

Banded Crystalline Spherulites in Polymers and Organic Compounds: Interior Lamellar Structures Correlating with Top-Surface Topology

Eamor M Woo^{1*}, Graecia Lugito¹, Cheng-En Yang¹, Shi-Ming Chang¹ and Li-Ting Lee²

¹Department of Chemical Engineering, National Cheng Kung University, Taiwan

²Department of Materials Science and Engineering, Feng Chia University, Taiwan

Abstract

By using several different polymers and compounds, organics or inorganic, low-molecular-weight or high-molecular-weight, this study has proven that they can be packed into concentric ring bands, usually circular, but other shapes like hexagons or flower-like petals can also be possible. With these traits taken into consideration, it is difficult to generalize the ring bands in spherulites to a single cause of lamellae twist/spiral. Instead, exposure of lamellae underneath the top layers beyond thin films becomes essential for shedding new light on all these intricately complex issues. The novel approaches in this study circumvent such limitation by interior dissection of PEA, which clearly reveals that no continuous spiraling twist, as the cross sections show a corrugated-board structure with layers resembling a peel-able onion, where each radially oriented layer is sandwiched with a tangential layer of lamellae.

Keywords: Ring-banded spherulite; Interior lamellae; Poly(L-lactic acid); Poly(ethylene adipate); Phthalic acid

Introduction

Compounds, organics or inorganic, low-molecular-weight or high-molecular-weight, can crystallize if their chemical structures are relatively ordered. In addition to many regular shapes that are widely known, crystals can be packed into concentric ring bands, usually in circular shape, but other shapes like hexagons or flower-like petals can also be possible. Banded patterns in spherulites mean that concentric rings (Note: sometimes not necessarily concentric rings with a common nucleus, but the crystal plates are aligned as spirals [clockwise or counterclockwise] from center to outer rims on the same substrate plane) are packed as a result of crystallization, usually under some specific conditions, such as temperature of crystallization, confinement, diluents, and/or solvent evaporation rates. In banded spherulites, the rings possess different optical properties, surface topology, and sometimes lamellar orientations. These banded patterns in spherulites are sporadically seen in crystallization of many materials; yet the mechanisms remain elusive and have been highly debated. Among the small-molecule compounds known to display rings in crystallized spherulites are: hippuric acid [1], phthalic acid [2], testosterone propionate [3], aspirin [4], D-mannitol [5], as reported by Kahr et al., and inorganic salts such as ($K_2Cr_2O_7$) [6-8]. In the fields of crystallography for small molecules, there are two proposals for accounting the ring bands: helical crystals, and rhythmic precipitation. There are also occasions that both mechanisms are simultaneously responsible for the banded patterns.

In addition to many literature reported on ring-banded spherulites in many other polymers, aromatic as well as some aliphatic polyesters, are among the most investigated materials for crystalline behavior including banded spherulites, such as poly(trimethylene terephthalate) (PTT) [9,10], poly(pentamethylene terephthalate) (PPT) [11,12], poly(octamethylene terephthalate) (POT) [13], poly(nonamethylene terephthalate) (PNT) [14,15], and poly(ethylene adipate) (PEA) [16-18]. The reasons these polyesters have been the focus of studies in crystal structures were due to that they always could be packed into the ring-banded spherulites within a certain temperature range. Most investigations approach 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, which suggest that the

internal lamellae assemblies also vary correspondingly.

Recently, biodegradable polymers, such as poly(L-lactic acid) (PLLA), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHB-co-HV), and poly(3-hydroxybutyrate) (PHB), etc. [19-23], have been shown to exhibit ring-banded spherulites just like many of other aryl-polyesters (PPT, POT, PNT, etc.) [9-15] or aliphatic polyesters (PEA, PBA, etc.) [16-18]. However, most investigators only focused on analyses based on top-surfaces of thin films, and very rarely the inner structures of banded materials were examined. Polymers are known to have chain folding from classical literature and some investigators including Lotz and Cheng [24] argued that chain folding induced surface stresses, which in turn were responsible for crystal twisting. By contrast, small-molecule compounds, including hippuric acid [1], phthalic acid [2], testosterone propionate [3], and aspirin [4], etc., do not have chain folding in crystals at all, but the crystals of some of the compounds also twist. Kahr et al [1-5], following the initiating arguments of a classical work by Bernauer [25] on many organic compounds using optical microscopy in 1929, have argued that temperature-gradient induced stresses, and other stresses, etc., may cause helice shapes in these small-molecule crystals. Apparently, the above comparisons between long-chain polymers vs. small-molecule compounds clearly hint that crystal twist is a habit that not necessarily is related to or induced by chain folding. A small-molecule compound, phthalic acid (PA), has been extensively investigated by Kahr et al. [2], in revealing ring-banded spherulites by evaporating PA from 20/80 water/ethanol solution at ambient temperature (25°C). This PA compound and its spherulites serve as a useful low-molecule model in comparison to the ring-banded long-chain polymer (PLLA) or aliphatic polyester (PEA), aryl polyester (PDOt) to be discussed in this work.

***Corresponding author:** Eamor M Woo, Department of Chemical Engineering, National Cheng Kung University, Tainan, 701-01, Taiwan, Tel: +886 6 275-7575 Ex. 62670; Fax: +886 6 234-4496; E-mail: emwoo@mail.ncku.edu.tw

Received April 23, 2015; Accepted April 16, 2015; Published April 22, 2015

Citation: Woo EM, Lugito G, Yang CE, Chang SM, Lee LT (2015) Banded Crystalline Spherulites in Polymers and Organic Compounds: Interior Lamellar Structures Correlating with Top-Surface Topology. J Adv Chem Eng 5: 120. doi:10.4172/2090-4568.1000120

Copyright: © 2015 Woo EM et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

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 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 retrieved from the ring-banded spherulites. However, these proposed correlations may be an Achilles-knee problem that should be tackled with more careful and deeper analyses, as they may run risks of the facts that twisted crystals may also be retrieved from ringless and non-banded spherulites.

To tackle the complex issues, novel approaches were taken in the work to examine the interiors of crystallized samples that have been prepared into bulk forms. In addition, thickness was varied from very thin to thick to observed changes in crystallized patterns. Top morphology and crystal patterns on the top surface in correlation with the interior crystal lamellae was established. 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 and testing for universal behavior in crystals that form ring bands. In addition, different types of ring bands were analyzed and mechanisms exemplified.

Experimental

Materials and preparation

Poly(L-lactic acid) (PLLA) of two grades, $M_w=11,000$ g/mol and $M_w=119,400$ g/mol, were purchased from Polyscience, Inc. (USA) and from NatureWorks, respectively. Poly(ethylene adipate) (PEA), with $M_w=10,000$ g/mol, $T_g=-52^\circ\text{C}$, and $T_m=43^\circ\text{C}$, was purchased as research-grade material from Aldrich Co. (USA). Poly(dodecamethylene terephthalate), (PDoT) was synthesized with a two-step polymerization from 1,10-dodecanediol and dimethyl terephthalate (DMT) with 0.1% butyl titanate as a catalyst. PDoT is an aryl polyester and has a structure similar to commercial poly(ethylene terephthalate) (PET), except that PDoT has a much longer methylene segment (12 CH_2 units) between the terephthalate groups in its main-chain repeat units. The weight-average molecular weight (M_w) and the polydispersity index (PDI) as determined by gel permeation chromatography (GPC, Waters) were 25,300 g/mol and 2.07, respectively. Phthalic acid (PA), with $M_w=166.13$ g/mol and $T_m=205^\circ\text{C}$, was purchased from Alfa Aesar, a Johnson Matthey Company. To ensure there was no impurity, those polymer materials were firstly dissolved into chloroform (CHCl_3) and filtered by PTFE syringe filter 0.45 μm and dried in vacuum oven for 7 days at room temperature. Samples of polymers (PEA, PLLA, PDoT) were prepared by dissolving each polymer into common solvent of chloroform, or other suitable solvents in various concentrations depending on film thickness required. Polymers were either drip- or spin-cast into thin films on glass substrates. For PEA, a few drops were repeatedly deposited on a glass substrate to stacked into a thick bulk sample (~ 100 μm). Degassing was performed at 45°C in a vacuum oven for 24 h to remove the residual solvent. The crystallization of polymers was conducted at a suitable temperature of crystallization directly from their melt state for displaying ring-banded spherulites.

Apparatus and procedures

A polarized optical microscope (POM, Nikon Optiphot-2), equipped with a Nikon Digital Sight (DS)-U1 camera control system and a microscopic hot stage (Linkam THMS-600 with T95 temperature programmer), was used to confirm the crystal morphology prior to the AFM and SEM observation. A sensitive tint plate with 530 nm optical path difference was inserted in between the polarizer and analyzer for enhancing the contrast of birefringence.

Scanning electron microscope (SEM, FEI Quanta-400F) was used to characterize both fractured and top free surfaces of bulk form PEA samples. PEA in thick bulk forms was heated to $T_{max}=90^\circ\text{C}$, rapidly dipped in a silicone oil bath set at controlled temperature of 28°C for crystallization. The fully crystallized bulk PEA samples were washed with petroleum ether before observation. The samples were fractured into halves, then coated with gold vapor deposition using vacuum sputtering prior to SEM characterization.

Atomic-force microscopy (AFM, diCaliber, Veeco Corp., Santa Barbara, USA) investigations were made in the intermittent tapping mode with a silicon-tip ($f_0=70$ kHz, $r=10$ nm) installed. AFM measurements were carried out to determine the phase images and height profiles in the morphology topology of thin-film samples.

Results and Discussion

Poly(ethylene adipate) (PEA)

Poly(ethylene adipate) has long been known to exhibit banded spherulite when melt-crystallized at $T_c=27-30^\circ\text{C}$. Many investigators seemed to be quick to jump into a presumption by following Keith and Padden who proposed earlier that thousands or millions of lamellae spiral and twist in coordinated fashion to generate such banding patterns seen in PEA. However, since the earlier proposal by Keith and Padden more than 60 years ago, no one ever attempted to answer why millions of lamellae were able to spiral coordinately to generate such smooth ring bands; or faced deeper questions why banding is displayed by PEA spherulites only in this narrow temperature range ($27-28^\circ\text{C}$), but not in any other temperatures? Furthermore, most polymer thin films in many investigations were not so thin enough to accommodate only one single layer of lamellar plates to do spiraling from nucleation center; there were actually tens or hundreds of lamellae (each averaging for 15 μm), i.e., many more than just one single layers that have to be co-spiral without any slips or mismatches to generate such smooth, or almost perfect, ring bands in spherulites. All past investigations on ring bands had been mostly based on analyses on top surfaces of thin films; then a deeper question for thoughts is that what happen to the lamellae underneath the top surfaces showing ring bands? The spiral of lamellae plates in accounting for the observed ring bands in spherulites has been conceived to be somewhat like that in α -helix in proteins. However, in proteins, it is known and well established that it takes strong intramolecular hydrogen bonds for stabilizing an α -helix in maintaining the spiral conformation; many investigators seem to have overlooked a very essential point that in crystal lamellae of most polymers, there are no such H-bonding for holding the lamellae in long spirals from the nucleation center all the way to the edge of the spherulites. Surface stress may cause occasional and irregular re-orientation of the lamellae plates, but consistent and coordinated spiral of the lamellae plates obviously need more convincing mechanisms than just stresses.

Observation as an example is placed on ring bands in poly(ethylene adipate) (PEA), whose top surface banding patterns and interior lamellar assembly would be compared. Figure 1 shows double ring-

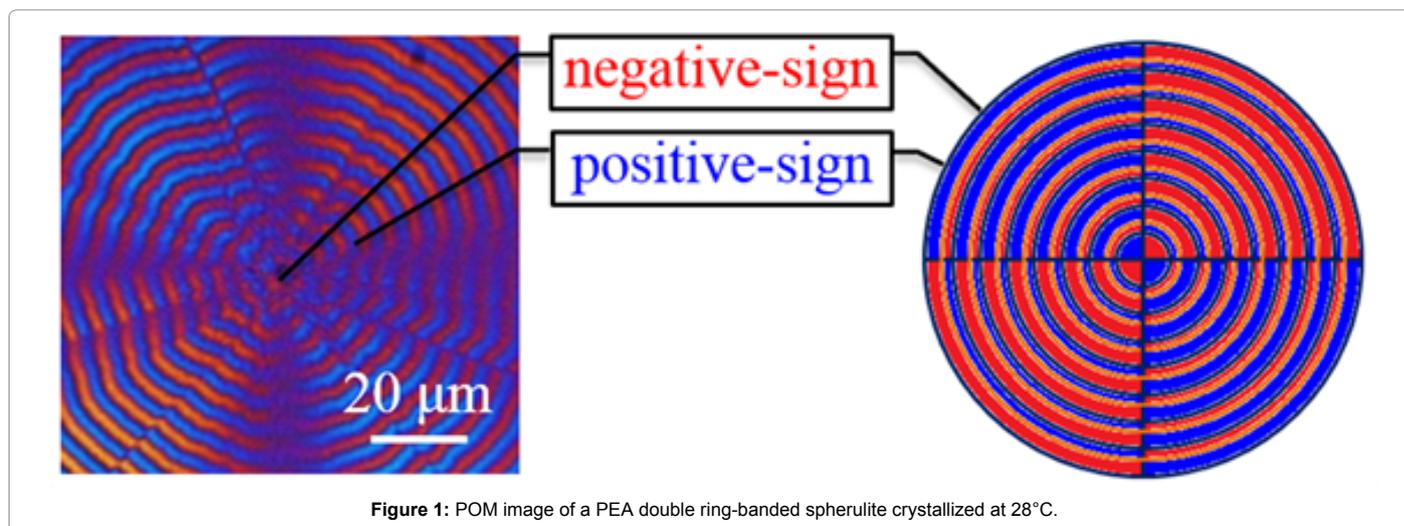


Figure 1: POM image of a PEA double ring-banded spherulite crystallized at 28°C.

banded spherulite of PEA crystallized at 28°C. At the beginning (center part), PEA spherulite shows the sign of negative-type spherulite, after about 4 μm in radius, the sign changes to positive-type for another 2.5 μm, and so on, composing the concentric pattern of alternating interference colors. One may sometimes misinterpret this kind of double ring-banded spherulite as negative single ring-banded spherulite due to its wider band of negative-type compared to the positive one.

The previous study clearly reveals the formation of mutually perpendicular orientations of crystal lamellae and its relation to the alternating birefringence in PEA double ring-banded spherulites [16-18]. Moreover, in this study, the interior architecture of bulk samples has been studied in order to give a manifest about the mechanisms and behavior of the lamellar assembly in case of PEA double ring-banded spherulite.

Poly(L-lactic acid) (PLLA)

In contrast to the ring band patterns composed of obviously blue/orange birefringence bands in PEA, poly(L-lactic acid) (PLLA), spin-cast to ~300-500 nm film thickness, can display concentric ring-banded spherulite with no birefringence colors. POM and AFM characterizations were performed on PLLA crystallized at $T_c=115^\circ\text{C}$, and results are shown in Figure 2. The POM graph, which demonstrates no birefringence colors in the banding patterns, is partially owing to the film thickness being smaller than (or roughly equal to) the visible optical light wavelength. The AFM analyses revealed concentric rings (of roughly hexagonal shape) in PLLA spherulites with inter-ring spacing ca. 7-10 μm, depending on the film thickness. An up-and-down topology for the ring-banded spherulite is clearly demonstrated by AFM analyses with height drop of 300 nm. The dramatic vertical and sudden drop from one band to the next one would rule out the possibility that lamellae are continuously spiral (twist) gradually from nucleous center to edge of the spherulites. Instead, one clearly sees that one band is almost detached from the next one, as the drop of height between the neighboring band almost equals to the film thickness, which means that the band drops to the substrate surface before it rises again to form the next bands in spin-cast PLLA ($T_c=115^\circ\text{C}$). Spiral or twist of lamellae plates would not cause a sudden drop to the substrate surface at all. The significant differences between the ring-band characteristics in PLLA spherulites from those in PEA spherulites should yield a hint that ring bands and their formation may not be from a same mechanism.

Ring bands in spherulites could be influenced with samples being covered or not by another top-glass. The fact suggests that the top topology responsible for the ring-banded patterns in the spherulites could be influenced or altered by physical contact with a top surface that makes contact with the lamellae (or crystal plates). Figure 3 shows POM graphs for high- M_w poly(L-lactic acid) ($M_w=119,400$, NatureWorks) crystallized at $T_c=130^\circ\text{C}$: (a) uncovered, (b) covered samples. If samples were crystallized with top surface free (no top glass cover on samples), the PLLA polymer was melt-crystallized at 130°C into ringless (no ring bands) spherulites; by contrast, with top glass on samples being crystallized, PLLA was melt-crystallized at 130°C into apparently ring-banded spherulites of large banding space (inter-ring spacing=100 μm). If chain folding and its effect on surface stresses between the lamellae were the sole causes responsible for the ring bands in spherulites, then top glass in contact with the lamellae should not be an influential factor for the ring-band patterns. The lamellae only make contact with the top glass in the interfaces between polymer and glass on top, and only the very top-layer lamellae are in contact with the glass, and the other lamellae inside should not be influenced at all. Furthermore, if making contact with the top glass would erase or diminish the surfaces between lamellae, then polymers on bottom glass substrates should also lead to ringless spherulites. However, these numerous results are opposite to such arguments, as all polymers showing ring banded spherulites have always been observed on bottom glass substrates.

Poly(dodecamethylene terephthalate) (PDoT)

Ring bands in a same polymer can exhibit many different types of patterns, which is difficult or almost impossible to justify all these ring bands to be originated from a single mechanism, e.g., lamellar spiral, that is responsible and workable for formation of all these wildly different patterns of ring bands. Examples are given in Figure 4 that shows ring bands POM patterns for poly(dodecamethylene terephthalate) (PDoT) crystallized at 90°C and 120°C, respectively. The pattern of ring bands in PDoT crystallized at $T_c=90^\circ\text{C}$ (Figure 4a) may be similar to those in PEA crystallized at $T_c=28^\circ\text{C}$ (Figure 1). However, the pattern of the ring bands in PDoT spherulites crystallized at higher $T_c=120^\circ\text{C}$ (Figure 4b) is completely different. Obviously, lamellar spiral/twisting does not seem plausible for the ring bands in PDoT crystallized at $T_c=120^\circ\text{C}$ at all (Figure 4b), as across the large pieces of bands (~50 μm), it is easy to tell from the POM graphs that there is no gradual spiral from the beginning to end of one large band. If there were spiral of the lamellae across the

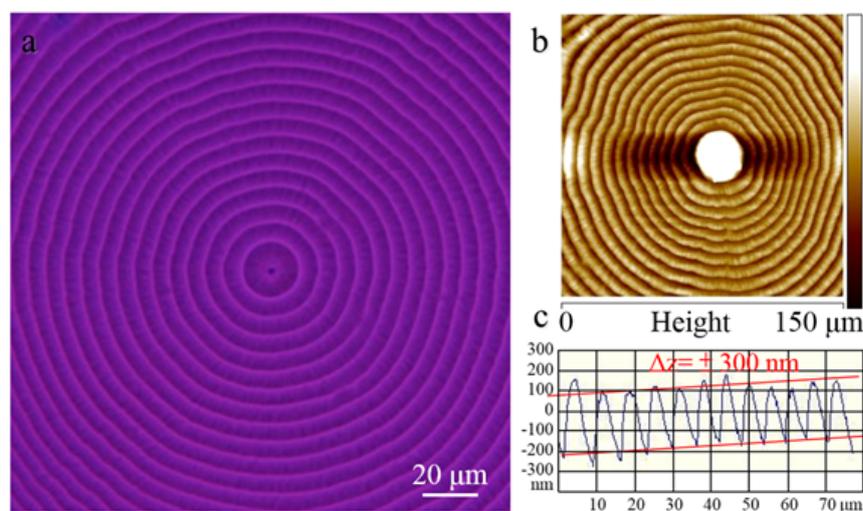


Figure 2: POM and AFM characterizations performed on low- M_w PLLA [$M_w=11,000$ g/mol, Polyscience, Inc. (USA)] crystallized at $T_c=115^\circ\text{C}$: (a) POM graph with 530 tint plate, (b) AFM height image, and (c) AFM height profile [film thickness=0.5 μm].

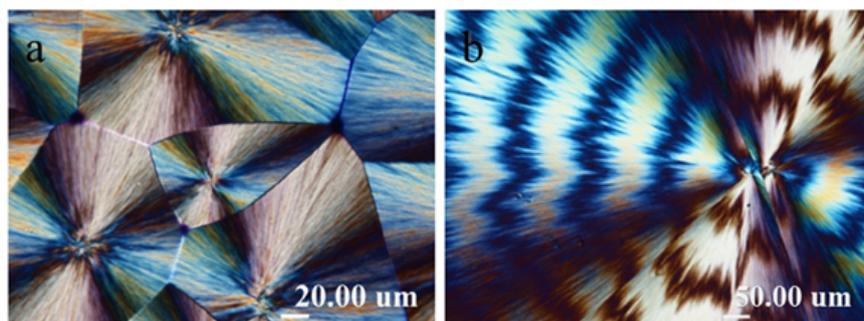


Figure 3: POM graphs for high- M_w poly(L-lactic acid) [$M_w=119,400$ g/mol, NatureWorks] crystallized at $T_c=130^\circ\text{C}$: (a) uncovered and (b) covered samples.

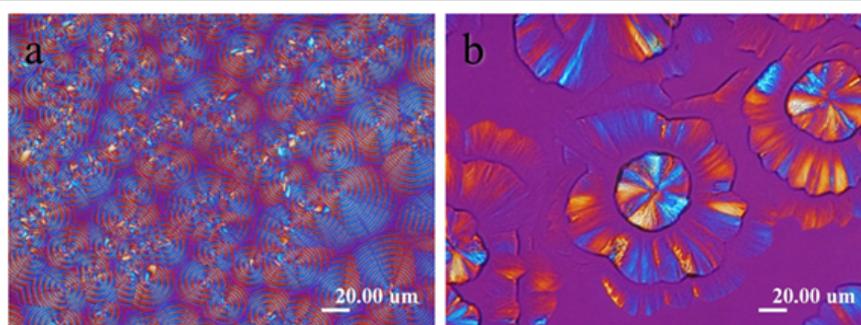


Figure 4: POM graphs for poly(dodecamethylene terephthalate) (PDOT) melt-crystallized at (a) $T_c=90^\circ\text{C}$, (b) $T_c=120^\circ\text{C}$, respectively.

band (spiral in radial direction), the POM birefringence would display gradual birefringence color transition. Obviously, the birefringence color remains the same across the band in the radial direction. In Figure 4a, the width of the band is too small (5 μm) to tell whether or not there is gradual spiral. But obviously, the two neighboring bands are of two opposite birefringence colors (Blue/Orange). It remains to be questioned whether these two opposite colors in two neighboring bands were a result of gradual "spiral/twist"? Or simply, there were two lamellae intersecting at perpendicular orientations? Again, dissecting

into the interior of the lamellae underneath these banding patterns was the only way to answer for clarification.

Ring-banded spherulites in phthalic acid

Phthalic acid (PA), a low- M_w organic compound, is known to show concentric ring bands in spherulites. Figure 5 shows POM graphs for PA (dissolved in 80% water+20 wt% ethanol), which was crystallized at ambient (28°C), 80°C, and 110°C, respectively. Note that ring bands in PA were formed in solvent-induced crystallization, but not in melt-

crystallization. The ring banded patterns in low- M_w PA spherulites are in every aspects very similar to those seen in the ring-banded spherulites of many polymers, such as poly(ethylene adipate) PEA or poly(butylene adipate) PBA. Contrary to the popular interpretations taken by many polymer scientists that ring banded spherulites in polymers are a result of chain folding in lamellae, which leads to surface stresses, which in turn cause lamellar spiral twists to form ring banded patterns in spherulites, it should be emphatically pointed out that PA, being a low- M_w organic compounds, there is obviously no chain folding in the crystals it packs into. With no chain folding or surface stresses in PA crystals, the ring banded spherulites in PA obviously cannot be attributed to chain folding induced surface stresses and lamellar spiral twists, etc. This fact yields strong evidence that ring bands in spherulites cannot be attributed to only a single cause.

Apparently, analyses of these banding phenomena have traditionally been limited to crystals in thin films and microscopic views on top surfaces of these thin films. How the crystal plates in interiors are connected to the top-surface topology in ring-banded spherulites has not been addressed. Poly(ethylene adipate) (PEA) was used as a model system for interior investigation. The results in this model system might be equally applicable to other polymers or even low- M_w organic compounds.

In Figure 6a, it can be seen that the tangential layers (in skin layers) occasionally bend, curve, or twist when traversing from tangential layer to the radial layer. However, the tangential lamellae are not physically extending between the two sequential layers, as what would be proposed in a continuous twist (spiral) going only in the radial direction. Internal views are apparent in revealing two main points of observations: (1) radial lamellae taper gradually and form thinner cilia-like lamellae before being attached by the next crystalline polymer chains tangentially in next layer; and (2) when there is no more cilia-like lamellae could be attached, yet the lamellae start to bend, curve, or twist 90° to continue the growth in the radial direction between the perpendicular layers located in the neighboring layers. But no matter they bend or curve, the radial lamellae are always positioned 90° to the tangential skin layers. It could be attributed to that the attachment of tangential lamellae to the cilia-like lamellae was detected as continuous bends, curves, or twists. Previous analysis on thin-film and thickness confined samples might have taken these traits as spiral or twisting of lamellae; however, as pointed out earlier, lamellae of radial and tangential directions do intersect at 90° (or nearly), but they do not spiral gradually from one to another at all. Opposite to such views generated from classical observations on thin-films samples, the internal dissection views on PEA bulks have clearly led to that there are always perpendicular radial lamellae plates between two tangential layers. Figure 6b shows that SEM characterization on PEA bulk

crystallized at $T_c=28^\circ\text{C}$, whose fractured interior shows alternating layers of radial and tangential lamellae intersecting at 90° to each other (not spiraling from one to another). The cilia fibrous layers are cleanly cleaved from tangential skins (composed by cilia-like lamellae), and radial lamellae are 90° perpendicular to the tangential skins. Each layer is composed of a tangential and a radial lamellae plate, together, these two perpendicularly intersected plates assume a dimension of 7-8 microns thick. Such internal analyses have also been discussed in a recent relevant study on PEA [17], and similar results have been shown. Here, further details of inter-lamellar intersection, yield views from a wider perspective.

Conclusion

By using several different polymers and compounds, organics or inorganic, low-molecular-weight or high-molecular-weight, this study has proven that they can be packed into concentric ring bands, usually circular, but other shapes, like hexagons or flower-like petals, can also be possible. Ring-banded spherulites in polymers can assume many types and inter-band spacing varies significantly, depending on T_c , polymer structures, film thickness, etc. Ring-banded spherulites of large spacing (20-50 μm) usually occur at higher T_c 's (130°C for PLLA, 120°C for PDoT). These large-spacing ring-banded spherulites are influenced by the top glass cover; for high- M_w PLLA, the spherulites are ringless if samples are uncovered with glass plates, but ring-banded if samples are covered with glass plates, when both are crystallized at same $T_c=130^\circ\text{C}$. On the other hand, the narrow-spacing ring-banded spherulites (spacing=5-10 μm) in PEA, PDoT, PLLA, PA etc, at lower T_c 's (28°C for PEA, 80°C for PDoT, 115°C for low- M_w PLLA, 28°C for PA) are not influenced by the top glass cover on samples; they all develop ring-banded spherulites regardless of top glass cover or not when crystallized at the same designated T_c 's for respectively compounds or polymers.

Obviously, there are three main traits for ring-banded pattern in compounds or polymers. (I) there are many types of ring bands (birefringent or not, large vs. small inter-ring spacing, etc.) in crystallized polymers; (II) ring banded spherulites can occur not only in polymers with chain-folded lamellae but also in low- M_w compounds with not chain folding at all; (III) top-glass cover on crystallizing samples can influence ring-banded spherulites of large spacing crystallized higher T_c 's but no effects at all on narrow-spacing ring banded spherulites crystallized at lower T_c 's of the same polymers. With these three traits, it is difficult to generalize the ring bands in spherulites to a single cause of lamellae twist/spiral; instead, exposure of lamellae underneath the top layers becomes essential for shedding new light on these intricately complex issues. The dissected cross sections show a corrugated-board structure with layers resembling a peel-able onion, where each radially oriented layer is sandwiched with a tangential layer of lamellae.

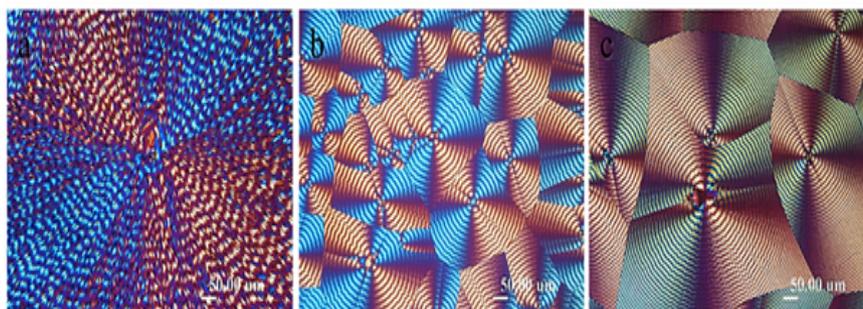


Figure 5: POM graphs for phthalic acid crystallized at (a) ambient, (b) 80°C, (c) 110°C, respectively.

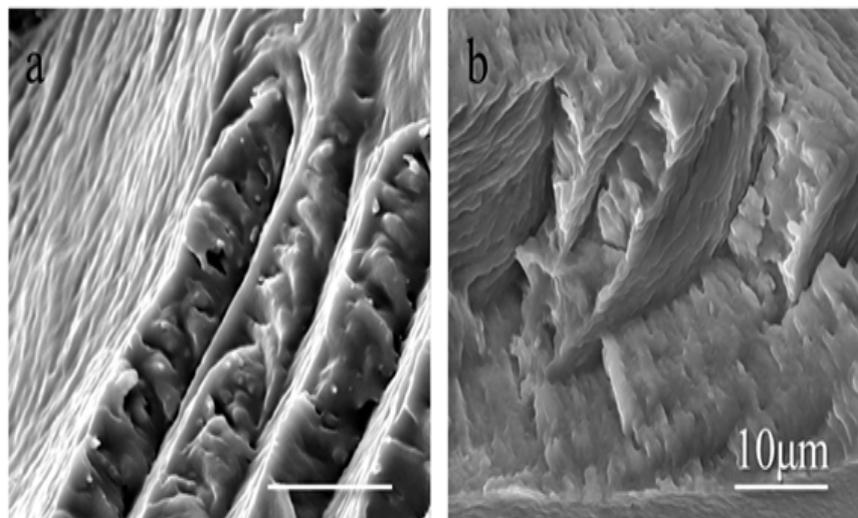


Figure 6: SEM graphs of the PEA bulk crystallized at $T_c=28^\circ\text{C}$: (a) radial and tangential lamellae perpendicularly interacting at 90° ; (b) tangential lamellae being cleaved cleanly from neighboring radial lamellae plates interacting at 90° .

Acknowledgment

This work has been financially supported by basic research grants (NSC 99-2221-E-006-014-MY3) in three consecutive years from Taiwan's National Science Council (NSC) – now Ministry of Science and Technology (MOST), to which the authors express their gratitude. This research was also partially supported by the Ministry of Education, Taiwan, R.O.C., in aim for the Top University Project to National Cheng Kung University (NCKU).

References

1. Shtukenberg AG, Freudenthal J, Kahr B (2010) Reversible twisting during helical hippuric acid crystal growth. *J Am Chem Soc* 132: 9341-9349.
2. Gunn E, Sours R, Benedict JB, Kaminsky W, Kahr B (2006) Mesoscale chiroptics of rhythmic precipitates. *J Am Chem Soc* 128: 14234-14235.
3. Shtukenberg A, Freudenthal J, Gunn E, Yu L, Kahr B (2011) Glass-crystal growth mode for testosterone propionate. *Cryst Growth Des* 11: 4458-4462.
4. Shtukenberg AG, Cui X, Freudenthal J, Gunn E, Camp E, et al. (2012) Twisted mannitol crystals establish homologous growth mechanisms for high-polymer and small-molecule ring-banded spherulites. *J Am Chem Soc* 134: 6354-6364.
5. Cui X, Rohl AL, Shtukenberg A, Kahr B (2013) Twisted aspirin crystals. *J Am Chem Soc* 135: 3395-3398.
6. Shtukenberg A, Gunn E, Gazzano M, Freudenthal J, Camp E, et al. (2011) Bernauer's bands. *Chemphyschem* 12: 1558-1571.
7. Imai H, Oaki Y (2010) Emergence of helical morphologies with crystals: twisted growth under diffusion-limited conditions and chirality control with molecular recognition. *Cryst Eng Comm* 12: 1679-1687.
8. Oaki Y, Imai H (2004) Amplification of chirality from molecules into morphology of crystals through molecular recognition. *J Am Chem Soc* 126: 9271-9275.
9. Chen HB, Chen L, Zhang Y, Zhang JJ, Wang YZ (2011) Morphology and interference color in spherulite of poly(trimethylene terephthalate) copolyester with bulky linking pendent group. *Phys Chem Chem Phys* 13: 11067-11075.
10. Wu PL, Woo EM (2003) Correlation between melting behavior and ringed spherulites in poly (trimethylene terephthalate). *J Polym Sci Part B: Polym Phys* 41: 80-93.
11. Wu PL, Woo EM, Liu HL (2004) Ring-banded spherulites in poly (pentamethylene terephthalate): a model of waving and spiraling lamellae. *J Polym Sci Part B: Polym Phys* 42: 4421-4432.
12. Wu PL, Woo EM (2004) Crystallization regime behavior of poly (pentamethylene terephthalate). *J Polym Sci Part B: Polym Phys* 42: 1265-1274.
13. Chen YF, Woo EM, Li SH (2008) Dual types of spherulites in poly(octamethylene terephthalate) confined in thin-film growth. *Langmuir* 24: 11880-11888.
14. Chen YF, Woo EM (2009) Annular Multi-Shelled Spherulites in Interiors of Bulk-Form Poly(nonamethylene terephthalate). *Macromol Rapid Commun* 30: 1911-1916.
15. Woo EM, Nurkhamidah S (2012) Surface nanopatterns of two types of banded spherulites in poly(nonamethylene terephthalate) thin films. *J Phys Chem B* 116: 5071-5079.
16. Meyer A, Yen KC, Li SH, Förster S, Woo EM (2010) Atomic-force and optical microscopy investigations on thin-film morphology of spherulites in melt-crystallized poly(ethylene adipate). *Ind Eng Chem Res* 49: 12084-12092.
17. Woo EM, Wang LY, Nurkhamidah S (2012) Crystal lamellae of mutually perpendicular orientations by dissecting onto interiors of poly (ethylene adipate) spherulites crystallized in bulk form. *Macromolecules* 45: 1375-1383.
18. Lugito G, Woo EM (2013) Lamellar assembly corresponding to transitions of positively to negatively birefringent spherulites in poly (ethylene adipate) with phenoxy. *Colloid Polym Sci* 291: 817-826.
19. Hsieh YT, Woo EM (2013) Microscopic lamellar assembly and birefringence patterns in poly (1,6-hexamethylene adipate) packed with or without amorphous poly(vinyl methyl ether). *Ind Eng Chem Res* 52: 3779-3786.
20. Hsieh YT, Ishige R, Higaki Y, Woo EM, Takahara A (2014) Microscopy and microbeam X-ray analyses in poly (3-hydroxybutyrate-co- 3-hydroxyvalerate) with amorphous poly (vinyl acetate). *Polymer* 55: 6906-6914.
21. Nurkhamidah S, Woo EM (2013) Unconventional nonbirefringent or birefringent concentric ring-banded spherulites in poly (L-lactic acid) thin films. *Macromol Chem Phys* 214: 673-680.
22. Nurkhamidah S, Woo EM, Tashiro K (2012) Optical birefringence patterns and corresponding lamellar alteration induced by solvent vapor on poly (L-lactic acid) diluted with poly (1,4-butylene adipate). *Macromolecules* 45: 7313-7316.
23. Lee LT, Woo EM, Hsieh YT (2012) Macro- and micro-lamellar assembly and mechanisms for unusual large-pitch banding in poly (L-lactic acid). *Polymer* 53: 5313-5319.
24. Lotz B, Cheng SZD (2005) A critical assessment of unbalanced surface stresses as the mechanical origin of twisting and scrolling of polymer crystals. *Polymer* 46: 577-610.
25. Bernauer F (1929) *Gedrilte Kristalle*. Gebroeder Borntraeger, Berlin, Germany.