Historically, in the past 60 years, continuous spiral twisting of polymer lamellae caused by chain folding induced unbalance surface stresses had been believed as a plausible mechanism for common optical ring-banding behavior in polymer spherulites. With progress of powerful advanced instrumentation and newer discoveries of diversified patterns (e.g., birefringent vs. non-birefringent; circular vs. hedral/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. 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 a single-crystal lamellae plate undergoing continuous spiral from center to peripheral of spherulite may need critical assessment for validity.

There are four critical points that we would like to bring forward for discussion. Firstly, 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. Secondly, 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. Thirdly, it takes synchronized twists of tens of thousands lamellae that all have to be identically shaped single crystals that might be a dauntingly impossible task for polymer crystals in order to build orderly ring bands in a spherulites as viewed in optical graphs. 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. 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. Thus, 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. Figure 1 summarizes the formation mechanisms of different periodic bands: radial-stripes bands (1) and various types of circular ring-bands (2-4) in polymer spherulites interpreted from surface and interior analyses.
The subjects in “periodic bands in polymer spherulites” would not be complete without subject of radial-striped spherulites in comparisons with circular ring bands. Radially striped spherulites of opposite birefringence will be demonstrated first 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. PEO/PVPh (80/20) spherulites appear to radiate out from the nuclei center, branch out, and bend to curvature, as they go from center to periphery displaying two contrast blue and orange striped bands. 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°. These perpendicular oriented crystals are forming contrast blue and orange stripes in POM graphs. 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) [1].

A more perplexing phenomenon is that a polymer, crystallized at a same Tc, 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(nanomethylene terephthalate) [2]. Two types of ring-banded spherulites are present in poly(nanomethylene terephthalate) (PNT), Type-1 is regular extinction ring and Type-2 shows banded ridges with slanted crystals. 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 circular ring-bands in POM graphs.

Circular ring-bands spherulites with a very long pitch (50~100 µm) are easily found in crystallization of PLLA [3-5].
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. SEM graphs of the fractured and water-etched interiors of PEO/PLLA (50/50) blend 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 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. These 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 [4].

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). POM graph 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, 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 [6-8]. 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 as shown in Figure 2 below.
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 periodical lamellar structures and inter-ring spacing. 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. 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.

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