten species of compounds. In a recent review, Kahr et al. [1] have thoroughly addressed growth-actuated bending and twisting of single crystals based on observations many organic/inorganic compounds. Crystals growing from the melt can be bent or twisted by stresses induced by temperature cooling from melt that generates a distribution along the single crystals; and perhaps also by stresses from other sources that may impose similar effects of crystal deformation. In the comprehensive review, Kahr et al. [1] discussed a few interesting cases of organic or inorganic small-molecule compounds, which are worthy

as comparative background information for addressing the similar issues in polymer crystals. A German chemist, Ferdinand Bernauer, [2] certainly was a pioneer on crystal deformation, who investigated more than 400 compounds and concluded that many of these molecular crystals can be made to grow as helices that can be observed under polarized optical microscopes. Bernauer studied these compounds and was mainly intrigued by observations of ring-banded spherulites displaying in them. One of the four hundred substances studied by Bernauer, hippuric acid (N-benzoyl glycine), grows from under-cooled melts as flat crystals, which display periodic birefringence color patterns with pitch (p) = 0.6 mm (600 μm) [2]. Many small-molecule compounds he examined display ring-banded spherulites when crystallized, and naturally they were attributed at that time as possible correlations between the twisted crystals and ring-banded spherulites. It should be noted here that this twist pitch (600 μm) in the single crystals of hippuric acid is order-of-magnitude greater and far away from the observed inter-ring spacing of ring-banded spherulites. Thus, proving twists in single crystals is one thing; but it still remains as another challenge to solve the problem of how to correlate meaningfully the twist of single crystals to the ring-banded spherulites that are composed of branched, twist, and bent polycrystals (i.e., crystals of multiple hierarchical crystal levels, and not the single crystals). We will show later in this article that there are other factors in complex spherulites vs. simple single crystals that should be examined for a more plausible mechanism of ring-banded spherulites. In addition, the pitch of helices of twisted single crystals, e.g., in hippuric acid or others usually are magnitude-of-order different from the pitch in ring-banded spherulites, which need more careful assessment for settling down a plausible and workable mechanism that takes into consideration of the much greater multiplicity of spherulites than that of signal crystals.

Crystals of organic-metal salts have also been studied. Huang et al. [3] have proven that potassium salts of 3,4,9,10-perylenetetracarboxylic acid grow as single crystals of straight-ribbon shapes; but the crystals twist into coils when dispersed in fluids that differentially solvate the surfaces, which obviously impose unbalanced stresses across the originally straight crystals before fluid exposure. This, of course, is a clear demonstration of stress-induced twisting in single crystals of originally grown flat-ribbon shape. Many of the compounds forming ring-banded spherulites originally reported by Bernauer [2] were re-investigated by Kahr et al. [4–9] in recent years for further details. Among the many small-molecule compounds known to display rings in crystallized spherulites are: hippuric acid [4], phthalic acid [5], testosterone propionate [6], D-mannitol [7], aspirin [8], and also in inorganic salts such as ($\text{K}_2\text{Cr}_2\text{O}_7$) [9–11]. The ring-banded patterns in small-molecule spherulites are sporadically seen in crystallization of many other materials; yet the mechanisms remain elusive and have been highly debated. In the fields of crystallography for small molecules, there are two common and simplified proposals for accounting the ring bands: helical crystals (induced by stress) and rhythmic precipitation (kinetically driven). There may be also occasions that both mechanisms are simultaneously responsible for the banded patterns. However, it has to be noted here that spherulites are not composed of many single-crystal-like lamellae radiating from a common center. Instead, however, true single crystals are not in spherulites, the polycrystals in spherulites are primary lamellae with various curvatures and branches, secondary branches. That is, the hierarchical crystal complexity in spherulites is much diversified than that in single crystals.

Chemistry of molecules, supramolecules, or natural crystals is full of examples of structured bent, twist, and helical geometry. We will not cite one by one here, but it is worthy to mention a notable example of natural silks – highly crystalline proteins – which have been demonstrated to form twist fibrils like double spirals [12]. The pitch of spiral protein molecules is typically a few nm, which of course is far below and cannot be correlated to the inter-ring spacing (2–10 μm) in most banded spherulites. The spiral molecules in proteins or other molecules and those stable spirals are held by strong intra-molecular hydrogen bonding forces, etc., are beyond the scopes of this article; but we only want to point out that spirals of different magnitudes in molecules cannot be brought to comparisons with ring-banded spherulites. In addition, the “pitch” of the fibril silk spirals is ca. 40 μm [12], which again is beyond the normal pitches (inter-ring spacing = 2–10 μm) observed in common ring-banded spherulites of any compounds. This again demonstrates that natural twist in many molecules, supramolecules, or crystal fibrils (or single crystals) are issues that should be carefully separated from probing the origins of ring-banded spherulites.

Furthermore, spherulite growth is governed by kinetic processes that involve species diffusion to crystal growth, which may put a limitation leading to periodic stops of growth owing to competition between the diffusion and growth. When this occurs, crystal habits may also be altered, likely in periodic patterns; which may superimpose on, or act collectively with, stress-related twist/bend of crystals in spherulites. That is to say, spherulites are order-of-magnitude higher in complexity than single crystals; therefore, both thermodynamic factors (stress-induced twist) and kinetic factors (growth fluctuation, growth difference in upper surfaces of films vs. bulk interior, etc.) must be simultaneously considered for constructing fuller pictures in describing the banded spherulites. As a matter of fact, ring-banded spherulites were not among the oldest discoveries in crystal materials displaying periodic patterns. Thirty years prior to the reports of ring-banded spherulites in crystallized compounds, Liesegang rings, first reported by German chemist Raphael E. Liesegang in 1896 and described further by Henisch [13] are related to kinetics of reactions periodically draining in a gel, where a drop of silver nitrate solution is cast onto a thin layer of gels with potassium chromate. The silver nitrate will begin to diffuse into the gel containing potassium chromate and react to form a region of precipitation into non-dissoluble “silver chromate” (Ag_2CrO_4 , dark brown-red color), followed by a region with no precipitate (light color); then reaction to precipitate and no precipitation in cycles until all reactants in gel are converted. Alternating repetitions of the cycles lead to distinct and sharp ring patterns (up to 10 or more rings) in final products. It would be easy to extend the theory to predict that if potassium chromate was not dispersed in gels but in an aqueous solution instead, then upon dropping the silver nitrate solution into the potassium chromate solution in a dish, the two reactants would react immediately into one single batch of precipitate and no alternating Liesegang ring

patterns would appear. Thus, apparently, rhythmic precipitation (cycles of reactions and stop to wait for diffusing species in gel) is a well-established consequence of diffusion-controlled reactions giving rise to the historically famous Liesegang rings in gels. Crystallization processes, like reactions, are kinetically controlled; and similar behavior may be expected in crystallization of polymer in thin films, just like the Liesegang reactions in a thin layer of gels. This similarity between reaction and crystallization kinetics should be born in mind when one approaches problems of ring-banded spherulites.

We will now direct attention to polymer spherulites with periodic ring bands. In addition to the numerous cases of ring-banded spherulites in small-molecule compounds widely reported since 1929, similar complex issues in polymers have long been explored by some outstanding work in the literature since 1950–1960s. Polyethylene (PE), the oldest synthetic olefinic polymer of commercial interests in 1940s, is one of the most widely studied materials in science community, to be followed by commercially useful aryl-polyesters and newcomers in recent years – biodegradable polymers. Until a more recent work from this laboratory on dissecting into the interior of poly(ethylene adipate) (PEA) [14] – an aliphatic polyester, much of the earlier proposed mechanisms since 1960 still could not yield persuasive evidence between the direct matching twist crystal pitch and optical inter-ring spacing in spherulites. This obstacle in polymer spherulites is similar to that in ring-banded spherulites of small-molecule compounds. In close similarity or resemblance to the numerous issues in small-molecule compounds, the lamellar twisting among all the proposed mechanisms is the most adapted model to account for the formation of the concentric ring bands in spherulites since 1960 [15–22]. Fujiwara [23] in 1960 used a then rudimentary tool of pin-holed lead to block an X-ray beam into “micro-beam” (square hole of $2.5\ \mu\text{m} \times 2.5\ \mu\text{m}$) in trying to analyze the then-proposed spiral lamellae in crystallized PE films. Of course, in present view, the X-ray beam size of $2.5\ \mu\text{m} \times 2.5\ \mu\text{m}$ (at hole) is just too large and intensity too low to be of any use. The beam size upon impinging the samples would be much larger than $2.5\ \mu\text{m}$. As the inter-ring spacing (one pitch) of ring-band PE spherulites was $3\ \mu\text{m}$; thus, the pin-holed “micro-beam” X-ray would cover the entire “pitch” or even a couple of pitches, leading to that the signals in essence were the averages of all “twist angles” – unable to reveal the “gradual and continuous rotation of lamellae” – a prevalent concept at that time. This attempt in 1960 illustrates how exhaustive works by many investigators were directed to trying to solve the problems in banding behavior in polymers. Explanations provided to account for lamellar twisting may be divided into two views. One alternate viewpoint proposes that rhythmic growth in polymers is associated with features that exist during growth or are generated by the growth process itself [24]. The “twisting” may be associated with screw dislocations [25], or surface stresses at chain-fold surface [26]. These two divided views in polymers are not too different from those already proposed in small-molecule compounds much earlier in the literature. By following the classical work of Keith and Padden’s hints [15,16], Bassett et al. [27,28] explored further possibilities of lamellar assembly in relation to the ring-banded patterns in polymer spherulites – mainly polyethylene (PE) at that time. If the polymer chains are tilted in the lamellae and screw dislocations are present, they have shown that the development of the lamellae in the screws can be asymmetric. In addition, if the twist of the leading lamellae is influenced by these additional lamellae in the screws, then the whole stack of leading lamellae would be asymmetrical. Lustiger and Lotz et al. [18] have further suggested that polyethylene (PE) lamellae undergo continuous twisting, rather than successive misalignment of essentially untwisted segments.

From the brief surveys on PE spherulites as discussed, most of the investigations in crystalline polymers followed the earlier arguments of stress – induced twist being related to ring-banded spherulites of small-molecule compounds, except that investigators on polymers further introduced a concept of chain-folding induced stresses in polymers, which is non-existent in small-molecule compounds having no chain folding in crystals. Polymers, with long chains unlike small-molecules, are known to have chain folding from classical literature. Some investigators, including Lotz and Cheng [22], argued that chain folding induced surface stresses, which in turn were responsible for crystal twisting. However, all polymers are known to chain fold in crystals, but not all polymers display ring-banded spherulites. In addition, by contrast, small-molecule compounds do not need chain folding in packing into crystals at all, but the crystals of some of the compounds also twist. In more recent and extensive work on small-molecule compound crystals, Kahr et al. [4–9], following the initiating arguments of the classical work by Bernauer [2] who pioneered on many organic compounds using optical microscopy in 1929, have argued that temperature-gradient induced stresses, and other stresses, etc., may cause helical shapes in these small-molecule crystals. Apparently, the above comparisons between long-chain polymers vs. small-molecule compounds clearly hint that crystal twist can be caused by stresses during or after crystallization, but is not necessarily related to or solely induced by chain folding.

However, in approaching the problems of ring-banded polymer spherulites, most investigators only focused on analyses based on top-surfaces of thin films, and very rarely the inner structures of banded materials were examined. A recent article [29] has just attempted to address the inherent constraint of analyses based on only the top-surface morphology of ring-banded polymers spherulites, which may not suffice in probing the complex issues of interior lamellae assembly accounting for the ring-band patterns. In addition to literature reports on ring-banded spherulites in aliphatic polyesters such as widely studied poly(ethylene adipate) (PEA) [14,22,30–32], many aromatic polyesters are among the most investigated materials for ring-banded spherulites, such as poly(trimethylene terephthalate) (PTT) [33–36], poly(pentamethylene terephthalate) (PPT) [37,38], poly(octamethylene terephthalate) (POT) [39], poly(nonamethylene terephthalate) (PNT) [40–42]. Further extension of the methylene unit length from the shortest two methylene units in poly(ethylene terephthalate) (PET) to very long 12 methylene units in poly(dodecamethylene terephthalate) (PDoT) [29] has demonstrated that ring bands exist in most aryl polyesters with 3, 5, or 7–12 methylene units, but the ring band patterns in spherulites differ when the chemical structures of the aryl polyesters vary in term of the number of methylene units. These polyesters have been the focus of studies in crystal structures because they always can be packed into ring-banded spherulites within a certain

temperature range. In addition to the traditional aliphatic polyesters or aryl polyesters, which are already well known to exhibit ring-banded spherulites, many newer biodegradable polymers, such as poly(L-lactic acid) (PLLA), poly(3-hydroxybutyrate) (PHB), and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHB-co-HV) [43–46], have been shown to exhibit ring-banded spherulites. The chemical structures of polymers play some roles in determining whether or not ring-banded spherulites can be formed in the polymers; yet, there are no general rules – not even the classical odd–even rule. This is seen in cases of ring bands existing in aryl polyesters with 3, 5, or 7–12 methylene units, but not in other aryl polyesters [poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT)]. Similar behavior is also seen in aliphatic polymers. Although polyesters such as poly(ethylene adipate) (PEA) [30–32] or poly(1,4-butylene adipate) (PBA) [47,48] easily form ring-banded spherulites. On the opposite side of poly(ethylene adipate) that easily forms ring-banded spherulites at $T_c = 26\text{--}30\text{ }^\circ\text{C}$, poly(ethylene succinate) (PESu), when crystallized at any T_c or blended with any amorphous diluents, would not form ring-banded spherulites at all [49]. Similarly, on the opposite side of poly(butylene adipate) (PBA) that easily forms ring-banded spherulites at $T_c = 28\text{--}31\text{ }^\circ\text{C}$, poly(1,6-hexamethylene adipate) (PHA) in neat form (with no diluent polymers) [50] virtually does not form ring-banded spherulites at any T_c 's. However, the normally ringless polyester poly(1,6-hexamethylene adipate) (PHA), can be made to form ring bands when blended with amorphous and miscible diluent such as poly(vinyl methyl ether) (PVME) [50]. Similar to PHA, poly(1,4-butylene succinate) (PBSu) in neat form (unblended) does not form ring-banded spherulites when crystallized at any T_c 's; but when blended with miscible crystalline or amorphous polymers, PBSu in blends can form ring-banded spherulites at temperature window of $T_c = 60\text{--}80\text{ }^\circ\text{C}$ [51,52]. Once again, the chemical structures of aliphatic polyesters do play a role in determining tendency of forming ring-banded spherulites; but there are no general rules.

An introduction of ring-banded polymer spherulites cannot be complete without mentioning a special type of ring bands with a pattern resembling multiple-petal flowers, which are concentric with the nuclei center but the rings and peripheries are shaped like a camellia flower. The camellia-shaped rings in polymer spherulites usually do not show alternating birefringence color changes, other than a sharp extinction bordering the rings. This type of ring bands (camellia-flower shaped) can be found in some polymers when cast onto very thin thickness (500 nm or thinner) on glass (or silicon wafer) and crystallized at specific temperatures, although the same polymers may not exhibit birefringence-color bands at all when crystallized in thicker films (1–30 μm) at any T_c 's. Isotactic polystyrene (iPS) is an extensively studied subject that exhibits such non-birefringent camellia-flower-shaped ring bands [53,54]. As iPS in solutions are cast to thin films ranging from 100 to 300 nm in thickness by spin-coating 1.0 wt% iPS-xylene solution onto clean glass slide, and crystallized at $T_c = 160\text{ }^\circ\text{C}$ (for 6 h), it is easy to observe such rings with inter-ring spacing (p) = 5 μm . Although the model of lamellae twisting is held for a long time by some investigators as the working mechanism for birefringence-color ring-banded spherulites in polymers, on a parallel interpretation is that the non-birefringent bands in spherulites may be driven by diffusion draining with crystallization growth stop – a mechanism that is by nature similar to the periodic reaction interruption in forming the Liesegang rings [13]. Diffusion depletion in explaining the special type of ring bands in iPS usually states that as the melt (molten species) becomes more and more depleted, lamellar growth stops. The “precipitation process” is usually sequentially from the top lamella downward, forming a curved front from top to bottom (in contact with the substrate).

Such non-birefringent color bands in thin polymer films are not just limited to iPS. For example, back in 1953, Schuur [55] already demonstrated that Gutta-Percha rubber, when diluted in paraffin oil and crystallized at $T_c = 42\text{ }^\circ\text{C}$, could develop the camellia-flower shaped ring bands although the mechanism was not fully understood at that time. Keller in 1955 [56] also reported similar behavior in melt-crystallized poly(ethylene terephthalate) (PET) as well as undried PET samples with *o*-chlorophenol or *m*-cresol when crystallized at 220–225 $^\circ\text{C}$ (which essentially were crystallized from PET/*o*-chlorophenol solution), showing camellia-flower shaped ring bands (named as “extinction bands”). Poly(ϵ -caprolactone) (PCL) is another well-known case of displaying camellia-flower shaped ring bands. Wang et al. [57,58] have shown that when PCL is crystallized (at 20 $^\circ\text{C}$ – room temperature) from an evaporating dilute PCL/toluene (5–50 mg/mL) solution cast on silicon wafer, the inter-ring spacing (p) of the camellia-flower shaped ring bands increases steadily with the solution concentration (5–50 mg/mL). Apparently, the inter-ring spacing is related to the film thickness. The birefringence and appearance/disappearance of these camellia-shape ring bands in PCL, like those in many other polymers, are governed by film thickness and the kinetics of solvent evaporation rates. A more detailed coverage to other numerous polymers with such behavior is not the goal of this article; the aims here are just to show that there are several different types of ring bands in polymers that differ in inner nature and outer shapes. Correspondingly, crystallization in various constraints or parameters (thickness, chemical structures, substrates, diluents, temperatures, etc.) leads to that the crystal packing in polymers can accumulate more complexity in the way periodic bands in spherulites finally appear.

Recently in 2012, Rosenthal et al. [59] took the tip of crystal twist by re-visiting the classical Keith-Padden model (twist due to surface stress induced by chain folding) to work on highly-birefringent and ring-banded poly(trimethylene terephthalate) (PTT). They have shown beautiful work using much more advance instrumentation such as small-angle X-ray scattering, and confocal optical microscopy than those available in the Keith-Padden's earlier time (1960); however, at the end they frustratingly admitted: “despite the formal agreement with the KP-model, the value of the chain tilt of 4 $^\circ$ alone does not appear to be sufficient for generation of the surface stresses required for twisted lamellar growth”, and they further stated: “the exact 3D-shape are needed to provide more insights into the nature of chirality of such supramolecular objects formed by achiral polymers.” This is a testimony how critical it is that 3D interior views are needed to construct a valid model for correct interpretations of ring-banded spherulites in many polymers. In the past 60 years or so, most investigations approached the issue from surface views on thin-film samples that have been crystallized in controlled conditions. For

different materials, the banding patterns may look similar, but the top-surface topological patterns differ subtly. These facts suggest that the internal lamellae assemblies also vary correspondingly.

An even more critical issue is that albeit the facts of stress-induced twisting in single-crystals of either small-molecule compounds or polymers, are there any correlations between the ring-banded patterns and the twisting of single crystals? Key point may be in providing direct evidence of whether or not the observed pitch of the twist single crystals is in agreement with the pitch of optical birefringent patterns in ring-banded spherulites. This single most critical evidence (twist pitch of single crystals being in agreement with optical ring interspacing in banded spherulites) appears to be missing in numerous works reported in the literature. Many investigators only focused on analyzing the twisting of single crystals and mechanisms therein, and argued that these twist crystals could be responsible for the ring-banded spherulites. Indeed crystals may twist in ring-banded spherulites, but they can also twist in ringless spherulites such as PEO. These proposed correlations based on the top surface of thin crystallized films may be an Achilles-knee problem that should be tackled with more careful and deeper analyses. By analyzing only top surface of thin polymer films with occasional crystal deformation owing to solvent etching, such traditional approaches may run risks of the facts that twisted crystals may also be retrieved from ringless and non-banded spherulites and interior lamellae packing still remains unknown. As the surface topology differs among different materials with banding patterns, the inner structures may also differ. Several polymers, mainly synthetic biodegradable polyesters, as well as small-molecule compounds, were used as models for comparison and testing the universal behavior in crystals that form ring bands. In addition, different types of ring bands were analyzed and mechanisms exemplified.

In this article, top morphology and crystal patterns on the outer surface in correlation with the interior crystal lamellae of ring banded spherulites in several common polymers was established. Novel approaches on dissecting the interiors of ring-banded spherulites in crystallized polymer bulks, as well as thin films, are discussed in details. Several ring-banded polymers are reviewed and analyzed for proposing a revolutionary model of interpreting formation mechanisms of ring-banded patterns. Ring bands in polymers, by nature, are of several dramatically different types that are distinguished by shapes, patterns, birefringence distribution, and height variation in ridge-valley regions. Interior lamellar vs. surface crystal that form ring bands of different types were analyzed and separate mechanisms exemplified. As the surface topology differs among different materials with banding patterns, the inner structures may also differ. Several polymers, mainly synthetic biodegradable polyesters, as well as small-molecules were used as models for comparison with the aim of describing the universal behavior in crystals that form ring bands.

2. Birefringent patterns in radial-stripe bands vs. circular ring-bands in polymer spherulites

The objectives of discussing radial-stripe bands in polymer spherulites as part of the subjects of periodic bands in spherulites should be first exemplified here. Most researchers have impression that circular ring band is the only noticeable periodic behavior in spherulites with distinct patterns of optical birefringence variations. This, however, is not true. There are many other types of “bands” in crystallized spherulites – including “radial stripes” with alternate birefringence colors as bands – periodic bands – because they alternately appear in spherulites, not as circular (or sometimes hexagonal) rings but as radial stripes of opposite birefringence. Band is a narrow stripe but not necessarily a circular ring. Thus, the subjects of “periodic bands in polymer spherulites” include not only conventional circular “ring bands” as most investigators are more familiar with, but also “radially-grown striped bands” that fewer investigators have noticed as periodic occurrence in polymer spherulites. Thus, the subjects in “periodic bands in polymer spherulites” would not be complete without these subjects of radial-striped spherulites for comparisons with circular ring bands. That is to say, “ring bands” are only a major sub-category under “periodic bands” in spherulites. These clarifications have been added into Section-2 for general readers to better appreciate the objectives of demonstrating a few cases of radially striped spherulites of opposite birefringence before moving into circularly ring-banded spherulites. There are some connections of mechanisms of formation and growth between the radial-striped spherulites and circularly ring-banded spherulites.

Poly(ethylene oxide) (PEO) is one of the polymers that never show ring-banded spherulites in any crystallization conditions, or when diluted by any amorphous/crystalline diluents. It, however, when blended with some strongly interacting diluent such as poly(*p*-vinyl phenol (PVPh), can be packed into hedritic spherulites with strongly birefringent stripes of blue/orange colors. This behavior makes it a useful model for comparing with polymers that form normal ring bands typically with alternating blue/orange rings. In this discussion, we set aside the camellia-flower type of “unusual” ring bands with no alternating blue/orange colors, as they are of a different category. Our discussion of ring-banded polymer spherulites thus begins with some interesting behavior observed in PEO/PVPh spherulites. Fig. 1 shows POM graph (A) and AFM phase images (B and C) of lamellar stripes in the spherulite of PEO/PVPh (80/20) melt-crystallized at 45 °C. Most well-rounded spherulites, in POM graphs with tint plates, would have two opposite colors in two mutually perpendicular quadrants separated by Maltese cross (extinction cross) as borders of these four quadrants. However, the hedritic spherulites of PEO/PVPh (80/20) blend melt-crystallized at 45 °C display no Maltese cross. Instead, the POM graphs easily reveal that the crystallized spherulite possesses dendritic (hedritic) patterns of two opposite colors (orange and blue) and the blue/orange stripes appear to “intertwine” with each other. The lamellar bundles in PEO/PVPh spherulites appear to radiate out from the nuclei center, branch out, and bend to curvature, as they go from center to periphery. But why the lamellae bundles possess two opposite birefringence colors? And do these lamellae really “intertwine” each other? Apparently, if one takes these

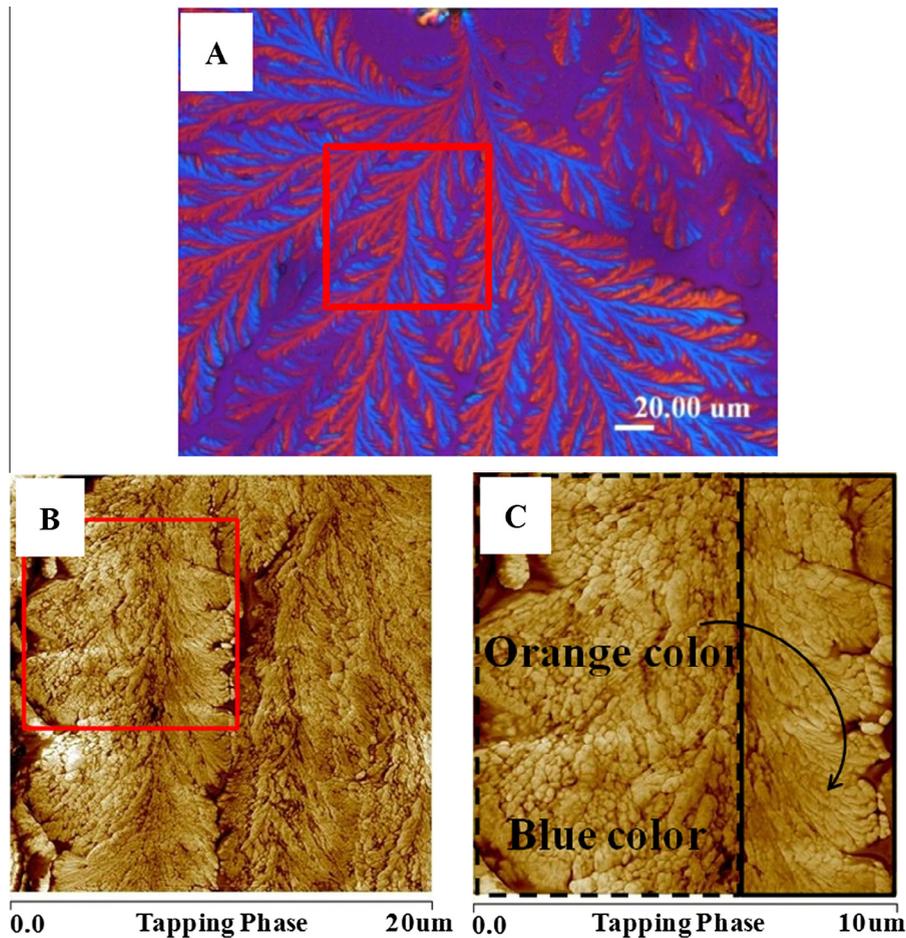


Fig. 1. POM graph (A) and AFM phase images (B and C) zoom-in to lamellar stripes in the dendritic spherulite of PEO/PVPh (80/20) melt-crystallized at 45 °C. The AFM phase images is enlarged area of the red block area in the POM graph. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

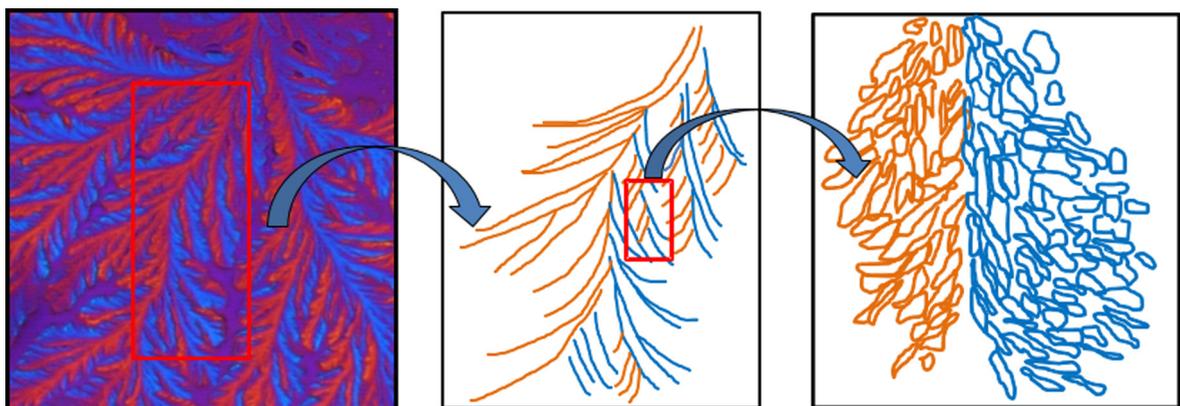


Fig. 2. Summary schemes for PEO dendritic lamellae in PEO/PVPh (80/20) blend crystallized at $T_c = 45$ °C.

radially-oriented lamellae stripes and re-arrange them in circumferential order, one would get alternating blue/orange birefringence ring-banded spherulites instead.

The POM graph does not have sufficient resolution for revealing the morphology details of dendritic lamellae in the PEO/PVPh spherulites; thus, AFM characterization results are used for assigning the lamellae and their shape/orientation

with the colored stripes in POM. The results in correlating the AFM micrographs and POM graphs show clearly that intertwining stripes of two opposite colors, representing lamellae of different orientations, are simultaneously present in the same quadrant of spherulite. At lower T_c (30 °C), the orange quadrants are vertical (slanted at +30°, while at higher T_c (>40 °C), the quadrants are no longer distinguishable; instead, the intertwining lamellae of both colors are seen in same quadrants of the spherulite, and these lamellae of orange/blue colors radiate out radially side-by-side and from the center to edge of the spherulite.

Summary schemes in Fig. 2 show the results of AFM analysis, in direct correlation to the POM results, reveals that all the orange-color-stripe lamellae are oriented to -45° , while all blue-color-stripe lamellae are oriented to $+45^\circ$. Thus, the lamellae of orange/blue colors in PEO/PVPh hedritic spherulite represent an obvious crystal habit where lamellae in spherulites are not single crystals. As spherulite grows, lamellae extend out from the center and they curve or bend to respond the stresses; in the meantime, branches are derived from the main lamellae usually at a fix angle corresponding to PEO's unit cell geometry. The AFM images clearly reveal that the lamellae or branches are oriented at roughly $\pm 45^\circ$ and are approximately perpendicular to each other, forming blue and orange stripes in POM graphs. Cheng and Lotz et al. [60] have shown by AFM imaging that as neat PEO (unblended but fractionated to different M_w 's) is confined to ultrathin films (~ 50 – 100 nm) on silicon wafer, it may crystallize into a dendrite or "seaweed"-like morphology similar to the morphology of PEO/PVPh (80/20) shown in Fig. 1. However, as the PEO films in their study were ultrathin, they were not able to correlate the PEO lamellae assembly to optical birefringence patterns as what we have demonstrated in Fig. 1.

The lamellae in these two opposite birefringence colors do not twist or flip from flat-on to edge-on; they are just oriented (or branch out at an angle) differently to assume opposite crystal axis and birefringence color as a result. With this in mind, one may ask whether similar morphological situation can exist in the opposite blue/orange ring-banded spherulites? We will show this is a very likely extension from alternating hedritic stripes to banded rings in spherulites.

Similar hedritic spherulites with opposite blue/orange stripes are also seen in poly(L-lactic acid) (PLLA) blended by mixing with 20 wt% atactic poly(methyl methacrylate) (aPMMA) [61]. A POM micrograph (upper side of figure) and three AFM images (lower side of figure) for crystallized PLLA/PMMA (80/20) at $T_c = 115$ °C is shown in Fig. 3. The fibrous lamellae with strong birefringence (orange-color dominated) in POM graphs are further revealed for clearer morphology using AFM phase imaging. Once again one sees that these fibrous lamellae are actually not all in the radial direction but have a habit of bending and intersecting perpendicularly, with the radially oriented lamellae and their bundles assuming the birefringence color

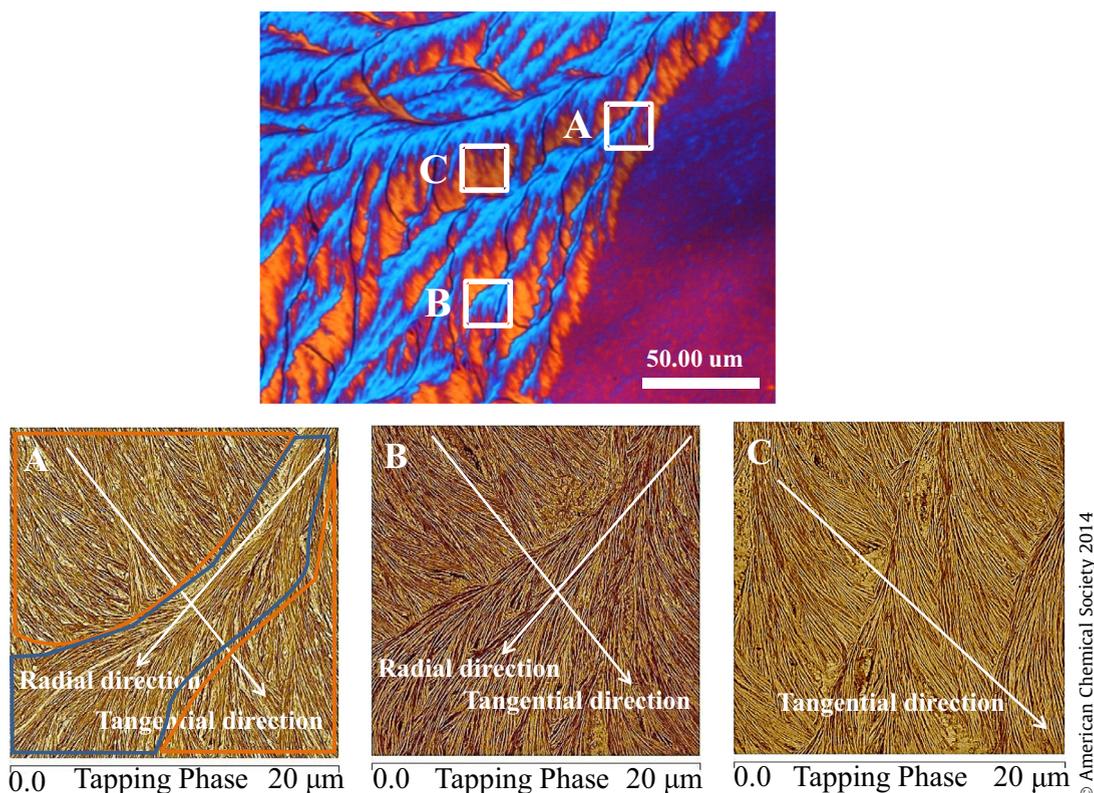


Fig. 3. POM (upper) and corresponding zoom-in AFM phase images (lower) by zooming into localized regions (square blocks-A, B, C) of colored stripes in POM graphs for spherulite of PLLA/aPMMA (80/20) melt-crystallized at $T_c = 115$ °C. Graph was re-produced with permission from Ref. [61]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of the spherulite quadrant, but the tangentially intersecting lamellae assuming the opposite color. Note also that the lamellae in blue and orange stripes are both fibrous from top view and they do not “spiral” or twist from one to another; they simply are branches mutually intersecting at approximately perpendicular orientations. This is a useful piece of information when later we go to examine the morphology of lamellae to prove how they assemble in alternating color ring-banded spherulites. That is to say, although continuous spiraling of a single-crystal plate from edge-on to flat-on is one way of reverting the optical birefringence in periodic pattern, it is not the only mean. Lamellar branches of same edge-on plates evolving or meeting at perpendicular orientations can display alternating birefringence colors. One even has to be more cautious that polymer spherulites in reality are generally not composed of single-crystal lamellae that spiral monotonously from the nuclei center to periphery. Rather, the lamellae more likely evolve into highly branched and curved geometry.

Most of the PLLA lamellae (Fig. 3) are branched and bent with curvature of either clockwise or counterclockwise direction. Although discussion on lamellae curvature is not the scope, it is noted here that hedritic spherulite with curvature are a common feature in many polymers including PLLA. Iwata et al. [62] in studying spherulites of stereo complex PLLA/PDLA have revealed that PLLA/PDLA blends with equivalent molecular weights, the straight-shaped edge-on lamellae were observed, while the direction of lamellar curvature in the polylactide (PLA) stereocomplexes with nonequivalent molecular weights is the same as that of PLLA having lower molecular weights.

3. Effects of solvent etching on distorting lamellae in ring-banded spherulites

Investigators probing correlations between ring-banded spherulites in polymers and crystal twists (or spirals) have always performed analyses based on characterization results on thin polymer films on substrates of glass or silicon wafers. To enhance the signals reaching the “interiors” of thin films on substrates, investigators sometimes perform sample etching by organic solvents. Many investigators claim to separate lamellae from spherulites by solvent etching, and obtain evidence of “twist” of lamellae after solvent treatments on crystallized samples showing ring-banded spherulites. Among several common solvents used by investigators for etching the crystals, methylamine (CH_3NH_2 , MA) perhaps is the one that may deliver the most obvious distortion of crystal forms and may also impose chemical changes in polymer chains. PEA and poly(3-hydroxybutyric acid-co-3-hydroxyvaleric acid) (PHBV) are two polymers that are widely studied for their ring-banded morphology and correlations with crystal twisting. We have proven in a recent work that exposure of polymers to MA liquid or vapor can completely change the chemical structures and altered the crystal forms of these aliphatic polyesters [63]. Fig. 4 demonstrates the effect of MA reactions on chemical and morphological alterations in crystal forms of three polyesters: PEA, PHBV, PTT, where POM graphs before and after MA exposures are compared. Crystals of aryl polymers (with benzene rings) such as poly(trimethylene terephthalate) (PTT) may be relatively less deformed, but minor extents of chain scission are still observed. Aliphatic polyesters such as PEA are much more susceptible to chemical reactions with MA, and as a result, the crystal morphology after MA exposure is completely changed. Fig. 5 shows POM and SEM graphs of PEA before (A, B) and after (C, D) MA etching. The original chemical and ring-banded crystal morphology of PEA (crystallized at

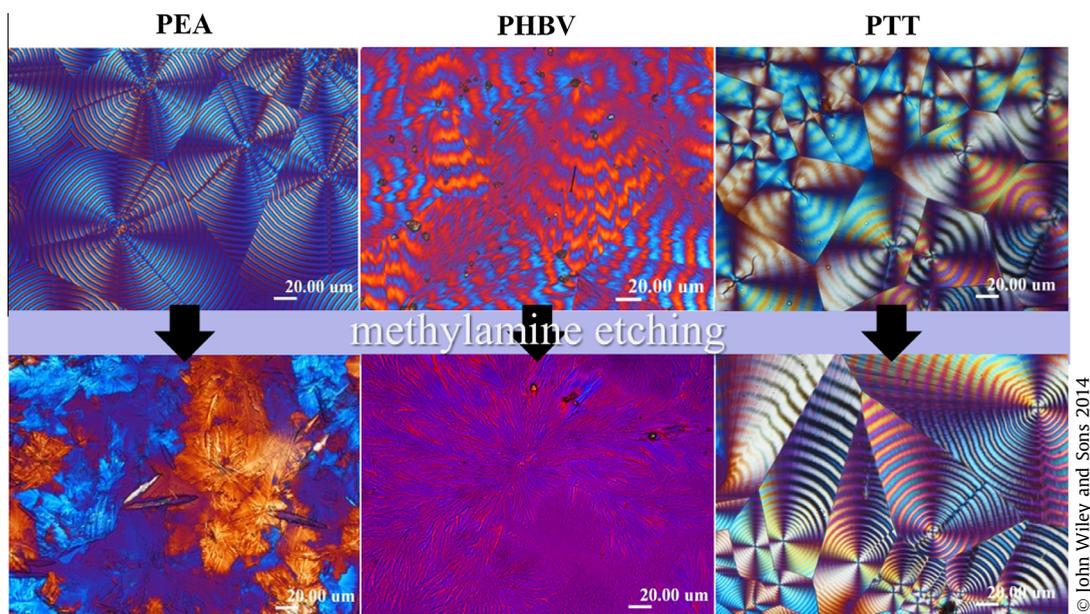
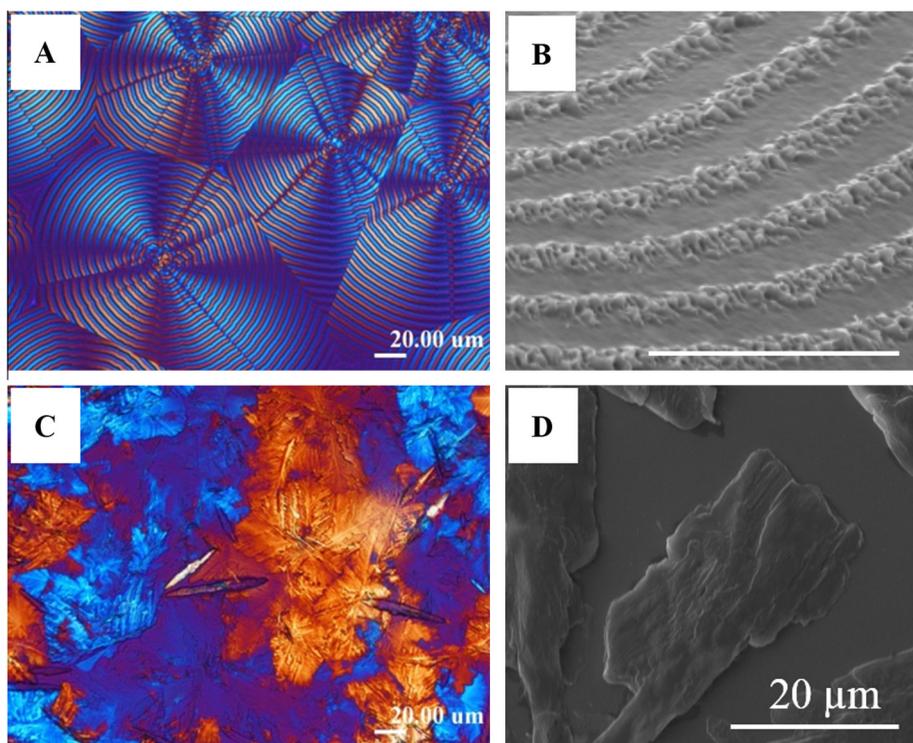


Fig. 4. Chemical and morphological alterations effected by methylamine reactions on Polyesters: PEA, PHBV, PTT. Top: before MA etching, bottom: after MA etching. Graphs are re-produced with permission from Ref. [63].



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Fig. 5. POM and SEM micrographs of neat PEA crystallized at 28 °C: (A and B) before etching, and (C and D) after MA-vapor etching for 24 h. Reproduced with permission from Ref. [63].

$T_c = 28$ °C) have been completely damaged by MA solvent exposure. The ring-bands in PEA crystallized at $T_c = 28$ °C are erased, as PEA has reacted with MA to become a different species. The SEM graphs clearly show that the original surface crystals forming ring bands are deformed after exposure to MA solvent. Similar changes are seen in PHBV after MA solvent exposure.

Wang et al. [64] ever discussed about evidence of twisting lamellae in poly(3-hydroxybutyric acid-co-3-hydroxyvaleric acid) (PHBV) using MA-vapor etching on crystallized lamellae, and claimed that the lamellar twist is responsible for ring bands. However, as discussed in Figs. 4 and 5, the chemical reactions between the MA-vapor and PHBV and resultant crystal deformation might have occurred, which was ignored in their interpretations. Methylamine by nature, like methyl alcohol and water, is a good solvent to many organic compounds including polymers. However, Gibbs [65] since a hundred years ago, has reported and cautioned that in addition to the outstanding solubility, MA also possesses capacity of reacting with many organic compounds into different chemical structures. Such reactivity of MA certainly may also involve many organic polymers. This caution on the reactivity of MA with organic compounds perhaps has gone unnoticed for hundred years. Many recent investigators used MA for etching polymer samples to expose lamellae behind the ring band patterns in crystallized spherulites, mistakenly believing that only physical etching took place in MA-etching, leaving the etched polymers chemically intact and unaltered. Results in Figs. 4 and 5, in support of the caution given by Gibbs [65], have pointed out the concerns in probing the evidence of crystal twists by using organic solvents such as MA on the surfaces of polymer samples. In short, one has to be cautious in dealing with validity of such evidence so obtained by chemical etching in studying ring-banded spherulites. Even without concern of chemical reactivity between the solvents and polymers, the physical alteration of stresses by exposure to solvents may also induce significant changes in crystal forms. As mentioned earlier, Huang et al. [3] have proven that the originally single crystals of straight-ribbon geometry of potassium salts of 3,4,9,10-perylene tetracarboxylic acid can be twisted into coils when dispersed in fluids that differentially solvate the surfaces. The coiling of originally straight single crystals is obviously induced by fluid exposure to cause unbalanced stresses across the originally straight crystals before fluid exposure. Chemical or solvent etching on ring-banded spherulites in crystallized polymer films can certainly induce similar effects. Care should be exercised to discern morphology changes by solvents.

4. Circular cracks accompanying ring bands in spherulites

One of the most puzzling phenomena in ring-banded spherulites of some polymers is that circular cracks may accompany the patterns of ring bands. The location of cracks approximately coincides with the borders between the “ridge” and “valley” of the ring bands. Woo et al have reported cracked and ring-banded PLLA and probed possible mechanisms and correlations

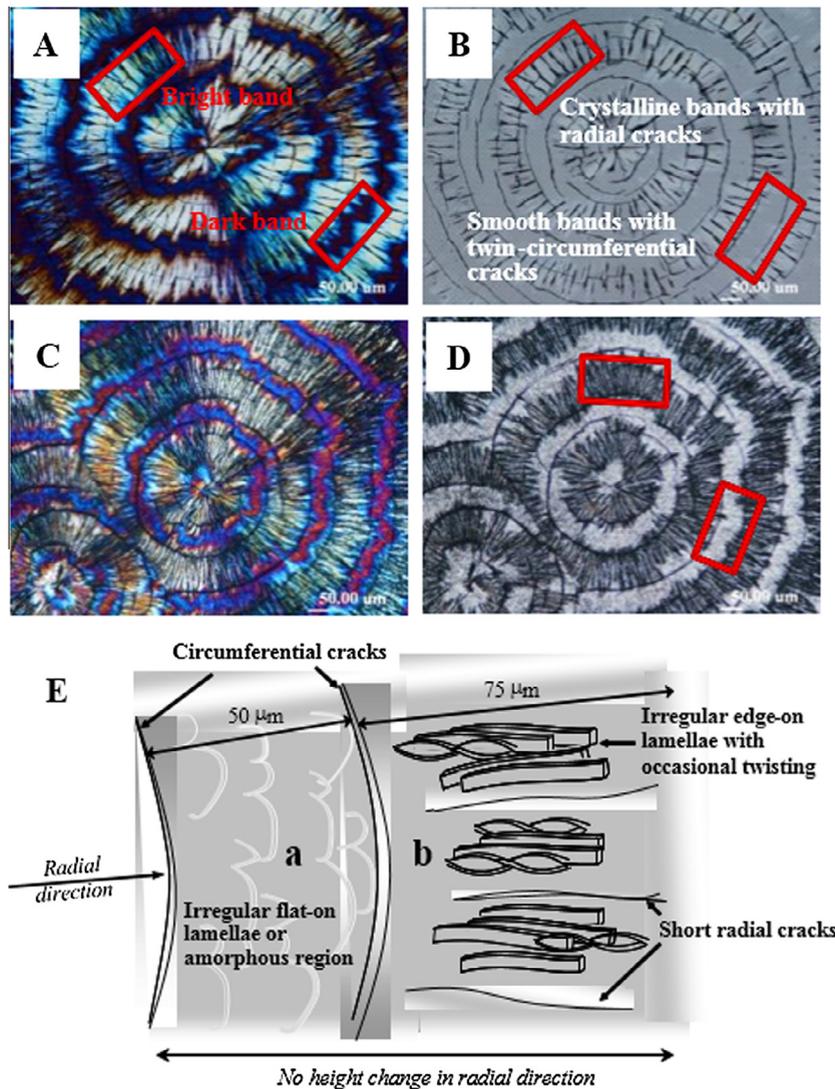


Fig. 6. POM (left column) and OM (right column) graphs of PLLA isothermally crystallized at 125 °C with a top cover for: (A) and (B) un-etched; (C) and (D) solvent-etched samples; (E) scheme illustration for alternating amorphous dark band (a) and crystalline bright band (b). Reproduced with permission from Ref. [66].

[66]. Fig. 6 shows POM (polarized) and OM (unpolarized-light) graphs of PLLA ($M_w = 11,000$ g/mol) crystallized at $T_c = 125$ °C and cooled to room temperature (28 °C) [film samples confined by top glass cover during crystallization]. Neat PLLA usually does not form ring bands, but it crystallizes into ring-banded spherulites in two conditions: (1) with top glass cover, or (2) blended with miscible diluents such as PEO [66]. Ring bands of large inter-ring spacing ($p = 75\text{--}100$ μm) and cracks of radial and circumferential orientations are apparent as shown in Fig. 6A in PLLA thin films crystallized at 125 °C with top glass cover. Typical ring bands in crystallized PLLA ($T_c = 125$ °C) are composed of a much large ridge band of 60–80 μm with blue birefringence color and a much narrower valley band of \sim ca. 20 μm with opposite orange birefringence color. The large pitch (or inter-ring spacing) is equal to the total width of ridge + valley bands = ca. 75–100 μm (depending on T_c). A simple helical twist of lamellae would create symmetric ridge and valley bands in roughly equal portions; by contrast, the highly asymmetric thick ridge band vs. thin valley band in ring-banded PLLA spherulites are seen. In later discussion, we will further demonstrate with proven results that the large PLLA lamellae of top surface of spherulites in thin films take an up-and-down wavy to create the alternating ring bands, and not helical twisting by using AFM height analysis. That is, not only the ridge and valley bands in the large-pitch PLLA spherulites are highly unmatched in the ridge/valley band widths, but there is no gradual modulation of birefringence colors across the pitch. The second main characteristic of PLLA spherulites is that two types of cracks are present accompanying the ring-banded patterns. Short radial cracks and long circumferential cracks are visible in the OM graphs (Fig. 6B). These cracks are not random or sporadic, but all oriented almost exactly according to the ordered patterns of the ring bands. The short radial cracks are confined within the ridge bands; and the long circular cracks

border between the valley and ridge bands. On the other hand, if PLLA is crystallized into ringless patterns (with no top cover, at $T_c = 120, 125, 130, 135$ °C), crystallized PLLA films upon cooling still develop cracks but these cracks in the ringless PLLA spherulites are irregular with no fixed patterns. Apparently, the long continuous circumferential and short radial cracks in ring-banded PLLA spherulites are attributed to different origins from those in the ringless spherulites. Why do the circumferential cracks accompany the ring bands of PLLA spherulites and tend to locate in the transitions between the ridge and valley bands? There must be weak interfaces between lamellae of different orientations. In addition to the clearly established correlations between the crack patterns and ring bands in PLLA, Woo et al. [66] have also proved in the work that the crack depth is approaching the film thickness, with the crevices going all the way from top-surface to touching the glass substrate. That is to say, the lamellae in ring-banded spherulites are cracked into periodic discontinuity and the lamellae may not be continuous from nuclei to periphery. In addition, the scission of lamellae coincides with the periodic valley-ridge interfaces. This would be puzzling and hard to comprehend from the points of views of continuously spiral lamellae extending from center to edge of spherulites. If the classical Keith-Padden's proposal [15,16], i.e., lamellae continuously spiral as single crystals all in synchronizing pace (i.e., edge-on gradually twisting to flat-on, back and forth) is used to create the ring bands in crystallized PLLA, then why are there circular cracks that form a sharp and sudden segregations of the supposedly continuously spiraling lamellae? In principle, cracks are expected to be located in the interfaces of crystals or in stress-concentrated areas. For continuous single-crystal-like spiraling lamellae (if were true), there may be radial interfaces between the neighboring long lamellae plates; but there should be no tangential interfaces in the long continuous crystals. Additionally, if there are twisting stresses in the continuous spirals, they should be averaged out in the spiral length, and not concentrated as a sharp border between the valley and ridge. The sharp-border circumferential cracks most likely suggest that there are interfaces of crystals of different species between the ridges and valleys. This is exemplified in a preliminary scheme (Fig. 6E) showing different crystal species meeting at interfaces. More details mechanisms for lamellae assembly accounting for the ring-banded PLLA spherulites are to be discussed later in 3D interior dissection.

In addition, the optical birefringence colors in the long-pitch PLLA crystals are examined to evaluate if there is color modulation in accordance with the gradual rotation. Recently, Kahr et al. in a review article [1] commented on one of compounds with spiral crystals originally prepared from hippuric acid by Bernauer [2], where the crystals grew from melts originally as flat ribbons. They showed that between crossed polarizers, the spiraling crystal ribbons of uniform thickness show a remarkable progression of dark bands to colors of all spectrums that correspond optic axes rotating around the [100] axis, etc. [67], and the gradual rotation around the [100] axis in spiral hippuric acid creates transitional modulation covering all optical birefringence colors. However, by contrast, in all ring-banded spherulites of PLLA, the birefringence color transition in the ridge and valley is usually abrupt with a sharp border and not gradual shifting that is expected with a continuous spiral. This observation (sharp abrupt transition) is also reflected in the crack behavior of the ring-banded PLLA spherulites, whose inter-ring spacing is very long up to 75–100 μm . Unlike the short pitches in some polymers such as PE or PEA, the long "pitch" in PLLA spherulites is supposedly sufficient for resolving the optical spectrums of various colors, but the fact is that no gradual transition of all birefringence colors is seen in ring-banded PLLA spherulites. The twisted single crystals of hippuric acid can show the gradual modulation of the interference colors across the twist pitch [4], but PLLA crystals, if indeed continuously twisting like the hippuric acid crystals, do not show similar modulation of optical birefringence colors expected for gradual rotation with axis of 360° in one pitch). There must be some good reasons. As mentioned earlier, plausible answers are hard or impossible to get if one only examines the ring bands of polymers only from the top surfaces and does not open up and analyzes the fine interiors of the PLLA lamellae to find out how the lamellae actually assemble themselves in forming these ring bands as seen in PLLA spherulites.

5. Interior lamellae in large-pitch ring bands

The very long pitch ($p = 75\text{--}100$ μm , inter-ring spacing between two neighboring ridges of the bands) of crystallized PLLA ($M_w = 11,000$ g/mol) makes it a perfect model for proving or disproving whether or not the mechanism of continuous spiral lamellae works to create the periodic ring bands. For other polymers such as PE or PEA, the inter-ring spacing is 3 or 6 μm , respectively. One full turn (if spiral works) is completed in the short length of 3 or 6 μm , or half-turn from edge-on to flat-on orientations is half of the pitches (1.5 or 3 μm), which makes it hard or impossible to evaluate transitions, if any, even by microbeam size of 1–2 μm from the modern synchrotron X-ray sources [it should be noted that further reduction of micro-beam diameter is physically possible, but intensity may be too strong to cause melting or chemical degradation of polymers]. Ambiguity originating from the very short inter-ring spacing in most ring-banded polymers is one of main reasons that arguments on crystal spirals and ring bands continue since 1950s.

The very large pitch of 75–100 μm in ring-banded PLLA spherulites is a completely different situation. For probing the interior lamellae morphology of large-pitch PLLA ring-banded spherulites, water-soluble polymer PEO was used for blending with PLLA (50:50 by weight). The reason that PEO was used for probing the interior PLLA lamellae was two folds: (1) PEO is miscible with PLLA and acts as diluent to induce orderly ring bands in PLLA, and (2) PEO is easily water soluble and can be readily etched out from the PLLA lamellae without risk of deforming the crystal shape. A recent work [43] attempted to resolve the puzzle of large-pitch PLLA spherulites by using PEO/PLLA mixtures that are crystallized in films with some thickness (10–20 μm) and the crystallized films show apparent ring bands. Etching out the PEO component from the interior of PLLA lamellae creates a pseudo-3D construction. Fig. 7 shows (A) POM graph of PLLA/PEO (50/50) crystallized at $T_c = 110$ °C,

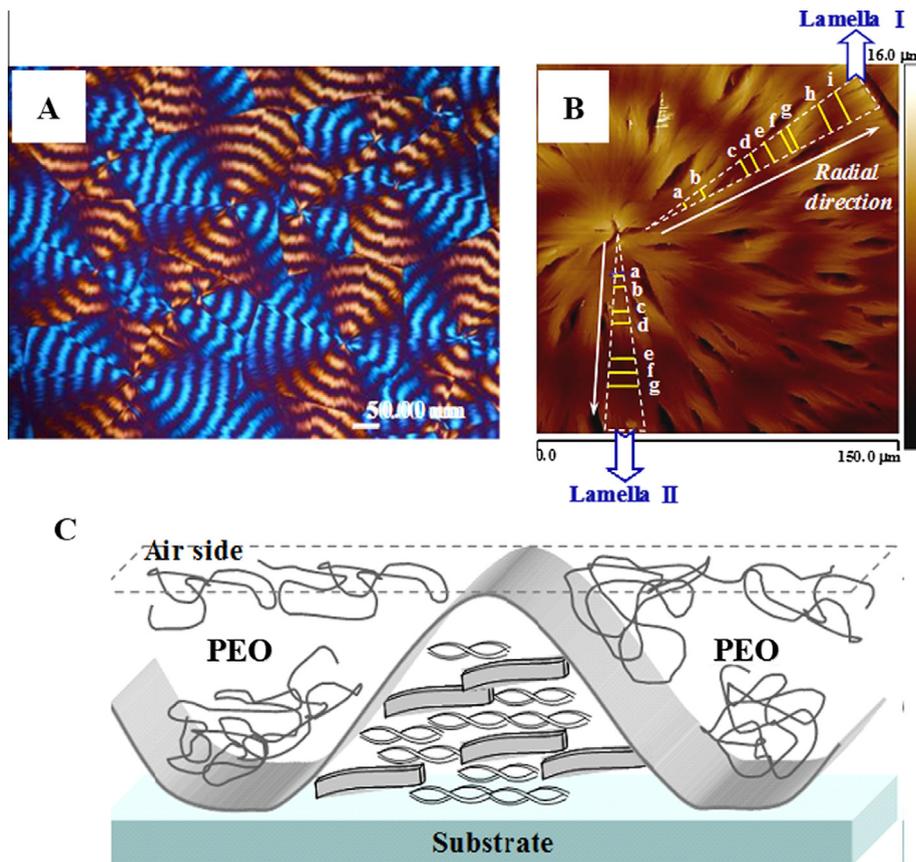


Fig. 7. (A) POM graph, (B) AFM height image on a single spherulite in water-etched PEO/PLLA = 50/50 blend crystallized at 110 °C. Two discrete macro-lamellae (I, II) marked for height profile analysis, and (C) scheme for crystal species in large-pitch ring bands. Reproduced with permission from Ref. [43]. Copyright (2012) Elsevier.

(B) AFM height image, and (C) schematic illustration of large-pitch ring bands in PLLA from the interior morphology analyses. The band spacing in PLLA/PEO (50/5) crystallized at 110 °C is ca. 50 μm from the POM graph. The AFM height profiles (Fig. 7B) as above prove beyond doubt that the outer lamellae do not spiral across the entire length, but they go periodic up and down waving and the waving pitch (50 μm) exactly matches the optical birefringence inter-ring distance (50 μm). The top-layer lamellae, from the AFM height analyses, wave up and down in the radial direction with no or very little tilting/spiraling in the transverse direction (scheme in Fig. 7C). Furthermore, the interiors lamellae, after etching out the water-soluble PEO, are revealed that in the cavities underneath or between the top waving lamellae, there are smaller lamellae (micro-lamellae) that twist, bend to different angles from the top lamellae. However, the twist/spiral pitches of these smaller lamellae are much smaller and in order of magnitude do not match the optical birefringence band spacing seen in POM morphologies. These twist/bend lamellae underneath the waving lamellae are actually crystal branches that grow from the main waving lamellae.

More advanced analyses on interior of lamellae in ring-banded spherulites with crack patterns of crystallized PLLA/PEO mixtures have yielded critical evidence on understanding not only the true mechanism of ring band formation, but also how and why cracks (radial and circumferential types) accompany and follow the ring band patterns [67]. Fig. 8 shows SEM graphs of the fractured and water-etched interiors of PEO/PLLA (50/50) blend also expose interesting correlations between the lamellar plates and crack orientations. Interior lamellae assembly is also exposed for clear correlation with the ring band patterns on the top surface. Lenticular-shape radial cracks are visible only on the ridge band (bulge band) of spherulites on the top surface and are oriented in the radial direction. The ridge band is composed of parallel lamellae plates that are perpendicular to top surface of polymer films; thus, cracks between the parallel edge-on crystals are visible (in SEM graphs) on the ridge band. The schemes in Fig. 8E and F reflect the actual fractured morphology in SEM graphs, which clearly show that voids are not only on the top surface but also on the hidden interior exposed by the fracture surface, as indicated by the arrow marks. On the other hand, with increasing PEO contents in PEO/PLLA blends, the water-etched PEO/PLLA (70/30, 80/20, and 90/10) blends exhibit more irregular twisting PLLA micro-lamellae, resembling seaweeds. Crystal twists are seen; however, the twists are a result of branching lamellae taking a different orientation to fill the space. The optical pitch of 70–100 μm is not due to lamellae twist along [100] axis.

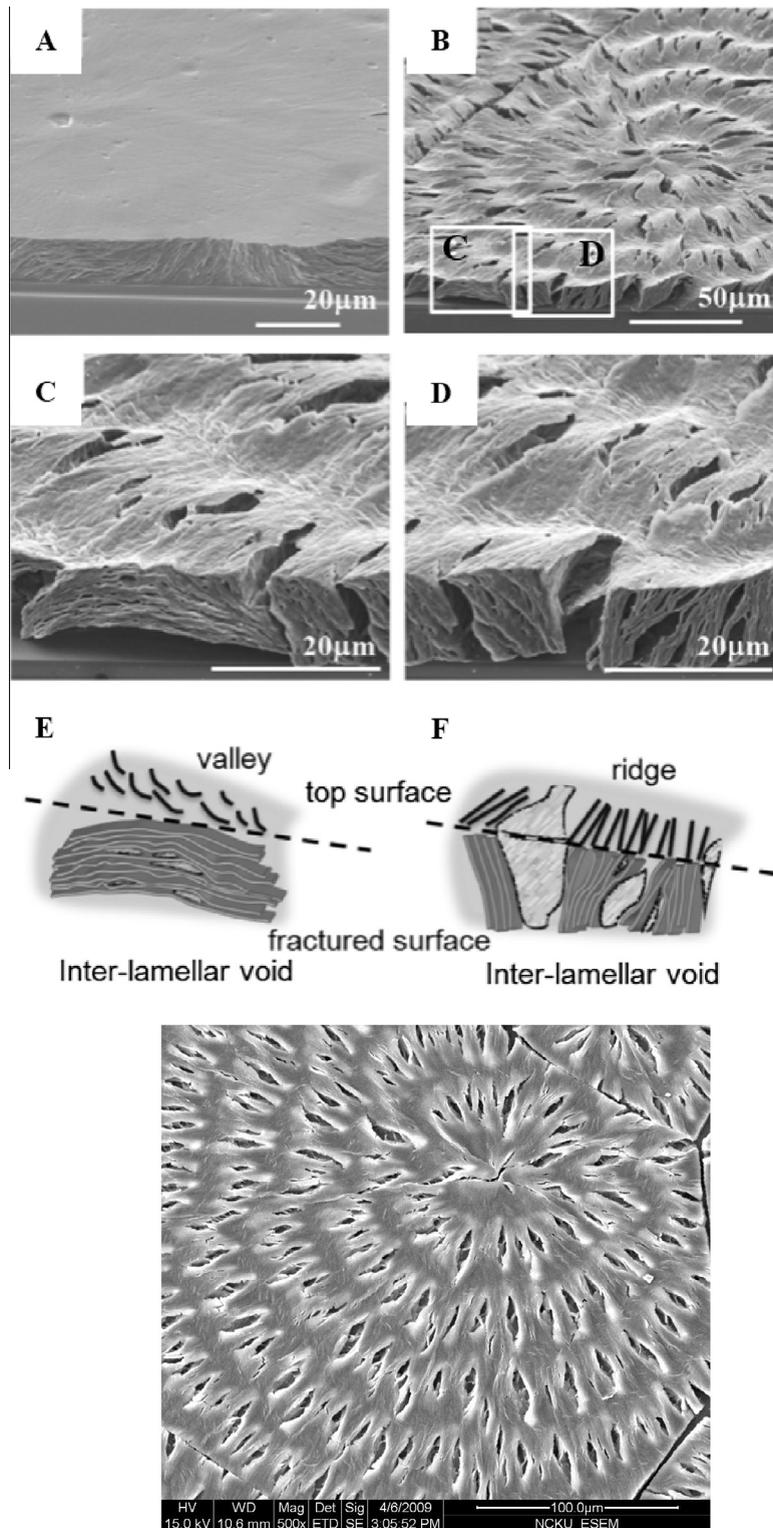


Fig. 8. SEM graphs for fractured surface of PEO/PLLA (50/50) blends crystallized at $T_c = 110^\circ\text{C}$ then cooled to ambient temperature ($25\text{--}28^\circ\text{C}$) of: (A) unetched sample, (B) water etched sample, (C) zoom-in valley "Region-C", (D) zoom-in ridge "Region-D". (E) and (F) are schemes for PLLA micro-lamellae at valley and ridge, respectively. Reproduced with permission from Ref. [67].

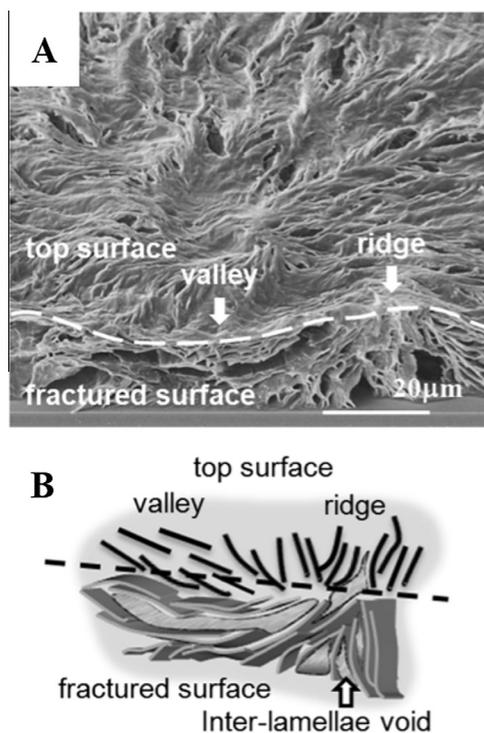


Fig. 9. SEM graph (A) and scheme (B) for fractured interior lamellae of water-etched PEO/PLLA (70/30) blend crystallized at $T_c = 110^\circ\text{C}$ then cooled to ambient temperature. Reproduced with permission from Ref. [67].

The top surface of ring banded PLLA/PEO (50/50) shows radial cracks only in the ridge band, and no cracks are visible in the valley band. Detailed SEM analysis on the interior lamellar morphology of the water-etched PEO/PLLA blends reveals that the lamellae orientation in PLLA spherulites is highly correlated with the crack patterns. Radial cracks are present on the ridge band (see SEM graph in Fig. 8D or scheme in Fig. 8F) because the multiple layers lamellae of polycrystals are mostly edge-on. Conversely, in the valley band, lamellae of polycrystals are oriented flat-on. There are still cracks (oriented in circumferential direction) in the valley band (see SEM graph in Fig. 8C or scheme in Fig. 8E), but they are sandwiched between the flat-on lamellae in the valley, thus the cracks in the valley band are not visible from the top surfaces. The observations on the lamellae assembly differences in the ridge and valley bands, however, summarize that one does not see a single-crystal lamella rotating as a helice continuously from the nuclei center to the periphery of spherulite to induce the periodic ridge-valley bands. Rather, the lamellae are polycrystals like multi-layer card-boards, which collectively are assembled in edge-on orientation in the ridge band. The valley-band lamellae, as side branches from the ridge-band lamellae, are assembled collectively in flat-on orientation. It is also very apparent that if analyses were restricted only on the top-surface morphology of crystallized PLLA/PEO (50/50) films, it would have been impossible to reveal such critical evidence for ring-banded PLLA spherulites.

As the PEO content is further increased to much higher than 50 wt%, say 70–90 wt%, the PEO/PLLA (70/30 or 90/10) mixture, upon crystallized at 110°C (or any other T_c 's) no longer maintains an ordered ring-band pattern like those in PEO/PLLA (50/50) mixture. Instead, there are irregularly positioned bulge (ridge) vs. concave (valley) regions in the spherulites of crystallized PEO/PLLA (70/30) films. Cracks are also irregularly distributed on the top surface of crystallized spherulites [67]. Interior morphology can be exposed by fracturing across the thickness of crystallized PEO/PLLA (70/30, 80/20, 90/10) mixtures prepared as films with convenient thickness (20–40 μm), followed by scanning electron microscopy (SEM) characterization. For brevity, only one representative composition (PEO/PLLA = 70/30) is discussed here. Fig. 9 shows SEM graph (A) and an illustrative scheme (B) for the interior lamellae of water-etched PEO/PLLA (70/30) blend crystallized at $T_c = 110^\circ\text{C}$ then cooled to ambient temperature. The lamellae on the top surface of spherulite appears to irregularly twist and bend. There are no longer continuous ring bands, but only irregular spots of bulges vs. concave regions. Similar interior analyses reveal that the lamellae on the bulge spots of spherulites are packed with edge-on polycrystals while the concave regions are packed with flat-on polycrystals. All are polycrystals and the cracks are on top surface of the bulge spots, and no surface cracks are seen on the concave regions. However, the fractured interior (SEM graph – bottom portion of Fig. 9A) clearly reveals circumference-oriented cracks sandwiched between flat-on lamellae. Once again, in this ringless (or highly frustrated bulge-concave topology), there are no single-crystal lamella rotating as a helice continuously. The flat-on polycrystal lamellae appear to be branches growing from the edge-on lamellae that are also multi-layer polycrystals (Fig. 9B). Without

opening up the interior for analyses, the top-surface morphology (upper portion of Fig. 9A) of ring-banded PEO/PLLA (70/30) may mask the real inner crystal morphology responsible for the ring bands, thus likely leading to erroneous interpretations from analytical methods based on even modern advanced instrumentation. Top-surface crystal morphology can be oppositely or dramatically different from the crystal assembly hidden underneath the outer thin layers.

6. Spiral lamellae along ring bands in circumferential direction – Discontinuity between bands

The first study revealing interfacing discontinuous boundaries between subsequent ring bands in polymer spherulites appeared in a series of work by Woo et al. since 2008 to date [38–42]. In 2012, the most convincing evidence of discontinuity in lamellae first appeared in the literature from a work on PEA by Woo et al. [14], which was obtained via analysis on interior of PEA crystal lamellae (crystallized at $T_c = 28\text{--}30\text{ }^\circ\text{C}$ with distinct and orderly ring bands) that clearly display mutually perpendicular orientations, i.e., a corrugated structure resembling onion cross section. This view of discontinuity, as demonstrated in PEA ring banded spherulites [14], directly challenged the conventional models of continuous helical twist of lamellae in constituting the ring bands. It is worthy to bring up a few recent studies emphasizing the fact of discontinuity between subsequent bands in ring-banded spherulites. Schultz, in a recent 2013 publication [68], re-examined the old AFM images of 3-hydroxybutyrate-co-3-hydroxyhexanoate (PHBH) from their previous study in 2004 [69], and concluded that twisting is not continuous, but rather occurs quite suddenly and in an unexpected manner. In 2004, Schultz and his coworkers claimed in conclusion that “the lamellae change their orientation via continuous twisting” with some screw dislocation in PHBH [69]; oppositely, in 2013 re-visit of the original AFM data of the same PHBH system, he reverted the conventional continuous opinion to that discontinuity may exist in the bands [68]. This case also demonstrates that findings can be also generated by re-analyses of past work. Schultz in the 2013 re-visit work [68] mentioned that what observed does not accord with any extant models of crystal twisting. There are three items that they have noted: (1) the change in orientation of the growing lamellar ribbons is sudden, from edge-on to face-on; (2) the newly reoriented ribbon grows both forward and backward; (3) the tips of the newly reoriented lamellae eventually bifurcate forming giant screw dislocations. Simultaneous growth in that forward direction and backward is impossible unless the original lamellae spawn new subsidiary lamellae which can grow in both directions. In line with the work on the proven corrugate-board discontinuity in ring-banded spherulites of PEA in 2012 [14], an yet another study by Woo et al. [70] on ring-banded poly(3-hydroxybutyric acid-co-3-hydroxyvaleric acid) in clearer way has revealed that there are two opposite lamellae orientations in the ridge and valley band. Again, the lamellae transition with interfaces between the ridge to valley bands in PHBV [70], like what proven in PEA [14], is not in accord with the gradual and continuous rotation (from nuclei center to periphery) into helices and defied the conventional model proposals since 1950s.

The interior dissection of lamellae fully exposes that the opposite intersection of two crystal species is a result of inter-play between the main lamella and branching crystals, where the side branches are oriented to an almost perpendicular direction from main lamellae. Poly(3-hydroxybutyric acid-co-3-hydroxyvaleric acid) (PHBV with PHV = 12 wt%) was blended with poly(vinyl acetate) (PVAc), and composition was fixed at PHBV/PVAc (70/30 = wt. ratio), as this composition showed the most pronounced and well-ordered ring bands in spherulites. Films of PHBV/PVAc (70/30) blend were prepared by solution blending using chloroform (CHCl_3) as the medium. Fig. 10 shows POM micrographs (A, B) of ring-banded films; SEM morphology for top-surface ring bands (C, D) and fracture interior (E, F) in correlation with the top-surface ring bands of PHBV/PVAc (70/30) blend film (thickness ca. 10 μm) crystallized at $T_c = 110\text{ }^\circ\text{C}$ [70]. Effects of film thickness on the crystalline morphology are significant as very thin films ($\sim 1\text{ }\mu\text{m}$ or lower) of PHBV/PVAc blend show no ring bands at all, while PHBV/PVAc (70/30) films of thickness of 5–20 μm easily crystallize into ring-banded spherulites at $T_c = 100\text{--}130\text{ }^\circ\text{C}$. Note that ring bands can also exist in thicker films (30–50 μm) or even bulk form of PHBV/PVAc, but not by observation using optical microscopy as light does not penetrate into thicker crystallized films. Ring bands in thick bulks (30 μm or more) of PHBV/PVAc blend can be identified by SEM on the outer surfaces or fractured interiors. There is critical evidence that should be pointed out here. First, the inter-ring spacing is ca. 10–12 μm for ring bands at $T_c = 100\text{ }^\circ\text{C}$ (Fig. 10A), or 18–20 μm for ring bands at $T_c = 110\text{ }^\circ\text{C}$ (Fig. 10B) [inter-ring spacing was estimated from the scale bar]. By further examining the POM graphs of ring bands of spherulites at $T_c = 100\text{ }^\circ\text{C}$, in Fig. 10A, apparently, the rings are not concentric with respect to a common center; instead, the rings in PHBV/PVAc are spirals of S-shape or inverted S-shape (like the pattern of spiraling snail shell viewed from top). That is, spirals of both clockwise and counterclockwise turns are co-existent. Note that these types of spirals along the rings are different from the spiral sense in the Keith-Padden’s original proposal [15,16] (as discussed in Introduction), where they claimed lamellae spiral synchronizingly from a common center to edge of spherulites to form helices in radial direction. The SEM graphs in Fig. 10 are even more striking in giving new interpretation of ring bands. Between the two consecutive ridge bands (black arrows, with inter-ring spacing ca. 20 μm for $T_c = 110\text{ }^\circ\text{C}$), there exists a smaller bulge ring (white arrows) in the middle of the valley band. Do not mistake this smaller bulge ring as another ridge band. From the inter-ring spacing clearly suggested by the POM birefringence color bands, the inter-ring spacing is ca. 20 μm ; but the inter-spacing between the smaller bulge rings and the true ridge ring (thicker bulges) is only ca. 9 μm . Thus, the position analysis proves that that smaller bulge ring is in the valley band. More strikingly, the lamellae in the thicker ridge bands take a spiral twist along the ring direction in clockwise sense; however, more intriguingly, the crystals in the smaller bulge ring (in the valley band) also take a spiral twist pattern, but aligned in opposite counter-clockwise sense. That is, the PHBV lamellae twist along the circular ring bands and not in the radial direction.

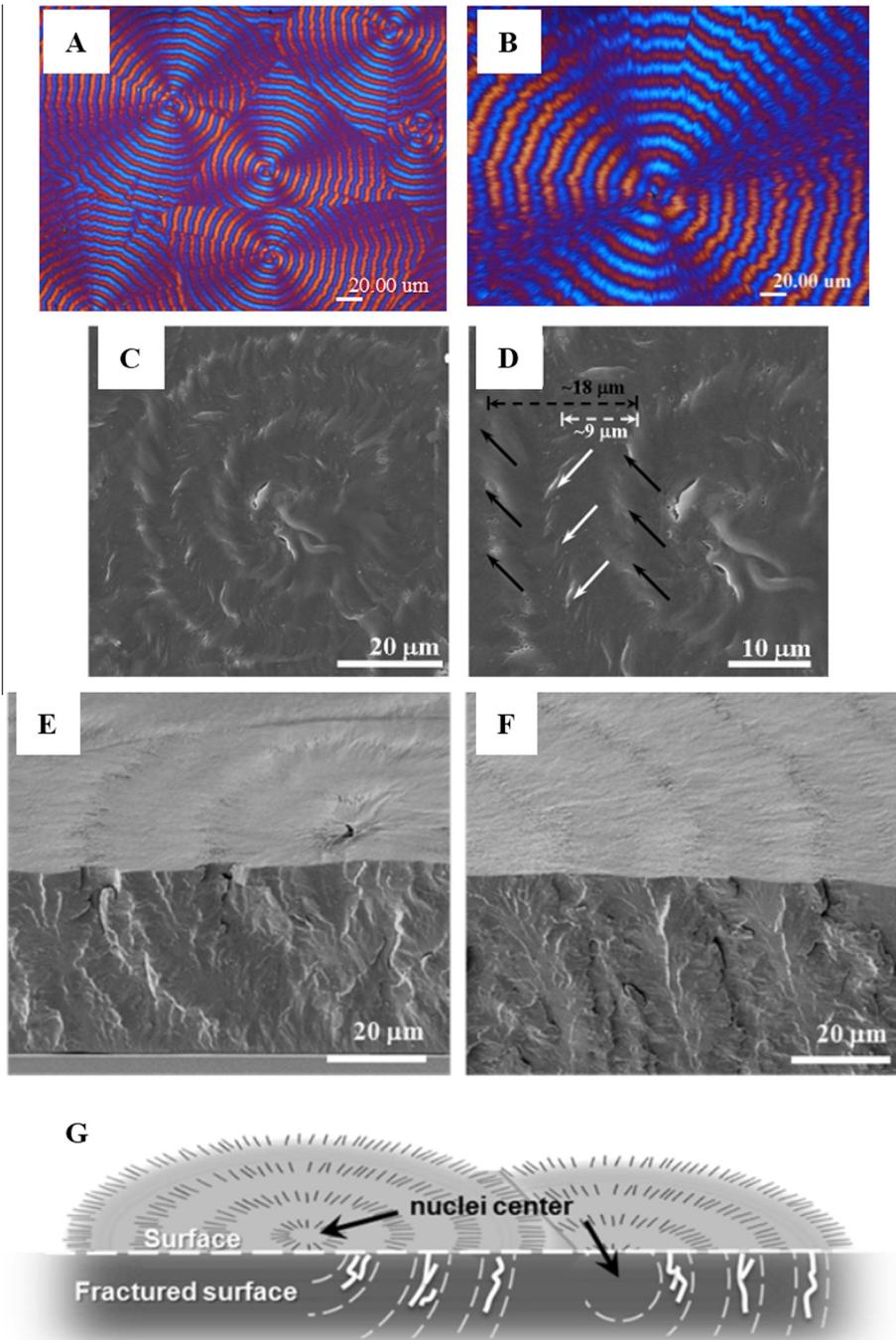


Fig. 10. POM micrograph (A and B); SEM morphology for (C and D) top-surface of ring-banded spherulites of solvent-etched PHBV/PVAc (70/30) isothermally crystallized at 110 °C, (E and F) fracture interior in correlation with the top-surface ring bands; and (G) scheme illustrated the correlation between top and fracture surfaces. PHBV with HV = 12 wt%. Reproduced from Ref. [70] with permission from the PCCP Owner Societies.

How could this morphology be interpreted? This would be an impossible phenomenon if one attempts to interpret such ring-band morphology according to the conventional Keith-Padden model [15,16]. According to the KP spiral model, the valley should be the location where radially-rotating spiral lamellae make a downward turn and there should be no bulge ring in the valley band at all. One will be lost and keeps on guessing all possibilities if just viewing and analyzing the top surfaces of thin-film samples of PHBV/PVAc that displays a small bulge ring in the valley band sandwiched by two much higher ridge bands. Further complexity is that the lamellae on the ridge bands appear to spiral along the ring of the ridge in clockwise

direction, but lamellae in the small bulge on midline of the valley band appear to spiral along the mid-line of the valley band but in opposite direction (counter-clockwise) [see SEM graphs in Fig. 10]. This peculiar morphology in PHBV/PVAc would have remained a mystery forever, even though analyses had attempted to perform etching procedures to peel off the top layers of ring-banded PHBV. A main key point to be solved is what crystal morphology is underneath the higher ridge bands and what is under the smaller bulge ring in mid-line of the valley band to account for the patterns seen in the top surfaces?

Extreme care is needed to analyze the seemingly “spiral” lamellae along the ridge band (black-arrow marked) and oppositely “spiral lamellae” (white-arrow marked) along the thin midline of the valley band (Fig. 10D) in ring-banded PHBV/PVAc. There must be some critical facts of lamellae assembly hidden underneath the top surface of ring-banded PHBV/PVAc (70/30) blend showing a smaller bulge ring between two consecutive ridge rings, and the lamellae in the smaller bulge ring in the valley bands are aligned oppositely to the lamellae in the ridge bands (clockwise vs. counter-clockwise). Opening the interiors and dissecting into the inner lamellae hidden under the top surface would provide a straightforward analysis. The bottom graphs (E, F) and schemes (G) for fractured interiors of ring-banded PHBV/PVAc (70/30, $T_c = 110^\circ\text{C}$) spherulites in Fig. 10 clearly demonstrate such critical evidence necessary to interpret the seemingly peculiar morphology that has never been seen or reported before. On the top surface of the spherulites (Fig. 10C and D), ring bands are apparent, with two ridge bands sandwiching a valley band. Peculiarly, a smaller bulge ring is located in the midline of the valley band. The inter-ring spacing (from centerline of ridge band to next ridge band) for PHBV/PVAc (70/30, $T_c = 110^\circ\text{C}$) is ca. $20\ \mu\text{m}$ (see scale bar). The fractured surfaces (Fig. 10E and F) reveal amazingly novel results that have never been reported for ring-banded spherulites, to be described as follows. Directly underneath the small bulge (in midline of the valley band), there is a tangentially oriented lamella (perpendicular to the top-surface). These tangential lamellae (brighter crystals in SEM graphs) point roughly upward to top surface but are curved into gentle arc-shape owing to grow into a sphere. The tangential lamellae (pointing upward) reach to the top exterior surface to become smaller bulge in the midline of the valley. In between the tangential lamellae (brighter crystals), feather-like branch crystals evolve at an angle (ca. 60°) to the tangential lamellae to fill the space between the tangential lamellae. As branching grows on both sides of the tangential lamellae, the branching crystals grow on both sides of the tangential lamella and impinge on the midway with the branching crystals from another neighboring tangential lamella. This impingement of branching crystals from both sides occurs in the interior as well as the top surface. On the top surface, the branching feather-like crystals impinge and bulge into periodic ridge bands, just like mutual crush of two earth tectonic plates to create a raised mountain in geology. Thus, underneath the valley band of top surface, there is a tangential lamella in interior of ring-banded spherulites; meanwhile, underneath the ridge bands of top surface, there are feather-like branching crystals (oriented $60\text{--}90^\circ$ to the tangential lamellae) growing to meet and impinge each other. The crystal axes of the tangential lamellae and branching crystals differ by an almost perpendicular angle ($60\text{--}90^\circ$), thus resulting in the observed blue/orange birefringence rings in POM graphs.

Fig. 11 further shows AFM (A) and POM (B) graphs for top-surface of ring-banded spherulites in PHBV/PVME ($T_c = 110^\circ\text{C}$, top surfaces slightly etched using water/acetone solvent). The AFM image of PHBV/PVME (70/30) top surface reveals similar characteristics as seen earlier in SEM micrographs (Fig. 10). The AFM images reveal seemingly spiral lamellae extending out from the band, and lamellae appear to bulge out in the ridge band, but the lamellae then swing the tips to opposite direction as they slope down and there exist a thinner crystal band in the mid-line of the valley band. The POM graph (Fig. 11B) shows clearly the ring bands are not concentric sharing a same common center; instead, the bands are actually composed of two helicoids (like a flattened spiral snail shell). From only the top views on the outer surface of the ring bands, lamellae appear to be “spiral” in the radial direction and these crystals on ridge and valley bands appear to be “helicoidal” along the rings in opposite clockwise vs. counter-clockwise directions. But once again, these views on top surface of thin films might involve many overlooked problems. The interior lamellae and their assembly would totally override the seemingly justified interpretations based on top-surface morphology. As discussed earlier, the top-surface morphology of ring-banded spherulites can be

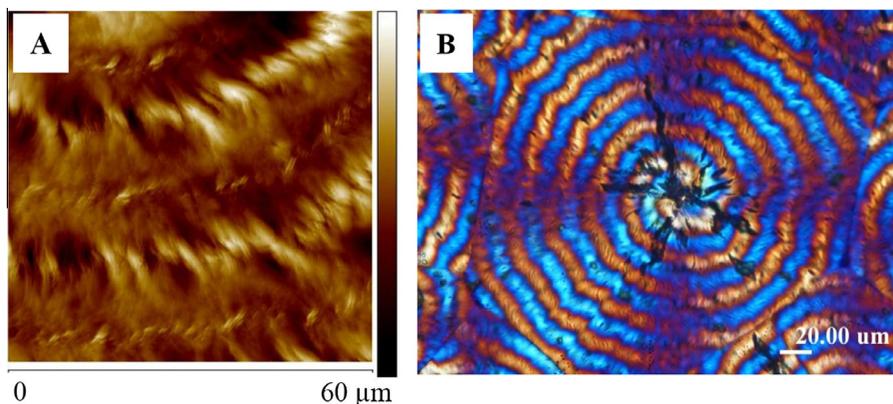


Fig. 11. AFM image (A) and corresponding POM micrograph (B) for top-surface ring-banded spherulites of solvent-etched PHBV/PVAc (70/30) isothermally crystallized at 110°C after etching with water/acetone = 1/3.

tangential lamellae do not emerge to the top surface to become the “ridge band”; oppositely, it is the impingement and perhaps compounded with some complex twist/bend of the branching crystals on the top surface (60–90° angle to the tangential lamellae) that create the “ridge band. The tangential lamellae mainly are located directly underneath the valley bands; but they do come up to the top surface to form a smaller bulge on midline of the valley band. This lamellae assembly may be contrary to intuition of continuous spiral, but this is the true fact from the dissected morphology of interiors, at least for the case of crystallized PHBV/PVAc ($T_c = 110^\circ\text{C}$). This mechanism of perpendicular lamellae in PHBV/PVAc also fully accounts for the fact that spherulites are composed of polycrystals with branches as spherulites grow outward. More importantly, the mutually perpendicular orientations of the tangential lamellae and branching feather-like crystals (pointing 60–90° to the tangential lamellae) nicely account for another fact that the birefringence color takes abrupt transition from the blue to orange bands in POM (Fig. 10), rather than gradual modulation into birefringence distribution that should be expected in gradually rotating helices.

7. Thickness effect on ring-band patterns

Ringless PLLA spherulites are resulted if the film thickness is kept at 10–20 μm (by drip coating of 4 wt% PLLA in chloroform) and crystallized at $T_c = 112^\circ\text{C}$. However, when the same PLLA polymer is made into thin enough (300 nm–2 μm , by spin-coating at control spin speeds), it may develop concentric ring bands of no alternating birefringence colors but with apparently periodic height alteration. PLLA ($M_w = 11,000$ g/mol) samples of two thickness levels were prepared by solution casting and spin coating using chloroform as solvent with concentration of 2 wt%. A drop of solution of the polymer was deposited and uniformly spread on a micro glass slide at 45°C and the solvent was allowed to fully evaporate in an atmosphere. Thin-film samples of PLLA were prepared by spin coating of PLLA solution onto glass slides using a spin coater (Chemat Technology Spin-Coater KW-4A) at 3500 rpm for 40 s. The film thickness prepared by solution casting or spin coating is about 1800–2000 nm and 350–400 nm, respectively. Concentric ring-banded spherulites of thin poly(L-lactic acid) (PLLA) films have been observed via melt-crystallization at $T_c = 112^\circ\text{C}$ from 350 up to 2000 nm of film thickness. The POM graphs in Fig. 12 clearly demonstrate that by controlling the film thickness, non-birefringent or birefringent concentric ring-banded spherulites can be obtained. More strikingly, the ring patterns (shape and inter-ring spacing, etc.) differ in a systematic trend according to variation of film thickness [45]. The shape of concentric rings changes from hexagon to circular shape as thickness is increased from 400 nm to 800 nm, and birefringence color becomes more apparent with film thickness at 2000 nm (2 μm) or more. However, there is a narrow range of film thickness for displaying such concentric ring bands in crystallized PLLA films. Eventually, as the film thickness exceeds 3 μm , the concentric ring bands completely disappear abruptly and the spherulites become ringless. AFM image analyses (Fig. 12-bottom) reveal that the “ridge band” of such concentric ring bands is composed of all flat-on lamellae while the “valley band” is not really a “band”, but just a sharp and narrow boundary between two wide ridge bands where the flat-on lamellae drop collectively and suddenly to nearly the glass substrate (according to the height profile analysis). The AFM height profile analysis also reveals that the all flat-on lamellae in the ridge band rise gradually at the beginning of the band, to a maximum tip, then drop suddenly to near the glass substrate with an asymmetric parabola shape [45] from lateral view. That is, no spiral twists are seen in AFM analyses on the concentric ring bands in PLLA films with thickness of 400–2000 nm. All lamellae are flat-on in the ridge band, but crevices are in the “valley band”.

There are two critical pieces of evidence that can be derived from the ring-banded spherulites in thin PLLA films: (1) lamellae on the ridge band are all flat-on and height analysis reveals no gradual twist into helices, (2) the up-and-down profile across the bands assumes an asymmetric parabola. Thus, once again, the morphological evidence of this special type of concentric ring bands (crystallized from thin PLLA films) suggests a lamella assembly that totally contradicts the vision based on classical models of gradual helical twist of a single lamella in creating the ring-banded spherulites. In the concentric ring bands of thin-film PLLA, the lamellae on the ridge bands are all flat-on with no twisting (AFM height profiles), and the ridge

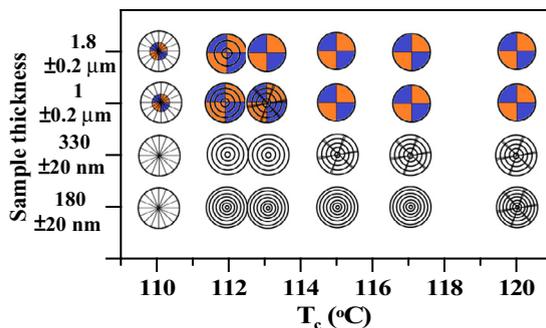


Fig. 13. Schematic diagrams to illustrate the effect of T_c and sample film thickness on ring band patterns or formation of either ringless or ring-banded spherulites (polymer = PLLA, $M_n = 11,000$ g/mol). Diagrams re-schemed from corresponding POM and AFM analyses.

bands are packed with crystals but the sharp narrow valley bands are just a narrow crevice (AFM phase image) where the flat-on lamellae drop periodically before rising again in next cycles. AFM analyses with height profiling capacity on twist curvature and height variation, unavailable in classical time, unambiguously reveal that these flat-on lamellae on the wide ridge bands remain flat and untwisted in the four zones of the ridge bands: beginning, middle, maximum peak and final sudden drop [45]. The “valley” is a narrow crevice with no crystals, and it is actually the interface boundary between two subsequent wide ridge bands. This kind of band patterns in thin crystallized PLLA films (400–2000 nm) [45] suggests that kinetics of diffusion and crystallization growth takes a similar route (periodic draining of species) as the factors controlling the formation of the classical Liesegang rings [13]. The thickness of the films determines the duration of growth and chain species draining duration, and thus, it also determines the width of the ridge band (Fig. 12 shows the thicker the films, the wider the ridge band – up to 2000 nm thickness). As the PLLA film thickness exceeds 3 μm (3000 nm), diffusion may no longer be a factor; thus, no concentric ring bands develop in the crystallized PLLA films thicker than 3 μm [45]. This unique type of concentric ring bands in thin films (400–2000 nm) of neat PLLA, as demonstrated in Fig. 12, is very different in nature of crystal assembly and optical birefringence from the ring bands of alternating blue/orange birefringence seen in thicker films (10–20 μm) or bulk forms of PLLA/PEO or PHBV/PVAc blends as discussed earlier in Figs. 10 and 11.

Effects of both film thickness and crystallization temperature (T_c) can be collectively summarized in schematic diagrams in Fig. 13 for PLLA ($M_n = 11,000$ g/mol). The diagrams in the figure show spherulite patterns as functions of both film thickness and T_c . The T_c window for formation of the concentric ring bands is restricted to occur between $T_c = 112$ to 120 $^\circ\text{C}$. If T_c is kept at 112 $^\circ\text{C}$ (the lowest bound of T_c for ring bands), the ring bands patterns vary systematically with film thickness. At very low film thickness (180 nm) with $T_c = 112$ $^\circ\text{C}$, the concentric ring bands in PLLA are of a very narrow inter-ring spacing and bands have no birefringence contrast (but height of valley and ridge bands is clearly discernible in AFM images). At higher film thickness (300–400 nm), the band inter-spacing increases proportionally to the film thickness, and the concentric ring bands in PLLA are still of no birefringence contrast. Finally, at film thickness of 1.0–1.8 μm , the band inter-spacing keeps increasing proportionally to the film thickness, but the concentric ring bands in PLLA are now with apparent birefringence contrast with a distinct narrow extinction between the bands (the narrow extinction is now understood by AFM analysis to be sharp crevice with no crystals owing to sudden drop of lamellae to glass substrate). In general, at film thickness exceeding 1 μm and T_c greater than 112 $^\circ\text{C}$, the PLLA spherulites become ringless with no concentric ring bands at all. Rings or no rings, as well as the banding patterns of ring bands, all vary with film thickness and T_c , indicating kinetics and growth rates of spherulites, as controlled by film thickness and T_c dictate whether or not concentric ring bands can form. Collectively, the evidence of the lamellae assembly and corresponding interior or top-surface morphology summarized in Figs. 10–13 all points out that mechanisms for probing origins of ring bands may vary with respect to different types of ring bands in spherulites. A single model based on only analyses of top-surface morphology of thin-film samples may lose critical opportunities of viewing the entirely diversified ways of crystal packing into ring bands that differ in nature and vary in interior lamellae assembly.

8. Diversified types of ring bands in same polymers

Classical work on ring bands in polymers usually assumed that one single type of ring bands can be present in polymers, such as PE, PEA, and PBA. However, in reality, one of the most striking features in ring-banded behavior of polymers is that a same polymer, in various thickness or compositions with other diluents, can exhibit different types of ring bands that vary in nature and characteristics. This feature also makes it hard to justify that there is one single mechanism universally responsible for all these widely different types of ring bands. Poly(ϵ -caprolactone) (PCL) does not form ring bands when crystallized at any T_c in neat forms (unblended, undiluted) with the normal thickness range (5–20 μm) that displays clear optical birefringence contrasts in POM. However, as PCL is made into very thin (nanometers to less than one micrometer), concentric ring bands (band spacing ca. 4 μm) of closely packed concentric rings but with periphery resembling camellia-flower patterns are present in crystallized PCL films on silicon substrates [71]. Wang et al. [71] investigated PCL in thin films with such ring bands (crystallized/dried at room temperature 20 $^\circ\text{C}$, thickness = 200–300 nm), and attribute such concentric ring bands to a cause of diffusion and growth, which is basically the same controlling factor described by Liesegang [13] one hundred years ago for reactants diffusing in gels to form Liesegang ring bands. Note also that such ring bands in the PCL thin films (200–300 nm) are similar in nature and patterns as those reported in more classical studies on iPS thin films [53,54]. For crystallized PCL thin films, Wang et al. [71] also reported a band-to-nonband transition that is observed above a threshold growth rate, and this leads to occurrence of a band-nonband composite morphology of PCL crystals (with the banded region on central portion and the non-banded region on periphery region of spherulites). The banded region is composed of mainly flat-on lamellae, while the non-banded region is composed of edge-on (tilted) lamellae. Therefore, once again, such ring bands in PCL thin films certainly cannot be described by lamellae continuous rotation/twist spirals to form alternating ring bands, as the banded region in PCL spherulites is packed only by flat-on lamellae. It is not until the non-banded region in PCL spherulites that lamellae are tilted into edge-on. The morphology of all flat-on lamellae on ring bands is similar to that in PLLA thin films as well [45].

Thus, PCL, when confined to very thin thickness (200–300 nm), develops the ring bands described as being controlled by a rhythmic growth-diffusion mechanism; however, the same PCL polymer does not form any ring bands when film thickness is increased to 10–20 μm where optical birefringence is clearly discernible in POM. This behavior in PCL thin films of 200–

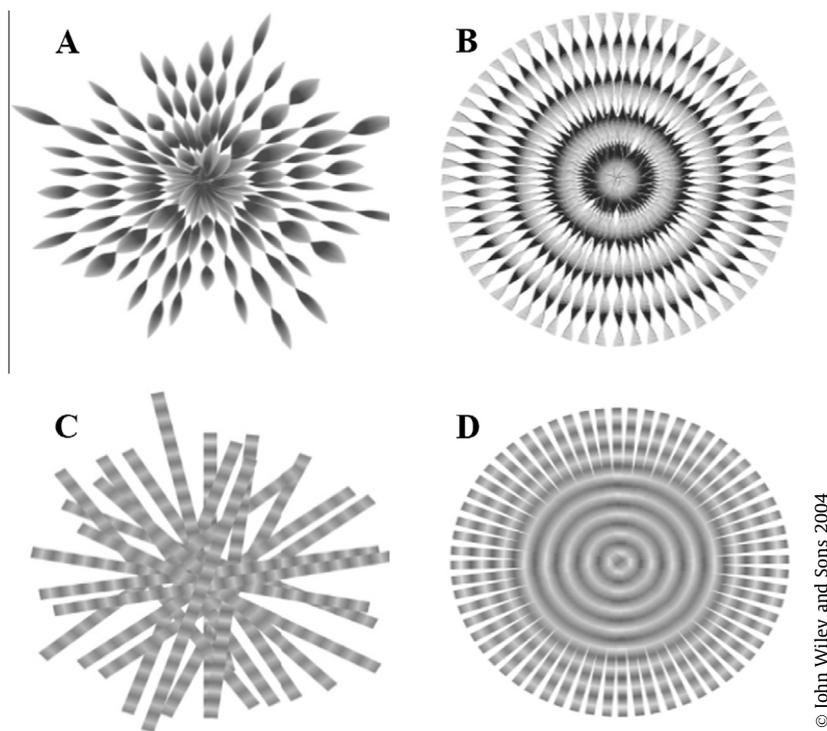


Fig. 14. Schemes for 2D ring bands from: (A) all spiraling lamellae from a common nuclei center with offset paces, (B) all spiraling lamellae from a common nuclei center with synchronized paces; (C) all flat-on lamellae from a common nuclei center with non-synchronized wavy up-and-down paces, (D) all flat-on lamellae from a common nuclei center with synchronized wavy up-and-down paces. Reproduced with permission from Ref. [37].

300 nm [71] is similar to that of PLLA thin films below 2000 nm thickness [45]. Apparently, for different polymers, the thickness range within which such non-birefringence concentric ring bands would develop is different.

It may be theorized that both confinement of thin-film thickness and mixing with diluents are potential kinetics factors that drive mechanisms of appearance or absence of ring bands in polymer spherulites. Film thickness and presence of diluents (solvents, polymers, or additives) tend to change the diffusing rate vs. growth rate during polymer crystallization. Furthermore, regardless of the types of ring bands in polymers developed from various different conditions (diluents, thickness, chemical structures), it is critical to remind a generalized behavior, which is that ring bands always occur in crystallization at relatively high degree of super-cooling. The extent of super-cooling required for banding may differ among polymers; but for banding to occur, it has always to be at a substantial degree of supercooling. For banding to appear in polyethylene (PE), the supercooling degree is 30 °C or more (within a range). For PHB or PHBV, the supercooling is ca. 30–50 °C (ring-band patterns may vary with supercooling). Similar observations apply to other polymers with ring bands. That is, if polymers are crystallized at temperatures extremely near their T_m , no ring bands appear; and the resulted spherulites will always be ringless (usually dendrites or hedrites, or even single crystals). Therefore, ring bands in polymers are associated with crystallization growth kinetics as one of main influencing factors. Perhaps, at extremely lower supercooling, i.e., higher T_c close to T_m , the growth rate is low while the species diffusing rate is comparatively high enough to supply polymer chains to crystals with no periodic interruption.

9. Discrepancy between pitches for spiral lamellae and optical inter-ring spacing

What types of lamellae assembly can possibly pack into periodic ring bands in spherulites? In the two-dimensional (2D) plane of thin films, there are several ways leading to either ordered or slightly disordered rings (with zig-zag patterns). Fig. 14 shows four schemes of ribbon-like (single-crystal) lamellae that are packed to form ring-banded spherulites in 2D thin films. The four schemes depict that waving lamellae, regardless spiral or non-spiral, all synchronizing from a common center, can generate periodic patterns on the top surface of 2D thin films. Specifically, Scheme-A and Scheme-B depict ring bands by all spiraling lamellae from a common nucleus center. The irregular pattern is due to offset paces of spiraling lamellae (Scheme-A), only fully synchronized paces will generate ordered ring patterns (Scheme-B). All flat-on lamellae in up-and-down waving growth can also generate bands. Scheme-C shows all flat-on lamellae from a common nucleus center with non-synchronized wavy up-and-down paces, and scheme-D is generated with synchronized wavy up-and-down paces. All these models and their resulted ring bands assume that the polymer lamellae are single-crystal like, with no branches as they grow; and they only spiral or wave up and down monotonously. Apparently, by disregarding the crystal

birefringence, there are several ways, and not just spiral, for lamellae to pack into ring bands in 2D thin films. Certainly, there may be yet other more intriguing ways, yet still undiscovered by investigators so far, of packing into ring bands as seen in the POM patterns. However, these models might have been over-simplified and some problems were overlooked. One of the main problems is that the polymer lamellae are not single crystals with no branches in spherulites. Furthermore, what forces are in polymer crystal lamellae responsible for holding the lamellae in continuous spirals, and for synchronizing the rotations all in paces to form concentric rings? Bassett [20] has shown in an assessment on polymer spherulites (banded or ringless) that the spherulites are complicated polycrystals and that numerous branches evolve from main lamellae with branching angle between adjacent dominant lamellae indicating local forces. Later forming secondary or infilling lamellae grow within the framework of dominant lamellae, but often at an angle to it so that they are differently oriented to applied stresses and so liable to deform in different ways. It is particularly worthy to note (Fig. 12 SEM micrograph in Ref. [20] – Bassett, 2007), which shows the interior of a linear polyethylene (PE) spherulite crystallized at $T_c = 128^\circ\text{C}$ demonstrating three regions of main lamellae vs. branches: (A) the long and diverging dominant lamellae, (B) the shorter subsidiary lamellae growing from them, and (C) infilling lamellae. As a matter of fact, Figs. 13–15 of the same Bassett's work [20] also clearly demonstrate that the crystals in the ring bands are full of subsidiary branches (twist/bend as fibrillar crystals) generated from the main lamellae. This beautiful SEM result on crystallized PE by Bassett in 2007 have clearly demonstrated that crystallized PE spherulites and the crystals in the ridge or valley bands are not by single-crystals at all. Collectively, in either non-banded or ring-banded PE spherulites, the PE lamellae are not single-crystal lamellae doing monotonous and synchronizing rotations. This observation can be similarly seen in many other polymers. Such accurate description on growth of polymer spherulites suggests that the single-crystal scheme in spherulites, either banded or ringless, may be over-simplified to lose the reality. Classical models of lamellae twist based on the assumption of single-crystal like crystal plates in polycrystalline polymer spherulites need to check against this experimental fact.

However, the schemes in Fig. 14 only demonstrate possibilities in top-view on 2-D thin films. Possibilities of lamellae assembly into periodic bands in interior 3D bulk of spherulites actually are more and usually overlooked by most investigators. Problems overlooked for crystal assembly in ring-banded spherulites are not just what discussed in the previous schemes for 2D patterns. Furthermore, one cannot expect that all ring-banded spherulites only grow in 2D thin films on glass or silicon wafer substrates. What will happen if the single-crystalline spiral lamellae grow in 3D spheres (in most bulk polymers) in thicker or bulk forms? Questions arise: how do the single-crystal lamellae spiral “synchronizingly” when they evolve from the nucleation center to “create” ring bands in 3D spherulites? Fig. 15 shows a scheme revealing possible 3D screw-like spirals from a common nuclei center. A series of questions arise. In 3D space, these spiral single-crystal lamellae cannot possibly form a synchronized up-and-down ring band as these spirals reach the outer surface; instead, they will be individual dots of the crystal tips. Additionally, as single-crystal lamellae undergo spirals with no branches, there will be even much larger crevices in the outer peripheries – which are of course opposite to the common facts seen in all polymer spherulites. On the other hand, if numerous branches grow extensively along the spiraling lamellae, then the entire pictures will be beyond what possibly can be described by the simple Keith-Padden model for ring bands. Additionally, all single crystals and their branches will point to different solid angles; so how do they synchronize to create “ring bands” in 3D space? In polycrystalline spherulites, it may be just too over-simplified to assume that the spiraling lamellae rotate and maintain

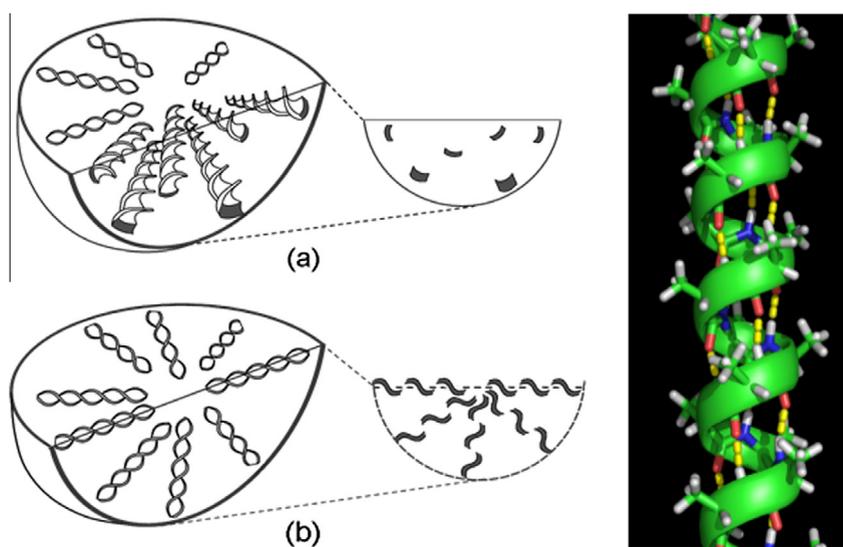


Fig. 15. Scheme for 3D spiral lamellae in constructing a ring-banded spherulite. Inset to the right is a model for an alpha-helix with hydrogen bonds (yellow dots) by Zsolt Bikadi [commons.wikimedia.org/wiki/File:Alpha_helix.png]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

“single crystals” and twist continuously from the nuclei center all the way to periphery without any branching as they grow – This is opposite to the findings so far in all spherulites.

Inset to the right side of the 3D scheme for spiral crystal lamellae in Fig. 15 is a molecular model for alpha keratins – protein molecule – are amply determined to have an alpha-helix (spiral) structure, formed of repeating 7 amino acids' residue fragments. The spiral shape in alpha-keratin is known to be held by regular intra-chain H-bonding, as shown in the scheme inset. Since Keith-Padden's proposal in 1950s attributing the ring bands in PE to a possible cause of spiral lamellae, numerous researchers have dwelled on searching for evidence of spiraling lamellae that resemble spiraling molecules such as alpha-keratin shown as inset on right side of the figure. For spiral protein molecules, there are strong hydrogen-bonding forces in precise monomer sequences to hold the shapes in stable forms; by contrast, for polymer crystals, there are none of such forces. Chain-folding in polymers was proposed as a cause to induce unbalanced surface stresses as a plausible reason for spirals of lamellae [22]. In an elegant argument about possibility of single-crystal lamellae twist for bands [22], Lotz and Cheng examined the factors that induce lamellar twist, by also taking into account the rather contradictory experimental findings, and suggested possible means to approach molecular insights on the origin of the lamellar twist. In the review article [22], they presented a few cases of TEM evidence of spiraling single-crystal lamellae, such as polyethylene or polyesters, with periodicity pitch ranging from 500 nm (PE) to 1.5 μm (polyester), reported in the literature. They, however, did not comment on the facts that these periodicity values are far different from and do not match the optical inter-ring spacing in these polymers. They concluded polymer chain-fold induced surface stresses were responsible for the scrolling. However, same scrolling single-crystal lamellae are also amply reported in the literature for small-molecule compounds [1]. Chain folding is absent in crystals of small-molecule compounds; but same ring bands and same scrolling/bending/twist lamellae can also occur in many small-molecule crystals. This fact suggests that if indeed stresses are responsible for crystal twists, the crystal twists are not necessarily from chain-folding stresses.

In addition, there may be some overlooked problems in attributing the lamellae spirals to chain-folding stresses. Chain folding in lamellae of polymers is long proven to be not all regular adjacent re-entry. There have been numerous classical studies on polymer chain folding, and it is not the scopes of this article to cite all here. For just one example, a classical study on PE single crystals by Sadler and Keller [72] has suggested that model for regular adjacent re-entry of chain folding does not correlate with experiments. Without regular re-entry of chain folding, it certainly would be difficult to expect stresses generated from numerous types of chain folding – if indeed present – to be consistent enough for holding the spirals in regularly rotating shape. Furthermore, one has to prove two critical aspects beyond spiral lamellae: (1) that all crystals twist and rotate in synchronizing paces to create ring bands, and (2) that the pitch of spirals exactly matches inter-ring spacing observed in optical birefringence patterns for ring-banded spherulites. Proofs and evidence for these two aspects of spiral/twist in lamellae may not be easy tasks.

As mentioned in Introduction, many small-molecule compounds and their crystals also show same ring bands as polymers do. In the meantime, lamellae scrolling into spiral shapes are also demonstrated in many small-molecule compounds [1]. Historically, there have been many attempts trying to retrieve lamellae from ring-banded spherulites and proving their spiral shapes, either by microtoming specimens from polymer films then TEM characterization, solvent-etching thin films and characterization using AFM or SEM, or directing X-ray micro-beam on thin polymer films with ring-banded patterns, etc. Thus, it is critical to prove that not only polymer lamellae may scroll (by whatever causes), but the periodicity of spirals should support the observed optical inter-ring banding. However, in the past 60 years, although there have been reports attempting to prove that polymer lamellae do twists, like the many demonstrated occurrences in small-molecule compounds, there has been no direct evidence showing lamellae spiral pitches matching optical inter-ring spacing. The following literature surveys summarize the discrepancies between the optical pitch and TEM evidence presented for “spiral lamellae”. For classical PE ring bands, the POM inter-ring space is known to be $\sim 4 \mu\text{m}$. Numerous investigators attempted to search evidence of lamellae spirals in past 60 years. Keller and Sawada did an early work on digging into interior of bulk PE in 1964 [73], and reported ring-banded PE with optical inter-ring ca. $4 \mu\text{m}$ and lamella spiral pitch using TEM to be ca. $\sim 1 \mu\text{m}$ (shown in Figs. 21, 23, and 24 of Ref. [73]). The mismatching discrepancy between the optical ring spacing and TEM spiral pitch is about $4 \mu\text{m}/1 \mu\text{m} = 4$ times. Additionally, Kunz et al. in 1995 [74] presented morphology of screw-like PE lamellae using TEM, and they claimed a spiral pitch to be ca. $\sim 100 \text{ nm}$ (shown in Fig. 4 of Ref. [74]), which is far different from the results of lamellar spiral of $1 \mu\text{m}$ reported earlier by Keller and Sawada [73]. The discrepancy between the optical ring spacing and TEM lamella spiral pitch (in Kunz et al.'s work) is about $4 \mu\text{m}/100 \text{ nm} = 40$ times for PE. This discrepancy is 10 times even much larger than the Keller and Sawada's work on PE 30 years ago in 1964. PLLA, when blended or blocked with other amorphous polymers, easily shows ring-banded spherulites at $T_c = 110 \text{ }^\circ\text{C}$. A study by Chao and Ho et al. [75] on polystyrene-PLLA block copolymer showed optical inter-ring space being ca. $\sim 30 \mu\text{m}$, but the TEM result of the same publication indicated lamellae spiral with a pitch ca. $\sim 100 \text{ nm}$ (shown in Figs. 5 and 9 of Ref. [75]). Thus, the discrepancy between the optical inter-ring space and TEM characterization on lamellae spiral pitch is about $30 \mu\text{m}/100 \text{ nm} = 300$ times for ring-banded PS-PLLA block copolymer. This is a very significant disagreement between the TEM result and optical ring patterns. Poly(trimethylene terephthalate) (PTT) is also a widely studied subject for ring-banded spherulites. For PTT, the optical inter-ring space (ring-banded spherulites as seen in POM graphs) is known to be ca. $\sim 5 \mu\text{m}$ (varying slightly with T_c up to ca. $10 \mu\text{m}$). Wang et al. [33] showed the lamellae spiral pitch in PTT using TEM analysis to be ca. $\sim 100 \text{ nm}$ or less (shown in Figs. 3 and 10 of Ref. [33]). Thus, the discrepancy between the optical ring space and TEM lamellae pitch in Wang et al.'s study is $5 \mu\text{m}/100 \text{ nm} = 50$ times, or up to 100 times for ring-banded PTT. In addition, Maillard and Prud'homme [76] studied PLLA in ultrathin films (15 nm) and tried to correlate chain chirality to physical origins of lamellae curvature. They

showed the lamellae of PLLA in ultrathin films (15 nm) can exhibit various scrolling, twisting, or bending into S-shape (PLLA), or Z-shape (PDLA) curved edge-on lamellae, along with straight branched dendrites, but no continuously spiraling lamellae are present in the specimens. However, their aim was not to search for relationships of spiraling lamellae and ring bands in PLLA, as in such ultrathin films of polymers, there would be no ring bands. These C- or S-shape lamellae most likely are associated with nuclei crystals that eventually will grow to complete spherulites if film thickness is sufficient. As a matter of fact, it has been long known that polymers displaying banded spherulites also show C- (Z-shape) or S-shape lamellae, according to Bassett and Hodge's study on PE in 1978 [77]. It is a critical question to answer how and why the crystal lamellae starting at a central point finally grow to form a circular-shape spherulite, with or without ring bands. In addition to the extension of initial dominant lamellae (either Z- or S-shape), there must be branching and spraying that accompany growth of dominant lamellae, just like the shish-kebab structures in classical PE or other polymers. This fact further suggests that monotonous growth of lamellae in a long spiral form to fill spherulite may not be realistic, and alternative views must be attempted. The key is to probe how they evolve, and the issues remain still highly debated.

PHBV shows ring-band optical patterns similar to PHB, but the former has a much larger inter-ring spacing ($\sim 60\text{--}70\ \mu\text{m}$ at $T_c = 90\ ^\circ\text{C}$ for PHBV with 12 mol% HV) than the latter. In 2010, Wang et al. [64] used a methylamine (MA) etching technique in searching for evidence of spiral lamellae in ring-banded PHBV, and they claimed to find evidence of lamellae spirals in MA-etched PHBV. We have earlier discussed that MA can chemically alter the structures and physically distort the PHBV crystals significantly [63]. By disregarding the MA's effects on chemical changes in PHBV, Wang's study [64] showed SEM results for MA-etched PHBV lamellae that assumed a spiral conformation with spiral pitches equal to ca. 20, 10, 25, and 30 μm (estimated from the scale bars) for PHBV with HV = 0, 8, 12, and 40 HV mol%, respectively (shown in Figs. 1 and 3 of Ref. [64]). Not only the lamellae spiral pitches irregularly vary with the HV contents in PHBV, but none of the reported spiral pitches (20, 10, 25, or 30 μm , respectively) did not match the known optical ring spacing for PHBV (60–70 μm). It should also be emphatically pointed out here that the lamellae of top surface of PHBV (upper 1 or 2 microns of films of ca. 10–20 μm) of ring-banded PHBV in Wang et al.'s study [64] may indeed show spiral rotation like single crystals as revealed by SEM characterization; however, the interior crystals directly underneath the top-surface are dramatically different from what is viewed on top. If one examines the morphology of ring-banded spherulites of PHBV/PVAc blend (PHBV with HV = 12%) in Fig. 10, it is clear that the top-surface bands are where the interior lamellae emerge out and that the "spiral lamellae" on the thin mid-line of the valley bands are actually the tips of the inner tangential lamellae emerging to the top surface and accordingly, the "spiral lamellae" on the ridge bands are the branching lamellae that emerge to the surface and impinge each other. Wang et al.'s work [64] showed single-crystal-like lamellae (10 μm in width and 100–300 μm in length) spiraling on top surfaces of PHBV films (after etching); however, the inner crystals underneath the ring bands are actually polycrystals with a highly branched structure (Fig. 10). Once again, the comparisons affirm that views restricted to characterization/analyses on the top-surfaces of ring-banded polymer films, especially after chemical etching and crystal distortion, may be entirely different from the interior crystal assembly and likely misleading. In addition, Cheng et al. [78] showed nice spiral lamellae in synthesized polyesters with chirality and varying methylene unit length $-(\text{CH}_2)_n-$ [sample names abbreviated to PET(R*-9, 10) or PET(L*-10)]. They showed lamellar spiral pitch ranging from 200 nm to 1 μm (varying with methylene unit) induced by L- or D-chirality, but no optical banding pattern was reported. Thus, once again, studies in the literature perhaps only demonstrated that lamellae spirals can occur in crystals, but many studies have overlooked problems that the lamellar spiral conformation might not be necessarily related to the optical banding.

Albeit numerous studies repeatedly claimed lamellae of continuously rotating spirals being responsible for ring-band PEA spherulites (inter-ring spacing ca. 6–7 μm at $T_c = 28\ ^\circ\text{C}$), for some unknown reasons, there have not been any reports in the literature in the past 60 years that ever presented direct evidence of TEM or SEM results for spiral lamellae with pitches matching the optical banding patterns. This may be due to the facts that PEA specimen preparation may not be so amenable to SEM or TEM characterization, and that MA etching simply and entirely degrades the PEA structure and crystal shapes. Thus, from these representative surveys on classical PE crystals to recent PLLA or PHBV spherulites, it may be simply put that none of the evidence of lamellae spirals presented in numerous literature results ever matches the optical ring patterns in any polymers so far.

10. A polymer displaying multiple types of ring-banded spherulites

A more perplexing phenomenon is that a polymer, crystallized at a same T_c , may display two or more types of ring-banded spherulites that differ entirely in optical birefringence patterns and lamellae structures. The complexity in such phenomenon makes it even more difficult to interpret the banding behavior using a monotonous and continuous spiral lamella models. This is exemplified in a recent study on ring-banded behavior of poly(nonamethylene terephthalate) by Woo et al. [41]. Fig. 16 shows POM graph (A) and scheme (B) of poly(nonamethylene terephthalate) (PNT, with nine methylene units) crystallized at $T_c = 85\ ^\circ\text{C}$. Apparently, two types of ring-banded spherulites are present in the same sample: Type-1 has same birefringence color in neighboring bands (differing only in shades); Type-2 has much wider bands than Type-1 and two strongly opposed birefringence colors (blue/orange) in neighboring two bands. Regardless of T_c variation between 70–85 $^\circ\text{C}$, Type-1 ring-banded spherulites always co-exist with Type-2 ones, and the difference between Type-1 and Type-2 spherulites is always consistent.

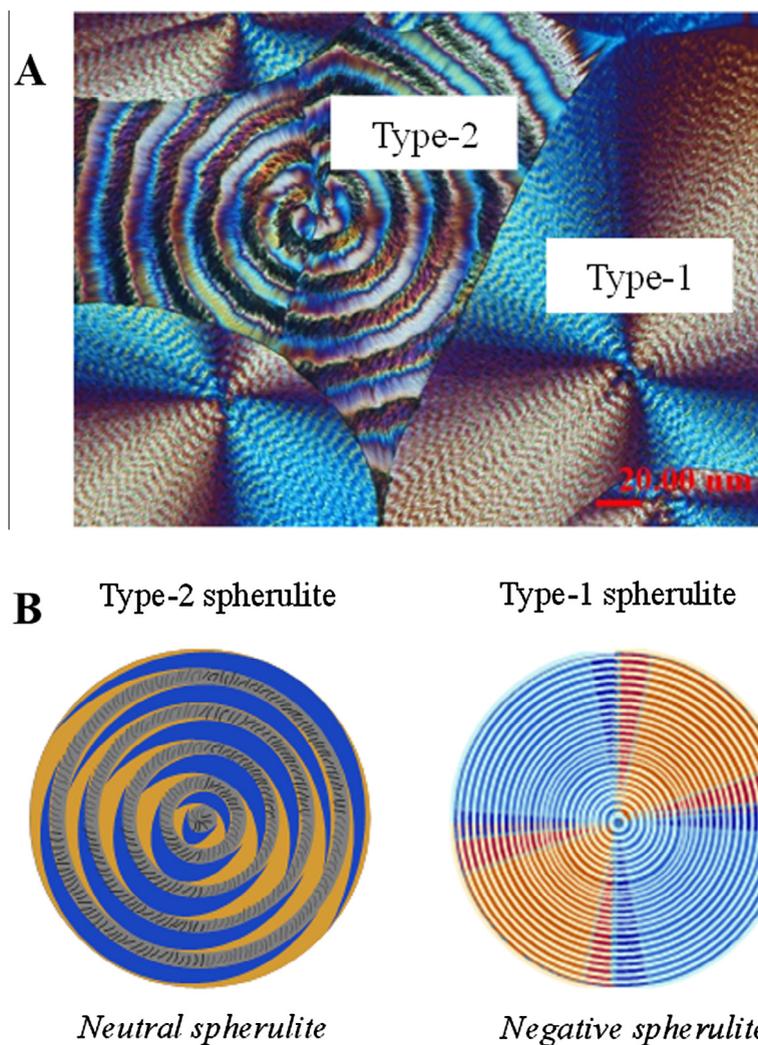


Fig. 16. POM graphs (A) of Type-1 and Type-2 spherulites in PNT films melt-crystallized at 85 °C; and schemes (B) for optical birefringence patterns associated with Type-1 (negative type) and Type-2 (neutral birefringence) ring-banded spherulites. Reproduced with permission from Ref. [41].

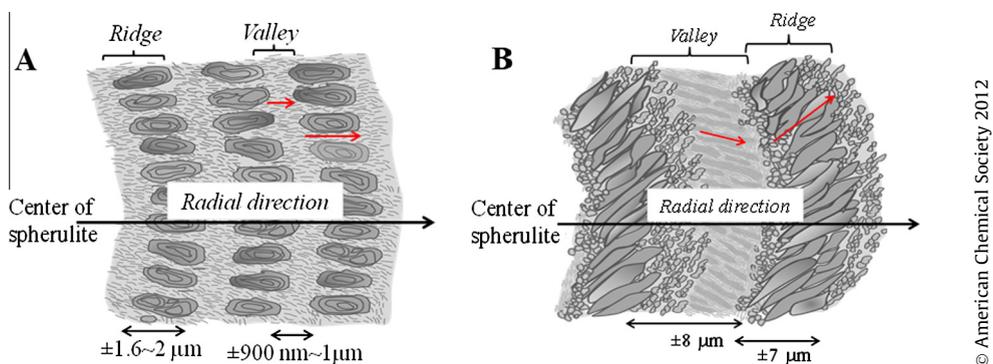


Fig. 17. Schemes for (A) dot-like crystals in ridge and flat valley in Type-1 spherulites vs. (B) spindle-shape crystals in Type-2 spherulites. Both types co-exist in PNT crystallized at a temperature between $T_c = 70\text{--}85\ ^\circ\text{C}$. Lamellar directions indicated by arrows. Reproduced with permission from Ref. [41].

The POM graphs demonstrate clearly two dramatically different optical birefringence and patterns in these two types of ring bands co-existing in PNT films crystallized at $T_c = 85^\circ\text{C}$; but details of the lamellae morphology and assembly in these two types of ring bands of PNT require analyses based on AFM. AFM results on PNT have shown that the crystals and their assembly in the rings of Type-1 differ much from those of Type-2 ring-banded spherulites, where Codes-1 and 2 are used only for conveniently distinguishing these two types of ring bands in PNT. For brevity, only representative schemes derived from detailed AFM analyses are shown in Fig. 17. For more details, refer to related results and discussion in a published work [41]. Scheme in Fig. 17A (results based on POM analyses) shows discrete dot-like crystals aligned in the ridge band of Type-1 ring-banded spherulite, while the valley is filled with similar crystals but the crystals in the valley band appear to be thinner. Such crystal assembly in Type-1 ring-banded spherulites agrees reasonably with the same optical color in POM graphs for the valley vs. ridge bands of Type-1 spherulites. By contrast, the crystal assembly in Type-2 (Fig. 17B) ring bands is entirely different from that in Type-1 ones. In the ridge band of Type-2 banded spherulite, spindle-shape elongated crystals ($7\ \mu\text{m}$ in length and $1\ \mu\text{m}$ in width) are lined up in the ridge bands, but all aligned at a ca. $+45^\circ$ angle to the radial direction; the valley bands are filled with thinner crystals (and barely distinguishable in AFM) of similar geometry, but all aligned at -45° angle to the radial direction. That is, the crystals in the ridge band of Type-2 spherulites are oriented perpendicularly to the crystals in the valley band. The perpendicular orientations in the valley vs. ridge reasonably account for the alternating blue/orange color bands in POM graphs for Type-2 spherulites. The AFM analyses on crystal assemblies of these two types of ring-banded spherulites in PNT fully support the results of optical inter-ring spacing and birefringence colors in the ridge-/valley bands. However, the morphology and topology on the top surfaces of these two types of ring-banded spherulites would not justify the model of continuous spiral lamellae for either type of the ring bands in PNT. The crystals on the ridge band (bulge band) of Type-1 ring-banded spherulites (Fig. 17A) are discrete and not continuous at all, and no features suggest that there is spiral rotation of lamellae from ridge to valley bands. Similarly, the crystals on the ridge band (bulge band) of Type-2 ring-banded spherulites are discrete spindle-shape and not continuous at all (Fig. 17B). The alignment of these spindle-shape crystals, oriented to 45° to radial direction, also does not suggest that there is a rotational spiral along the radial direction to generate the ring bands.

Our earlier study on interior dissection of crystallized PNT ($T_c = 75^\circ\text{C}$) on KBr [42] has revealed new horizons of interpreting ring-banded spherulites in polymers. Fig. 18 shows SEM graphs and schemes for interior dissection of crystallized PNT ($T_c = 75^\circ\text{C}$) with two types of ring bands: Type-1 and Type-2, whose top-surface banding patterns have been discussed in Figs. 18 and 19. Apparently, none of the two types of ring bands on top views show any relationships to continuous spiraling lamellae to create the banding patterns on the top surface of crystallized PNT. Furthermore, the interior dissection also shows that the lamellae assembly underneath these two types of ring bands (Type-1 and -2) differ substantially. Straight lamellae, fanning out from a nucleus center, are directly underneath the top surface of Type-1 ring bands, where dot-like crystals are seen to distribute in the ridge band of Type-1 spherulites. On the other hand, corrugated-shell interior, mostly

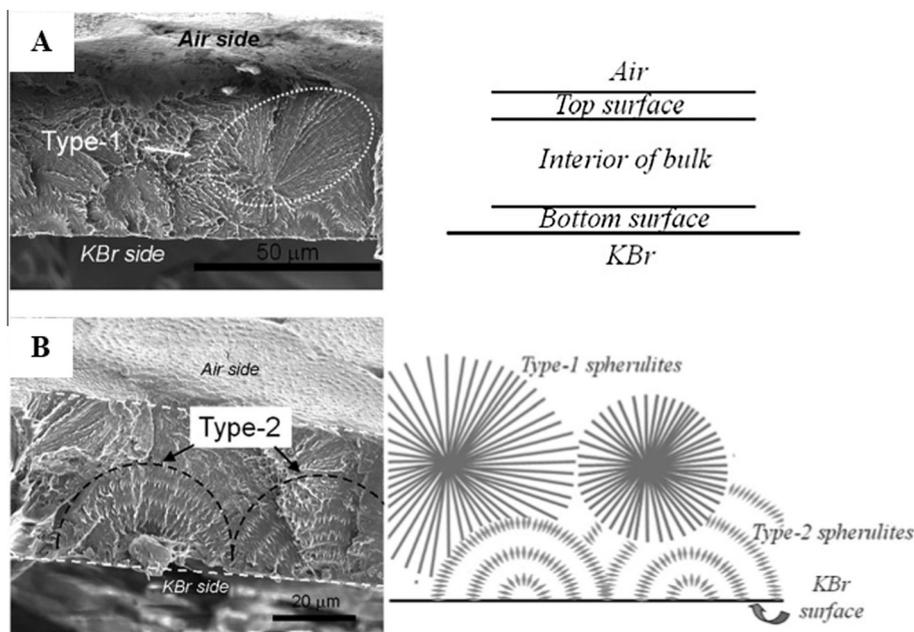


Fig. 18. SEM graphs and schemes for interior dissection of crystallized PNT with two types of ring bands: (A) straight lamellae underneath the top surface Type-1 ring bands where dot-like crystals distributed in ridge vs. (B) corrugated-shell interior underneath top surface Type-2 ring bands with spindle-shape crystals in ridge. Both types co-exist in PNT crystallized at a temperature between $T_c = 70\text{--}85^\circ\text{C}$. Reproduced from Ref. [42] with permission from the PCCP Owner Societies.

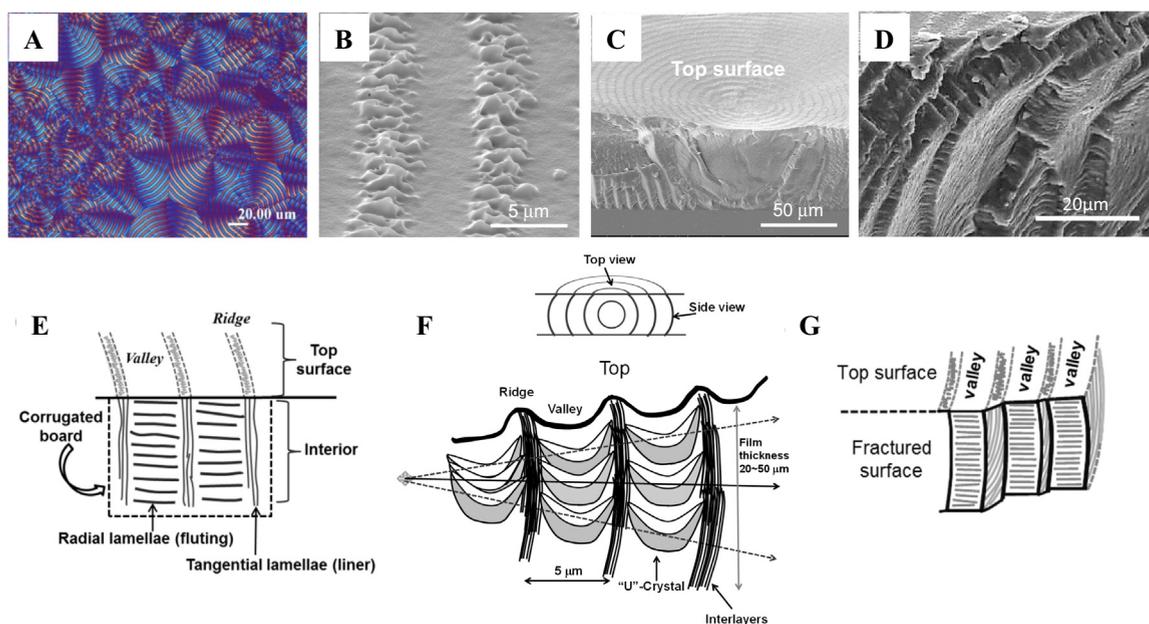


Fig. 19. POM and SEM graphs for top surface of PEA thin films (A and B); and SEM graphs for bulk 3-D interiors of PEA spherulites crystallized at 28 °C: (C) top surface and fractured cross section, (D) magnified cross section; and schemes (E–G) for correlation between top-surface and interior lamellar morphology. Reproduced with permission from Ref. [14].

nucleated from glass surface, are underneath the top surface of Type-2 ring bands, where closely packed spindle-shaped crystals, all oriented at 45° angle to radial direction, are seen in the ridge band of Type-2 PNT spherulite.

Type-1 and Type-2 spherulites, though co-existing in same PNT films crystallized at a same T_c , differ dramatically not only in the top-surface patterns, but also in interior lamellae assembly. They may also differ in nucleation sites or nuclei geometry, etc. Type-1 spherulites are nucleated in the central or upper sites of polymer films (or bulks), and the straight lamellae fan out and reach the top surfaces as dot-like crystals aligned in concentric rings. By contrast, Type-2 spherulites are nucleated near the bottom substrate interfaces, but some of the interior lamellae do not reach the top surface at all. For thinner films, Type-2 spherulites display corrugated-shell interior lamellae, and the interior lamellae have much better chances of reaching the top surface to display spindle-like crystals on the ridge bands of Type-2 spherulites. The reason that the spindle-like crystals on the ridge band are tilted at ca. 45° angle to the radial direction of spherulites is likely related to helicoidal growth of the corrugate-shell lamellae. These shell-like lamellae, upon reaching the top surface of Type-2 spherulites as the ridge band, all point toward the helicoidal direction.

11. Periodic crystal assembly with structural patterns matching optical inter-ring spacing

In 1956, Takayanagi and Yamashita [79] was one of earliest pioneers addressing the ring-band behavior in crystallized poly(ethylene adipate) (PEA). He approached the problem completely in the growth-kinetic points of view, and reported that there existed a cusp in $\log(G)$ vs. temperature plots, with a cusp (a sudden drop of growth rate) locating at ca. 29 °C for PEA with molecular weight $M_w = 9900$ g/mol, to 23 °C for PEA with $M_w = 1420$ g/mol (fractionated, but no reference to either number-average or weight-average). This temperature of growth cusp point coincided with the temperature at which PEA ring-band formation occurred. Thus, Takayanagi hinted that the ring-band formation is associated with kinetic growth rate, although at that early time the work was brief and preliminary. After 50 years, in 2005, Lotz and Cheng [22], following the Keith–Padden model on classical PE and using various results in the literature, proposed that chain-folding in polymer lamellae of PEA, PE, polyesters, etc., caused unbalanced stresses to induce continuous spiraling twists of crystal lamellae, whose synchronizing rotations in turn account for the ring-bands in crystallized PEA. In 2006, JJ Point [80], following the 1956 Takayanagi's work on PEA and Keith–Padden's spiraling PE model, attempted to theoretically fit with continuously twisting PEA lamellae from refractive index ellipsoid based on molecular polarizabilities calculated from the atomic coordinate of the PEA crystal reported by Turner–Jones et al. [81]. There are numerous other studies on ring-banded PEA spherulites in past 60 years since 1956, but this article will not review all here. From the above cited work, two extreme views: kinetics growth rates vs. thermodynamics equilibrium in response to stresses were both self-justified in their arguments based on the limited data from early-time analyses on thin-film PEA cast on glass substrates. More advanced analyses, however, are needed to crack-open the mysteries.

As discussed, poly(ethylene adipate) (PEA) is an intensively studied system for understanding the mechanisms responsible for ring-banded behavior. However, although numerous theorized claims by many investigators attempted to prove that

lamellae twist into helices and synchronizingly rotate to create ring bands, however, so far in the past 60 years, there has been no evidence presented by investigators to show that the lamellae pulled or retrieved from ring-banded PEA spherulites do show twisting with a spiral pitch matching the optical inter-ring spacing (i.e., 6–7 μm). Additionally, if the lamellae do rotate from a common nucleus center in radial direct to rotate along the [100]-axis, then, upon fracturing the crystallized PEA bulk, one should be able to see screw-like twists of numerous single-crystal lamellae that all radiate out from a common center in synchronized rotations all the way till the edges or top surfaces of spherulites. Any models or theoretical analyses, however elegant, need direct experimental evidence to justify and to testify. Why there have been no attempts in the past 60 years to address such puzzling issues in more straightforward approaches? A published work in 2012 from this laboratory proposed a uniquely novel approach by dissecting into interior of ring-banded PEA bulk, which was an approach that had not been used by investigators in the past 60 years [14]. Fig. 19 shows top-surface morphology of thin films in correlation with the interior morphology of fractured thick-bulk PEA (all crystallized at $T_c = 28^\circ\text{C}$) [14]. POM graph (Fig. 19A) shows clearly alternating blue/orange color bands, with inter-ring space of ca. 6–7 μm . SEM graph on top surface of PEA films shows bulged rings as the ridge band, with the valley band submerged (Fig. 19B), and the inter-ring space being ca. 6–7 μm , in perfect agreement with the POM patterns. Nevertheless, what is underneath the valley or ridge bands on top surfaces of ring-banded PEA spherulites has remained unknown or highly debated in the past 60 years until 2012 [14]. As demonstrated in this figure, the SEM micrograph onto the interior PEA bulk reveals clearly that the lamellae underneath the top surface of ring-banded spherulites are aligned in clearly layered structures resembling a corrugated board or an “onion-shell” structure. The radial-lamellae layer is equivalent to “flute”, and the tangential cilia-like lamellae are equivalent to the “liner” layer of a corrugated board. In addition, each of the interior shell-like lamellae corresponds to one ring band on the top surface, with width ($\sim 6\ \mu\text{m}$) of the interior layer (revealed by SEM) being exactly identical to the optical inter-ring spacing ($\sim 6\ \mu\text{m}$ by POM) on the top surface. The interior lamellae of PEA ring-banded spherulites are structured like a laminated corrugate-board, where the radial lamellae plates are directly underneath the valley band on the top surface. Oriented perpendicularly but situated between two flute-layers (the radial lamellae) of corrugate-board laminated layers, there is a thinner interfacial layer that is apparently populated by tangential lamellae (fibrillar crystals pointing upward), which protrude out from interior vertically to form the ridge band on the top surface of spherulites. That is, each of the corrugate boards is packed with alternating layers of the radial lamellae as flutes and the tangential lamellae as liner-layers that are oriented at ca. 60–90° angle to each other. These radial lamellae appear to be crystal branches growing at 60–90° angles from the fibrillar tangential lamellae. The flat radial lamellae, upon reaching the upper surface, form the valley band; and the fibrillar tangential lamellae form the ridge band upon reaching the top surface. Evidence of lamellae assembly and correlation with the ring-banded PEA spherulite becomes clearer and more straightforward upon dissecting the crystals underneath the top-surface ridge and valley bands.

The scheme inset at the bottom of Fig. 19E–G clearly demonstrates the above-discussed relationships between the top-surface ring patterns (ridge and valley) versus interior lamellae assembly in ring-banded PEA spherulites. The alternating flute/liner layers are directly underneath the top-surface ring-band patterns. The lamellae in these two layers intersect at an angle to be determined by the branching crystals. The flute-layer lamellae may not be totally flat, and the fibrillar crystals in the liner-layer are also not completely straight upward; but they can twist, bend, and scroll somewhat to response the stresses during growth. No lamellae, either in the flute or liner layers, undergo continuous spiraling like a single crystal. The clean cleavage between the interior layers underneath the ring bands as demonstrated in the SEM graphs of Fig. 19C and D strongly testifies that the crystals in the flute and liner layers are not continuous spirals (from the flute to liner layers and continuously from the center to periphery of spherulites). Instead, they are of two crystal species intersecting or branching at an angle.

More strikingly, all across the entire fractured interior surface of ring-banded PEA spherulites, one does not see continuously twisting spirals of single-crystal lamellae that rotate continuously to form alternating ridge-valley bands – neither on the top surface nor in inner interiors of PEA spherulites. The most solid evidence is that the corrugate-board layer thickness in the SEM results [radial (5 μm) + tangential (1–2 μm) layers = 6–7 μm] matches perfectly the optical inter-ring spacing in POM graphs for the ring-banded PEA spherulites. This most critical evidence (matching between the crystal assembly periodicity and optical ring inter-spacing) had never before been shown by previous investigators on PEA ring bands in the past 60 years [22,79,80]. This critical evidence would not have been possible without going into the interiors of lamellae assembly of ring-banded systems [14].

Once again, in similar approaches for solving the problems of crystallized ring-banded PHBV/PVAc ($T_c = 110^\circ\text{C}$) spherulites [70], dissection into the PEA interiors yields a novel and more workable mechanism that fully accounts for the fact that spherulites are composed of polycrystals with numerous branches as spherulites grow outward. More importantly, the mutually perpendicular orientations of the tangential lamellae and branching feather-like crystals (pointing ca. 90° to the tangential lamellae) nicely account for another fact that the birefringence color takes abrupt transition from blue to orange bands in POM. In the case of PHBV/PVAc ring bands (shown earlier in Fig. 10) [70], the tangential lamellae rise up to the top surface to correspond to the valley bands, while impingement of branching crystals accounts for the “ridge band”. This is slightly different from the case of PEA where the tangential lamellae (also polycrystals) directly go up to top surface to form the ridge band. However, similarity in both ring-banded PHBV/PVAc and PEA is that there are two alternating polycrystals that are tangential- and radial-oriented and mutually intersecting (or branching out) at an angle of 60–90°. A minor difference in the mechanisms of ring bands is that for ring-banded PEA (tangential lamellae being underneath the ridge band – see Fig. 19) vs. PHBV/PVAc ring-banded spherulites (tangential lamellae being underneath the valley band but the tangential

lamellae bulging up slightly to form a thin “island chains” in mid-position of the valley bands. Such difference in PEA vs. PHBV further demonstrates that the proposed mechanisms share general similar traits in accounting for the transition of blue/orange optical birefringence, but there are minute differences that have to be exposed by detailed analysis into interior crystals hidden underneath the top surfaces. By summarizing the above cases (PEA, PLLA, PHBV, etc.) and considering there are so many varieties of ring bands and variation in patterns, better and more accurate mechanisms for formation of ring bands in various polymers could be unveiled by analyzing the inner crystal assembly lamellae behind the top-surface crystals of ring-banded spherulites.

12. Common traits of ring bands in polymers including PEA and PHB

Barham and Keller et al. [82] were among the early pioneers in 1984 to investigate intensively the optically active polyester – poly(3-hydroxybutyrate) (PHB, with $M_n = 133,000$ g/mol). PHB (melt-crystallized at $T_c = 60–70$ °C) exhibits very similar ring-banded spherulites to PEA (melt-crystallized at $T_c = 28$ °C) in that both polymers display optically clear dual ring bands (blue/orange birefringence). They only differ in the inter-ring spacing: for PHB, $p = 12–45$ μm for $T_c = 50–90$ °C; which is twice as much as that for PEA, $p = 6–7$ μm (note for PEA, p does not change within $T_c = 27–30$ °C, but outside this range, no ring bands). It would be appropriate to compare PHB with PEA to discern some inner lamellae structures leading to their similar optical banding patterns. Barham and Keller et al. [82] reported that the inter-ring spacing (12–45 μm) in ring-banded PHB is roughly proportional to its spherulite sizes and growth rates ($r = 100–800$ μm and $G = 0.5–4$ $\mu\text{m/s}$, respectively, from $T_c = 50–90$ °C), while the PEA inter-ring spacing and spherulite size both remain much the same, not varying within $T_c = 27–30$ °C (ring-band region) [14]. Barham and Keller [82] used the conventional thin-film approaches for investigations of ring-banded PHB spherulites, but they took advantage of the particularly wide bands and large spherulite size in PHB to obtain X-ray diffraction patterns from selected-area parts of the spherulites. They claimed that they were able to deduce the orientation of the crystal axes within the spherulite. They attributed the b -axis of crystal lattices being along the bright band (orange band) and the crystal c -axis being along the neighboring dark band (blue band, and c -axis is the fiber axis in their assignments), with a -axis being along the radial direction of spherulite. Such assignments in their study made an assumption that single-crystal lamellae spiraled continuously from edge-on in the ridge band (bright) to flat-on in the valley band (dark). The spiral in a continuous single crystal requires that the a -axis [100] being toward the radial direction all the time during spiral rotation with the b -axis being along the valley band (dark). After rotating a half pitch (180°) from the flat-on valley to edge-on ridge band, the b -axis is now still pointing along the ridge band (bright), only with the c -axis rotating 180° (from upward to downward) to be still perpendicular to the radial direction of spherulites. But it should be emphatically pointed out here if the lamellae do continuously spiral along the a -axis to create periodic edge-on and flat-on rotation, one would not see the b - and c -axis being alternating along the ridge and valley bands – as affirmed by Barham and Keller's X-ray results on wide ring-banded PHB [82]. By interior dissection of PEA ring bands, the alternating layers (corrugated board structure) in the PEA bulk as shown in Fig. 19D and E will have the b -axis of crystals along the valley band (flute-layer lamellae) and c -axis to be along the ridge band (tangential liner-layer lamellae) in alternating patterns. That is, the single-crystal spiral lamella model violates the X-rays results by Barham and Keller [82], but the alternating corrugated-board polycrystals model would agree with the Barham and Keller's results. From the interior dissection on PEA bulk and direct evidence of the corrugate-board layer-structure matching the optical banding patterns [14], we know that the valley/ridge (blue/orange) bands in the PEA spherulites are not composed of single crystals continuously spiraling radial direction, but polycrystals of two opposite layers orienting to different directions. Thus, the crystal lattice axes that Barham and Keller assigned to the PHB ring bands (blue vs. orange bands) were most likely the averages of multiple polycrystals in the bands, and these polycrystals in alternating layers, with the collectively lamellae orientation and averaged optical properties, will have c -axis in the radial direction on one band (blue) but in the circumferential direction in next band (orange).

In addition to the common traits shared in the morphology of interior corrugate-layer structures of ring-banded polymers, another similarity in temperature windows of growth kinetics is also universal in different polymers. Finally, a common feature between the ring-band behavior shared in both PHB and PEA is worthy of mentioning. Barham and Keller [82] reported the formation of ring bands of the most regularity for PHB occurs at $T_c = 70$ °C \pm 20 °C (for PHB with $M_n = 133,000$ g/mol), which is near the maximum point of plotted curves for spherulite growth rates vs. temperature. According to the results of Takayanagi and Yamashita [79] and Woo et al. [14] on PEA, respectively, the formation of ring bands of the most regularity for PEA occurs at $T_c = 29$ °C \pm 2 °C (PEA, $M_n = 9000–12,000$ g/mol), which is also near the maximum point of plotted curves for growth rates vs. temperature. Neither of polymers displays ring-banded spherulites when crystallized at extremely low degrees of supercooling (high T_c), nor at extremely high degrees of supercooling (low T_c). To further support such claims, a separate study on poly(trimethylene terephthalate) (PTT, intrinsic viscosity of 0.92 dl/g but M_n unsupplied) by Chuang et al. is cited here [34], which furnished data of crystallization growth rates vs. formation of ring-banded spherulites of PTT in melt-crystallization vs. cold crystallization. They found a transition of banded to non-banded spherulites (during melt-crystallization) takes place at $T = 425–468$ K (or 152–195 °C, in Regime-II), which also corresponds to the maximum point of plot of growth rates vs. temperature; on the other hand, cold-crystallization of PTT, does not develop ring-banded spherulites (only a sheaf-like structure). Apparently, all three cases of polymers (PEA, PHB, PTT) showing ring-band behavior all exhibit similar trends in terms of crystallization kinetics vs. banding in spherulites. This, of course, cannot be taken to hint at the face value that it only takes high growth rates to develop ring bands in

spherulites. Nevertheless, the relatively high growth rates (near max. point) coupled with yet unmatched diffusion rates at those temperature windows may be a key role. The formation of ring bands in polymer spherulites appears to be associated with crystallization growth kinetic in similar and intricate ways. This universality of formation of ring bands driven by kinetic growth within a window can be extended to many polymers.

13. Conclusions

For understanding the nature of origins of periodic bands in crystals, it is critical to discern that there are several types of ring bands in spherulites that differ widely in band patterns and birefringence nature, and a single mechanism may not be sufficient to account for all these diverse patterns with interior lamellae assembled in various ways. When controlled to thin thickness (300 nm to 1 or 2 μm), concentric ring bands of no alternating birefringence colors can appear in crystallized polymers. In such concentric ring bands, lamellae do not spiral at all; instead, the “ridge band” (bulge region) is composed of all flat-on lamellae while the “valley band” is not really a “band”, but just a sharp crevice that is a narrow boundary between two wide ridge bands where the flat-on lamellae drop collectively and suddenly to nearly the glass substrate. For such concentric ring bands, kinetic process with periodic diffusion draining is most likely the main cause. Normally, ring bands of any kinds do not appear in polymers confined in ultrathin thickness (50 nm or lower). In such ultrathin confinement, polymers are less likely to pack into polycrystals with accompanying occurrence of periodic patterns. By contrast, ring bands of dual optical birefringence colors always occur in polymers of normal drip-casting thickness (several microns to 30 μm , or bulk forms). Moreover, both types of ring bands occur only in certain regime of spherulite growth in a specific temperature window. That is, thickness of crystallizing species and temperature of crystallization impose windows of occurrence for such periodic patterns. Crystallization is related to a kinetic process. Formation of ring bands in spherulites (either non-birefringent or birefringence types of ring bands) is usually limited in certain kinetic conditions, and will not occur in other kinetic conditions. Fine correlations need further analyses. Nuclei geometry and chirality of chain structures may further influence or govern the macro-shapes of periodic patterns, but this is out of the scopes of this article.

The reviews in above cases have shed new light in approaching complex issues in polymer crystallization showing periodic patterns. In the past 60 years, it had been repeatedly claimed by investigators that chain folding stress-induced lamellae to undergo continuous spiraling twists, which is the sole responsible factor for ring-banded polymer spherulites. However, interior dissection into inner lamellae in ring-banded spherulites of many polymers does not support such views, although dissection also reveals that polymer lamellae, in polycrystalline and highly branched forms, can twist, bend, or scroll in smaller localized scales that do not match the inter-ring spacing of optical bands at all (twist/scroll dimension usually far below the optical band spacing).

This work, based on newer approaches, proposes alternative mechanisms for understanding the origins of the ring-bands by showing the interiors of lamellae in spherulites with matched periodic lamellar structures and inter-ring spacing. That is, lamellae spirals identified in TEM or SEM characterization alone cannot be used as proofs that the spirals are indeed continuous and all synchronized in pace to cause ring bands in spherulites. This, however, does not say that stress-induced twists do not occur or exist in crystals of spherulites. Stresses on crystal lamellae can be from branching and impingement of growth, presence of amorphous polymers as diluents or external solvent exposure, as well as possibly from chain-folding; and lamellae in primary and secondary crystallization spiral, bend, scroll, tilt, or twist, etc. in response to these stresses. That is, crystal deformations from original flat single-crystal-like plates do occur and exist in polycrystalline spherulites – ring-banded or ringless alike, but the pitches of lamellae twists or spirals normally do not match the optical birefringence rings observed in spherulites. More strikingly, newer evidence supports that ring bands of alternating optical birefringence in polymer spherulites are packed by layered lamellae oriented in two nearly perpendicular angles (usually 60–90°, depending on geometry of crystal lattices of polymers), with their crystal axes differing sufficiently to give two sharply distinct birefringence colors in bands. The lamellae layer thickness, as revealed in interior SEM characterization, exactly matches the inter-ring spacing of optical bands in POM. Additionally, nonbirefringent concentric ring bands, usually occurring in specimens confined between 300 nm to a few micrometer thickness, and can be circular, camellia-flower-like, or polyhedron in shapes) are packed with crystal lamellae in entirely different ways from those in birefringent ring bands in thicker polymer specimens. The ridge (bulge) of non-birefringent periodic bands is packed like fish-scale assembly by fully flat-on lamellae with no twist or scroll; while the valley is either crevices or settled with minor amount of non-crystallizable species expelled by crystal fronts. Furthermore, interior dissection into ring-banded spherulites in bulk crystallized polymers does not reveal that the lamellae behave as single crystals and synchronize in spiral twisting in ordered paces. Rather, highly-branched polycrystalline lamellae fill the spherulites and the lamellae are aligned as a corrugate-board structure with liner and flute layers. The alternating flute/liner layers are directly underneath the top-surface ring-band patterns. The lamellae in these two layers intersect at an angle. The crystals in the flute and liner layers are not connected by continuous spirals; instead, they are of two species related to main and branched crystals.

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