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Graphical Abstract

Analysis of Crystal Assembly in Banded Spherulites of Phthalic Acid upon Solvent Evaporation

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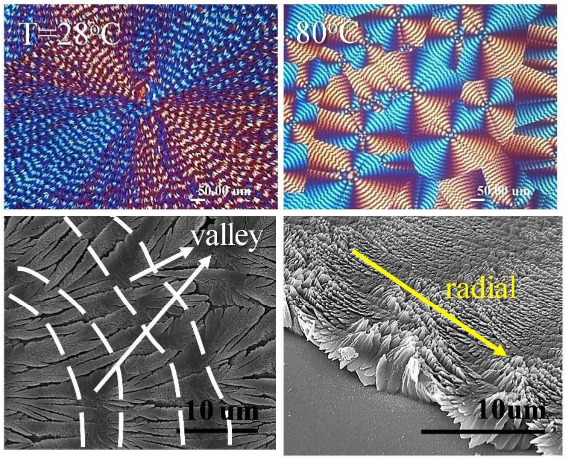

Differences are seen in the lamellar assembly of two alternative banded regions (valley and ridge) of phthalic acid spherulites solvent-evaporation crystallized either at higher temperatures (80 ^{o}C) or ambient (28 ^{o}C). The “ridge” of the band is composed of discrete crystals pointing upward, like high-rise buildings viewed from high altitude. The valley crystals are also discrete and all laid flat-on parallel to the substrate surface. From the fact of valley/ridge patterns being assembled like pieces of individual roof-shingle crystals pointing to two mutually intersecting directions, it is also consistent with the alternating optical bands of two birefringence shades.

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A low-M_w compound phthalic acid (PA) was chosen to investigate the packing mechanisms and lamellae assembly in ring-banded spherulites. Several solvents with PA were also investigated for appraising the kinetic effects on ring bands brought about by solvents. Structural effects were examined by morphology analyses on PA's two isomeric compounds, isophthalic acid and terephthalic acid. Optical birefringence and variation in the PA ring-banded spherulites crystallized at wide range of T_c (25–110 °C) was correlated directly to the top-surface lamellar assembly via characterization using atomic-force microscopy (AFM) and inner or lateral lamellae assembly were performed using scanning electron microscopy (SEM). Amazingly interesting features are seen in differences of lamellar assembly in the two alternative banded regions (valley and ridge) of PA spherulites solvent-evaporation crystallized at higher temperatures (80 °C) other than ambient (28 °C). The "ridge" of the band is composed of discrete crystals pointing upward, like high-rise buildings viewed from high altitude. The valley crystals are also discrete and all laid flat-on parallel to the substrate surface. All crystals, in valley or ridge, in peripheral or inner regions, are discrete and no continuous spirals from one to another. From the fact of valley/ridge patterns being assembled like pieces of individual roof-shingle crystals pointing to two mutually intersecting directions, it is also consistent with the alternating optical bands of two birefringence shades. Each of the bands is not from spiraling of a single continuous crystal, but packed by polycrystals and their aggregates that discretely grow in two different orientations.

Introduction

Small-molecule compounds, as well as polymers, are long known to crystallize into ring-banded spherulites under some specific conditions. Small-molecule compounds differ from polymers in the chain length and in the absence of chain folding in crystals. Many investigations by polymer physicists have theorized on an assumption of chain folding in polymers, and they have emphasized that polymers, owing to folding back and forth of long chains in crystals, exhibit chain-folding induced surface tensions/stresses in crystal plates as causes of continuous spirals. Such claims of stress-induced spiralling twists in polymers have dominated for decades as the most responsible factor for periodical bright/extinction optical birefringence in spherulites. However, in the literature, there are also ample studies by chemists on crystallization of small-molecule compounds that have demonstrated formation of similar ring bands of alternating birefringence rings in crystallized spherulites, either organics or inorganic salts.[1-12]

In 2006, Kahr et al.[3] investigated phthalic acid (PA) dissolved in an ethanol/water (20/80) mixture, and they reported that ring-banded spherulites could form from solvent evaporation-induced crystallization of PA solution casted on flat substrate as glass. AFM analysis revealed that the band spacing was 29 (±15) μm with height difference between ridge and valley being 150–250 nm. Such morphology of PA ring bands with similar band spacing can also be found in many polymers reported in the literature. In 2011, Kahr et al.[4] further investigated the crystal lattices of PA and proposed that phthalic acid crystallizes in monoclinic cell group and no polymorphs of PA have been detected, suggesting that polymorphism was not a cause for ring bands. Nevertheless, authors in those investigations still did not clearly expound the mechanisms of ring bands, other than excluding the possibility of crystal polymorphism. As the matter of fact, not just PA, but also many other small-molecule compounds are known to form ring-banded spherulites: mannitol,[5] testosterone propionate,[6] aspirin with salicylic acid,[7] resorcinol,[8] potassium dichromate ($K_2Cr_2O_7$),[9-12] etc. Crystallization and growth conditions, crystal polymorphisms, additives are factors that promote the appearance of twisted/spiral crystal in those compounds. However, the crystal "twist" seen is ultimately do not match the band spacing of the spherulites.[10] Apparently, issues of microscopic evidence of spiral twists, responsible causes of crystal lattices, additives, melt-

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†Electronic Supplementary Information (ESI) available: [Properties of the solvents, POM graphs of isophthalic acid dissolved in THF and DMF, terephthalic acid in DMF, and benzoic acid in ethanol/water (20/80) and ethanol at different evaporation temperatures, AFM height image and profile]. See DOI: 10.1039/x0xx00000x

crystallization vs. solvent-evaporation crystallization, etc., remain still elusive.

In two-dimensional molecular self-assembly, structures are depending on molecular building blocks, temperature at which self-assembly takes place, type of solvent, and other parameters that influence the kinetics and thermodynamics self-assembly process.[13] Our current work was focused on extension of PA crystals in attempt to probe the possible causes by investigating effects of evaporation temperature, solvents, chemical structures, and film thickness. Topology of top-surface lamellae assembly of banding patterns was analysed using AFM, while the inner lamellae assembly was dissected using SEM from lateral sides and free edges. A unique approach was taken, which analysis was not based on top views of crystals, but also from lateral or interior views across the thickness. Only via such approaches could new light be shed on causes and mechanisms of crystal assembly in banded spherulites not only in small-molecules compounds but also in feasible extension to interpreting those similar bands in high-molecular-weight compounds – polymers.

Experimental

Materials and methods

Phthalic acid (PA), C_6H_4-1,2-$(COOH)_2$, was obtained from Alfa Aesar, Inc. (USA), with M_w = 166.13 g mol^{-1}, T_m = 205 °C. Two other isomers of PA were also examined: Iso-phthalic acid (IPA) was supplied by Aldrich Chemical Co., Inc. (USA), with M_w = 166.13 g mol^{-1}, T_m = 341 ~ 343 °C. Terephthalic acid (TPA) was supplied by Aldrich Chemical Co., Inc. (USA), with M_w = 166.13 g mol^{-1}, T_m > 300 °C. Benzoic acid (BA) was supplied by Fluka Chemical Co., Inc. (USA), with M_w = 122.12 g mol^{-1}, T_m = 112 °C. Different solvents with different evaporation rates (boiling points, T_b) were used to evaluate the solvent effects on spherulites' patterns and lamellar assembly of PA and its isomers. The solvents used are 20% alcohol in aqueous solution (20%ethanol+80%water), demineralized water, ethanol, THF, and DMF as described in **Table S-1**.

PA (or other isomeric compounds – IPA or TPA, or benzoic acid) was first dissolved in solvent. Concentration of the solution was kept at 0.12 M, in accordance with previous investigations.[3,4,11,12] However, concentration variation within a small range was not found to be an influential factor on final crystal morphology. Film sample preparations of all small-molecule organic compounds were as follows. One or two drops of PA solution (0.12 M, 0.02 g ml^{-1} solvent) was drip-cast on the glass slides (placed on temperature-controlled hot stage for a specific T_c) until the solvent was totally evaporated for the compounds to fully crystallize. Crystal banding regularity and patterns might differ with the temperature of crystallization; thus, a range of different T_cs (casting temperatures) were examined for each sample. Sample thickness was kept at ca. 1–2 μm for POM characterization, as films beyond some thickness might have overlapped crystals. For SEM characterization, film thickness effects on crystal assembly were examined by preparing three levels of thickness in cast samples. For comparison of thickness effects on crystal assembly, a total of three film thickness levels were prepared: 1–2 μm, 3–4 μm, and 8–10 μm.

Apparatus and procedures

Polarized-light optical microscopy (POM, Nikon Optiphot-2) equipped with a Nikon Digital Sight (DS-U1) digital camera and a microscopic heating stage (Linkam THMS-600 with T95 temperature programmer) was used for the preliminary confirmation of different morphology spherulites in samples prepared by crystallization at the procedures described in the previous section. First-order retardation plate (530 nm) was also inserted in between polariser and analyser to produce contrast interference colours for all POM graphs.

Atomic-force microscopy (AFM, diCaliber, Veeco Corp., Santa Barbara, USA) investigations were made in an intermittent tapping mode with a silicon tip (f_0 = 70 kHz, r = 10 nm) installed. The largest scan range was 150 x 150 μm, and the scan was kept at 0.4 Hz for the overview scan and zoon-in regions. Thin films of neat PA (or IPA, TPA) were deposited on glass slides without cover, with an open face for AFM characterization.

Scanning electron microscopy (FEI Quanta-400 F, SEM). In addition to characterization on top-surface morphology of banded spherulites, the interior crystal assembly was viewed from lateral sides of the banded spherulites. Fractured surfaces and top surfaces of thin-film PA samples (or IPA, TPA) crystallized at solvent-evaporation (ethanol/water) temperatures of RT (28 °C) or 80 °C were characterized using scanning electron microscopy (SEM) for revealing the lamellar structure in the lateral fracture surfaces and top free surfaces, respectively. Those fractured samples were sputter-coated with gold vapour deposition using vacuum sputtering (2 mA, 10 x 60 s) prior to SEM characterization.

Results and Discussion

Figure 1 shows POM graphs for phthalic acid (PA) dissolved in ethanol/water (20/80) solution (conc. = 0.12 M), then evaporated to crystallize at different temperatures. The POM results in **Fig. 1** show clearly that PA cast films crystallized at T_c = 50 to 110 °C exhibit optical banding patterns and ring orderliness that are all similar. Oscillations around a more or less constant band spacing value of 20 microns are obtained from this system. This tendency is different from the tendency of most melt-crystallized polymers that increases with increase of T_c.[14,15] Unlike the formation of ring formation in melt-crystallized polymer systems that is governed only by crystallization kinetics, in solution-cast PA, it is also governed by solvent evaporation rate. The fact that these two temperature dependent governing rates are in contrast one another perhaps the reason why oscillations in band spacing occur. Although the ring regularity of PA ring-banded spherulites does not differ much when cast at 50–110 °C, it should be noted here that the general ordered regularity of ring bands in PA cast at these higher T_c's is very different from significantly twisted ring patterns in the PA ring-banded spherulites crystallized at room-temperature (25–28 °C) as reported earlier by Kahr, et al,[3,4] or in the twisted ring bands of crystallized $K_2Cr_2O_7$ at T = 25 °C by Imai et al.[11,12] The temperature of casting (or crystallization) in either PA or $K_2Cr_2O_7$ apparently does an influential effect on the patterns of ring bands by altering the crystal assembly in forming the spherulites. We will further address the crystal assembly in PA crystallized at T_c = 25 °C vs. that at T_c = 50–110 °C in latter sections.

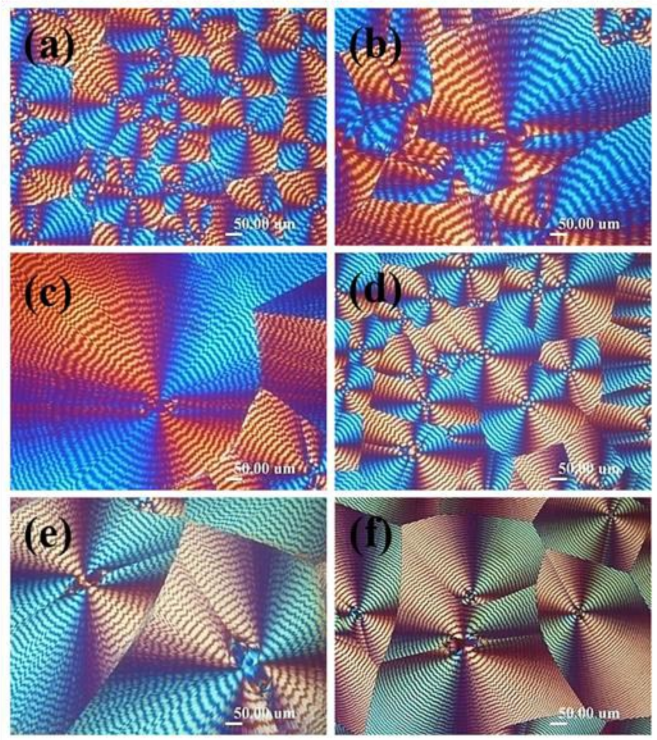


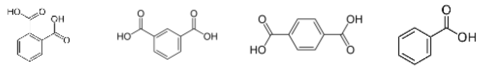
Figure 1. POM graphs of phthalic acid (PA) dissolved in ethanol/water (20/80) solution (0.12 M), then evaporated to crystallize at different temperatures: (a) 50 °C, (b) 60 °C, (c) 70 °C, (d) 80 °C, (e) 90 °C, (f) 110 °C [scale bars = 50 μm].

Careful examination of the POM graphs in **Fig. 1** for the ring-banded PA spherulites at different T_c's (50–110 °C) reveal that the concentric bands are all bordered with two colour-shades of a same birefringence colour. PA shows extinction-bright (black-white) rings in POM if without tint plates, hence a 530 nm tint plate was added to POM in characterizing the crystallized PA crystals. In crystalline spherulites, birefringence is described as difference between the refractive index in radial direction (n_r) and the refractive index in tangential direction (n_t). When $n_r - n_t = 0$, there is extinction/ transparency; but when $n_r - n_t$ = values other than zero, there are different colours (larger value) or shades (small value) of birefringence. In the ring-banded PA spherulites, no strict extinction bands ($n_r - n_t = 0$) exist, as only two bands of different shades (brighter-darker) alternatively repeat themselves in forming the ring bands. This optical patterns lead to useful tips of dissecting the inter-relationship with the crystal lamellae assembly to be discussed in SEM data in latter sections.

The ring-banded spherulites in the low-M_w PA compound, however, are quite similar in patterns to those found in many other polymers that are known to form similar ring-banded spherulites, to name just a few, such as poly(3-hydroxybutyrate) (PHB),[16-19] poly(nonamethylene terephthalate) (PNT),[20,21] poly(trimethylene terephthalate) (PTT),[22] polycaprolactone (PCL),[23] and poly(L-lactic acid) (PLLA),[19,24,25] as well as widely-studied poly(ethylene adipate) (PEA),[26,27] or classical polyethylene (PE).[28,29] The optical birefringence patters may differ among the ring-banded spherulites of either polymers or low-M_w compounds though. When tint-plate is equally used in POM characterization, the PA ring-banded spherulites are characterized by bright bands interspersed with darker (extinction) band; while the banded spherulites in many polymers (PEA, PHB, PTT, PNT, etc.) are distinguished by alternating addition (blue) and subtraction (orange) colour-bands, suggesting the crystal packing in these different birefringence patterns may differ correspondingly.

Similar alternating-birefringence ring-banded spherulites as those in PA have also been reported for other small-M_w organic compounds, such as: mannitol,[5] testosterone propionate,[6] aspirin mixed with salicylic acid,[7] as reported earlier by Kahr et al. These small-molecule compounds (mannitol, testosterone, and aspirin) reportedly can form banded spherulites from melt-crystallization (compounds melted and quenched to crystallization temperature, without solvent). By contrast, for PA to form ring-banded spherulites, not only it has to be crystallized from PA solution upon solvent evaporation, but also the solvents should be specific and solvent evaporation must be at some suitable T_c's range. These facts reflect that kinetics favourability is likely the only way to produce banded spherulites from PA. The kinetic favourability in PA ring-band formation also involves complicate interplays between the crystal growth and solvent evaporation, as PA does not develop ring-banded spherulites at any T_c when melt-crystallized from molten state without any solvents.

Table 1. Spherulitic morphologies examined by using POM for some small-molecule compounds in various solvent-evaporation systems.



	Phthalic acid	Iso-phthalic acid	Tere-phthalic acid	Benzoic acid
(20%ethanol -80%water) solution	ring-banded	insoluble	insoluble	ringless
water	mostly ringless	insoluble	insoluble	insoluble
ethanol	ring-banded	ringless	insoluble	ringless
THF	ring-banded	ringless	insoluble	ringless
DMF	ringless	ringless	ringless	✕

Effects of solvents and chemical structures of the crystalline species were investigated. PA morphologies resulted from solvent evaporation method of different solvents are summarized in **Table 1**, and graphical results are demonstrated in POM characterization to be discussed. For more detailed analysis and comparison of solvent effects, **Figures 2** and **3** show the POM crystal morphology and optical patterns in PA film-cast to crystallize from solutions of PA with various solvents. PA was dissolved in solvents other than the ethanol/water mixture, such as pure THF (T_b = 66 ^oC), ethanol (T_b = 78.4 ^oC), water (T_b = 100 ^oC), or DMF (T_b = 152 ^oC). The various PA/solvent solutions were subjected to similar solvent evaporation-induced crystallization by casting to controlled-T_c on hot plates and their crystal morphology characterized using POM for comparisons to those observed in PA with water/ethanol solvent. Results in **Fig. 2** show that PA in pure THF or pure ethanol could form partial ring-banded spherulites, although not as distinct or regular as those in PA cast from the ethanol/water (20/80) solution. Basically, PA in the ethanol/water mixed solvent of any weight ratios (x/y) could lead to ring-banded spherulites, differing only very little in the ring-band regularity or interring spacing. With PA in ethanol/water (20/80) solution, the temperature window within which the PA solutions could be cast into ring-banded spherulites appeared to be quite wide (from RT to 110 ^oC).

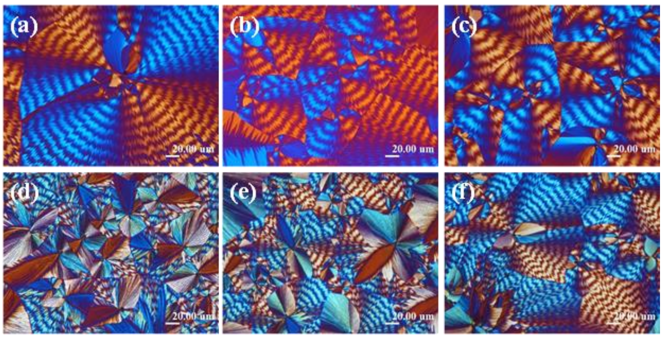


Figure 2. POM graphs of orderly ring-banded spherulites in phthalic acid (PA) dissolved in ethanol and crystallized at different evaporation temperatures: (a) 50 ^oC (b) 60 ^oC (c) 80 ^oC; versus partially ring-banded spherulites in PA dissolved in THF and crystallized at: (d) 50 ^oC, (e) 60 ^oC, (f) 80 ^oC [scale bars = 20 μm].

For slower-evaporating systems (PA in DMF or water), ring-band spherulites were not found at any casting temperatures. On the other hand, for very fast-evaporating solvents, such as PA dissolved in pure THF or ethanol, ring bands could form, but the regularity of banding patterns was not as good as in PA from the water/ethanol mixtures. The fact suggests that PA crystal bands were intimately regulated by the solvent evaporation rates to form ring bands in crystallized spherulites. As PA was cast and crystallized from the water/ethanol mixture, water acted as an evaporation regulator with ethanol in leading to the most uniform patterns of ring bands.

In the meantime, chemical structure effects of the compounds were examined, and results are shown collectively in **Figures S-1** to **S-5**. Two PA isomers, i.e., isophthalic acid (IPA) and terephthalic acid (TPA), could not dissolve in ethanol or water or ethanol/water mixtures at all. As these two isomers do not dissolve in water/ethanol mixtures, they cannot be compared to the morphology of PA in same water/ethanol mixtures. Nevertheless, they could be dissolved in DMF, but no ring-bands could form as TPA/DMF or IPA/DMF solutions were cast to crystallize at any Tc. Benzoic acid (BA), differing from PA by having only a single COOH in the benzene ring, also did not dissolve in water, but could be dissolved in the ethanol/water (20/80) mixture, pure ethanol, or THF. However, BA only exhibited ringless spherulite morphology (**Fig. S-4** and **Fig. S-5**), regardless of what solvents were used or at any temperature of evaporation. This is to say, although rapid solvent evaporation is essential in inducing extinction ring in crystallized low-M_w compounds, proper physical interactions between the compounds and solvents collectively govern the patterns of spherulites. The chemical structures of compounds, like numerous cases in polymers, influence the ease with which the compounds could be cast into ring-banded spherulites.

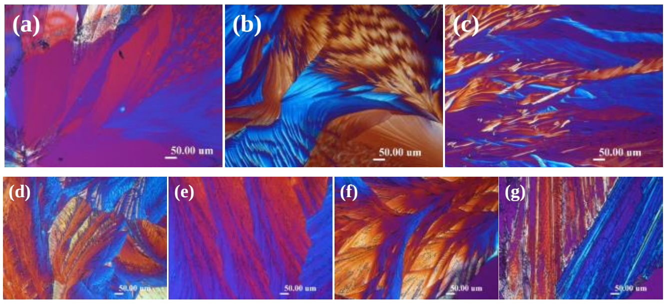


Figure 3. POM graphs of mostly ringless spherulites in phthalic acid (PA) dissolved in water and crystallized at different evaporation temperatures: (a) 60 ^oC (b) 80 ^oC (c) 100 ^oC; and strictly ringless spherulites in phthalic acid (PA) dissolved in DMF and crystallized at different evaporation temperatures: (d) 80 ^oC, (e) 110 ^oC, (f) 130 ^oC, and (g) 150 ^oC [scale bars = 50 μm].

Apparently, rhythmic precipitation is at work in generating rings in solvent-evaporated PA, but it does not work with all compounds or all solvents. PA could be under solvent-evaporation-induced crystallization cast into ring-banded spherulites within a wide range of temperatures: 28 – 110 ^oC (hot-stage controlled), although the banding regularity at lower RT was not as good as those cast at higher temperatures, e.g., T_c = 80 ^oC. The ring-band pitches and height difference between the valley and ridge in ring-banded PA, however, were found to differ with respect to T_c and film thickness. As an example, both AFM height image and height profile of PA banded spherulite crystallized from ethanol/water (20/80) solution-evaporation at T_c = 110 ^oC are shown in Figure S-6. These facts suggest that the kinetics of solvent evaporation influences the crystallization kinetics and final morphology of ring banded spherulites in PA. Morphology patterns and crystal lamellae of ring-banded PA spherulites at several solvent evaporation temperatures (from low RT to high 110 ^oC) were analysed. Lamellae packing in the banding pattern of PA cast at RT are significantly different from that cast at T_c = 80 ^oC, which can be revealed by SEM analysis in correlation with POM analyses.

Figure 4 shows SEM micrographs **(a-d),** POM graph **(e)**, and scheme **(f)** for the top-surface of phthalic acid (PA) solvent-evaporation crystallized at RT (28 ^oC). POM micrograph is illustrated for the birefringence patterns of the rings in PA cast at RT in correlating the lamellae assembly revealed by the SEM results. Owing to branching at irregular positions in these crystal plates, the banding pattern is correspondingly not regular (as shown in **Fig. 4(e)**). For more details, the SEM graphs (**Fig. 4(a-d)**) yield clear evidence that for PA crystallized at RT, all crystals are flat-on and parallel to the substrate, and the PA crystals are aligned collectively to point to radial directions, with minor slanting angles. There are no PA crystals twisting or spiralling from ridge to valley or vice versa. The ring bands in PA spherulites cast at RT are not very circularly regular, but with some zig-zag irregularity. The ridge band is filled with wider lamellae (all flat-on) pointing in radial direction and interfaced with neighbouring lamellae with visible crevices (voids). The valley band (darker zig-zag rings in **Fig. 4(a)**) is composed of numerous crystal branches that bend from the radial direction and evolve from slightly different positions of the main stalk crystals. That is, in the valley, the crystals are bent to deviate from the radially oriented ridge-band crystals, and are more compact with less crevices between the valley crystals. After crossing the valley region, the crystals in spherulites grow forward to form the next ridge region, where the crystal branches fan out in the radial direction to fill the increasingly larger space (i.e., growing spherulite with increasing radius); and again, the fanning-out of these crystal branches leave significantly unfilled crevices between the branches. This fact accounts for that the ridge crystals are wider and more significant voids between branches, while the valley crystals are narrower and almost no crevices between the neighbouring crystals. The ridge-valley cycles repeat to form ring bands. Note, however, both valley and ridge crystals are flat-on and parallel to the substrate surface, and they do not twist from edge-on ridge to flat-on valley to form a continuous spiral. The valley crystals do bend (or branch out) to deviate from the ridge crystals in the radial direction, with the cycles repeated periodically to form alternating ring bands.

Scheme drawing in **Fig. 4(f)** summarizes the detailed SEM crystal morphology in the RT-crystallized banded spherulites in PA films, which amply demonstrate that the banding pattern in PA apparently cannot be interpreted as a single crystal monotonously twisting to a continuous spiral. By contrast, numerous branching lamellae, all flat-on, fan outward in periodical "branching-precipitating" cycles to fill the increasingly larger peripherals of the expanding spherulites. Only via such a mechanism can the crystals fill the ever increasing spherulite; or else a monotonous lamella of fixed width in continuous spiral cannot possibly fill the space of an expanding spherulite at all. There indeed may be single crystals of some small-molecule compounds that can be grown to as long as 1 mm in suitable conditions, and these single-crystal plates can undergo twisting upon exposure to stresses, etc., as reported by Shtukenberg, et al.[1,5] However, for polycrystalline spherulites of polymers or small-molecule compounds (in melt-crystallization or solution grown), the crystal lamellae cannot grow continuously as long as several hundreds of micron-meters to twist into perfect spirals without discontinuity. It should also be pointed out here that in low-resolution optical microscopy, polymer spherulites may display long and seemingly continuous lamellae; however, in SEM or AFM micrographs, these "continuous" lamellae in spherulites actually are composed of numerous discrete crystal plates, or branches, etc., with apparent discontinuity in the crystal structural hierarchy.[20,26,27,30]

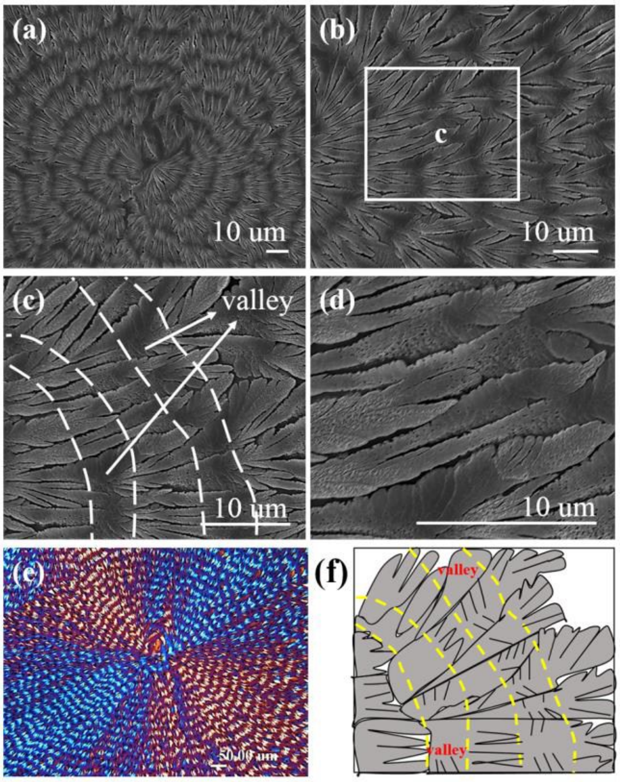


Figure 4. SEM graphs (a, b, c, d) with increasing magnifications as indicated on graphs, (e) POM micrograph [scale bar = 50 µm], and (f) scheme for top-surface of phthalic acid (PA) solvent-evaporation crystallized at room temperature (RT = 28 °C), where the banding pattern is not regular. Yellow dashed lines indicate border between the ridge and valley.

Morphology and crystal assembly of ring-banded spherulites in PA cast films at temperatures higher than the RT were also analysed. The lamellar-assembly morphology of the extinction bands in PA cast at RT is similar (or same as) to that reported earlier by Kahr et al.;[3] however, it will be shown later that PA cast at higher evaporation temperatures (T = 50–110 °C) and/or with thicker films, the extinction bands and corresponding lamellar assembly display an entirely different morphology. **Figure 5** shows SEM micrographs for the top surface of the phthalic acid crystallized at 80 °C at medium sample thickness (4–5 µm). The corresponding optical patterns of 80 °C-crystallized PA are as shown earlier in POM graphs of **Fig. 1**. The SEM analyses were intended to reveal the detailed crystal assembly on top surface that accounts for the optical patterns seen in banded PA spherulites. Apparently, **Fig. 5** shows that the concentric rings are composed of alternative lamellar assemblies that differ between the ridge and valley bands (or bright and dark bands in POM graphs). In the ridge region of banded spherulites, the crystal bundles (lamellae) point mostly upwards with the lozenge tips slanting upward to top surface. The crystal bundles generally are aligned at a slant angle to the radial direction (that is, the long axis of crystals in ridge is not entirely in the radial direction but the crystals all point upward from the substrate); by contrast, in the valley region, the crystal bundles point to the tangential direction and they lie flat on the substrate (the long axis of crystals in valley is aligned at a slant angle to the transverse direction). In all, the long-axis directions of the crystals in ridge and valley may not be a full 90^{o} to each other, but they differ substantially to cause birefringence contrast in valley vs. ridge bands. Connection between the radial-oriented and tangential-oriented crystals is not clear enough in this crystallized PA film of 4–5 µm thickness (T_c = 80 ^{o}C); but the crystals in the valley are generally thinner, and they appear to be finer branches of crystals evolving from the thicker radial crystals. Such assembly repeats itself to form optical ring bands. Apparently, crystals in the ridge band intersect perpendicularly with the crystals in the valley band. In addition, the crystals in the valley band tend to be more branched with finer textures. Nevertheless, one cannot say that a single crystal twists and/or spirals from ridge to valley, as these are not single crystals at all; they are polycrystals with multiple discrete branches bending 90^{o} periodically. Crystal assembly and transition from ridge to valley bands should be viewed more closely by analysing the crystallized PA films of a thicker structure to fully expose the lateral sides. The peripheral region of banded PA spherulites allowed lateral views on true crystal assembly to be conveniently analysed.

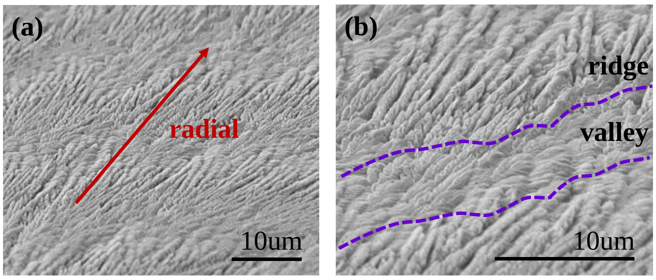


Figure 5. SEM micrographs for top-surface of phthalic acid (PA) crystallized at T_c = 80 ^{o}C with medium sample thickness: 4–5 µm. Border indicates interfaces between the ridge and valley bands.

PA thin-film samples (PA in ethanol/water solvent crystallized at 80 ^{o}C) were prepared to expose the broken lateral side of the films, where upon setting the sample vertically upward at tilted angles, the cross section of the sample's lateral side could be viewed with SEM electron beams from the top. SEM characterization was then performed on the samples where both the cross section of the thickness direction and top surface of the PA film could be simultaneously analyzed. **Figure 6** shows SEM micrographs of crystals in the ridge and valley regions of phthalic acid crystallized at 80 ^{o}C with banded spherulites (samples prepared to be thicker films of 8–10 µm). Focus was placed on the crystal assembly at ridge and valley bands in the peripheral vs. inner regions of the spherulite. The edge of the spherulites has helped to shed very clear light in revealing the alternating features of lamellae in constituting the ridge vs. valley bands in PA spherulites. The shingle-like PA lamellae resemble each other in the geometry dimensions, but differ in their pointing directions (or growth direction) – in the ridge band they point upward but in the valley band they point in transverse horizontal direction. All crystals, in valley or ridge, in peripheral or inner regions, are discrete and no continuous spirals from one to another. From the fact of valley/ridge patterns being assembled like pieces of individual roof-shingles pointing to two mutually perpendicular directions, it can be ruled out that bands are composed of same continuous crystals spiraling from valley to ridge from a common nucleation centre.

The inner regions of the spherulites, by comparison, are much more crowded with lamellae species, as shown in the zoom-in SEM image of **Fig. 6(b)** (inner spherulite region as marked). Such features as exemplified in the peripheral edges vs. inner regions of spherulites can be extended to predict that there would be subtle differences of lamellar assembly between the top free surface and the crowded inner layers of spherulites in crystallized films on a flat substrate. If one examines the inner regions of the PA spherulites carefully, one sees that similar alternating shingle-like crystals are packed in the valley and ridge bands, respectively. However, as they are more jammed in the inner region of the spherulites, one sees that the valley band is packed by crowded flat-on shingles but the ridge band is packed by squeezed shingles that are aligned orderly all at a slant angle to vertical directions. The PA ring-bands at high T_c (80 ^{o}C) tend to be more ordered than those at ambient or lower T_c's, and the crystal assembly likely may take a mechanism slightly from the conventional continuous twisting. The fractured cross section of ring banded PA spherulites exposed that these two crystal sets intersected at 90^{o} to each other, leading to alternating birefringence (bright/dark) contrasts. Such crystal assembly repeats itself to form optical ring bands. The ridge crystals appear to be oriented 90^{o} from the ridge to the valley. The ring bands are associated with the growth cycles (radial growth outward-branches with transverse bends), which repeat until the spherulites are filled and complete.

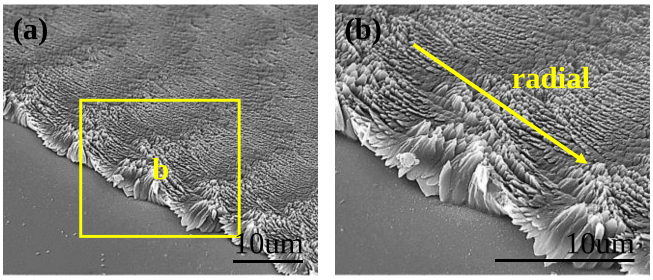


Figure 6. SEM micrographs of banded spherulite of phthalic acid (PA) with thicker sample (ca. 10 µm) crystallized at T_c = 80 ^{o}C: (a) peripheral vs. inner regions of banded spherulite, (b) zoom-in graph of squared region. Scale bars indicate magnifications.

To more emphatically illustrate these crystal assemblies in the ridge vs. valley of the concentric band in PA spherulites, a scheme is made and shown in **Figure 7**. The scheme represents a clear view based on the deeper analysis on the SEM results of the 80 ^{o}C-crystallized PA films. Each shingle-like lamella is more or less lozenge-shaped with dimension ca. 2–3 µm in width and 5–10 µm in length. Near the edge of the spherulites, these two crystal sets intersect at 90° to each other, leading to radially alternating optical birefringence (bright/dark) contrasts, as the SEM evidence has clearly revealed that the long axis of the lozenge-shape crystals are pointing to different directions in the valley vs. ridge band. Such crystal assembly repeats itself to form optical ring bands. Worth to mention here that even if these discrete crystals come from the independent growth of the undergo fragmentations as the lamellae become thicker and more rigid (Eshelby twists), we could not see any main twisted pole that connects one shingle-like lamella to the next and thus keeps the twisting effect last forever from the SEM figures. During the solvent evaporation, repeated precipitation of PA crystals occurs due to a complex interplay of several flows, allowing the crystal to arrange in two contrast alternating arrangements of vertical and horizontal.[31]

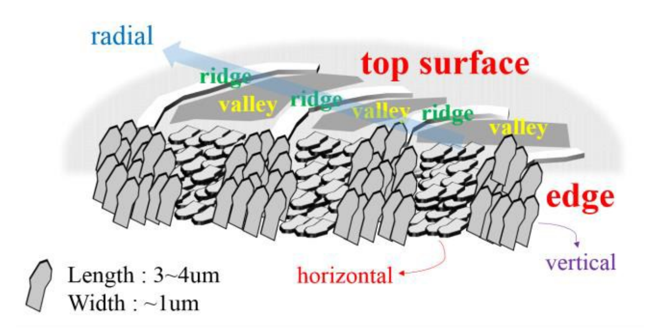


Figure 7. Scheme for crystal assembly as viewed from lateral surface and top surface, revealing an imbricate structure of discrete crystals assembly of two alternating directions.

To sum up, the above SEM result of Fig. 6 and scheme in Fig. 7 illustrate the main features of PA crystals upon solvent evaporation at 80 °C, which may need better refinement for proving three possibilities: (1) twisting of continuous crystals at low T_c's including ambient temperature, (2) discrete and perpendicularly oriented crystals at high T_c's such as 80 °C or higher, (3) do the same transition of crystal assembly exist in compounds other than PA? The complexity in ring bands of organic or inorganic compounds can be appreciated in the following discussions on numerous compound systems widely investigated in the literature.

Rhythmic precipitation, as a matter of fact, is not limited to PA from solvents or solvents/gelatine. It actually is also common in some inorganic compounds, such as aqueous potassium dichromate ($K_2Cr_2O_7$) first studied by Miers.[32] Extinction rings in crystallized spherulites of phthalic acid (C_6H_4-1,2-$(CO_2H)_2$, PA) were first described long time ago by Gaubert.[33] Spherulites, by essence of multiple crystals or anisotropic-oriented lamellae, are polychroism; and this means that the spherulite (either ringless or ring-banded) has the optical property of optically anisotropic crystals to exhibit different brightness and/or colour when the polarized light is transmitted through it. A further critical question to be asked is: how do the crystals or lamellae pack in a spherulite so that the optical birefringence would display the observed ring patterns? We attempted to address the issue in this work in details. By using gelatine (10% in solvents) to encourage periodical precipitation, Imai and Oaki [11,12] described the ring bands in $K_2Cr_2O_7$ as "type-2 spherulites" (T_c = 25 °C), whose radii twist helically and turn in heterochiral directions from the site of nucleation. It should be noted that the work by Imai et al.[11,12] on $K_2Cr_2O_7$ was done on T_c = 25 °C; however, our present work on PA already demonstrates that the temperature of PA casting (e.g., RT vs. 50–110 °C) can dramatically alter the ring patterns and crystal assembly therein. By extension of Imai's work on $K_2Cr_2O_7$, Kahr, et al.[3] further demonstrated that using gelatin was not essential in producing the extinction rings in PA or other similar compounds. They probed the origin of the differential circular extinction in PA using AFM analysis; they found that the crystals have heterochiral microtextures. They used AFM image of a banded phthalic acid (PA) spherulite cast at RT (ca. 25–28 °C ambient) to show that there is the difference in handedness in two sectors of spherulites. More recently, Imai et al.,[34] used interferometry and optical microscopy techniques to investigate the crystals of potassium dichromate $K_2Cr_2O_7$ grown in a gelatine gel at a fixed T_c of 25 °C to confirm continuous twisting phenomenon that has been proposed in other previous studies.[1,5] Our study in this work further extends that thickness of PA films and temperature of casting profoundly influence that morphology and crystal packing in banded spherulites– to such extend that crystals are aligned to not necessarily obey the rule of handedness. We used SEM analyses on PA crystals solution-grown at various T_c's (25 – 80 °C) in discovering new modes of crystal packing that differ from earlier results for small-molecules grown in gels, and these results can likely stir up newer thoughts for future work on refining the mechanisms. Such critical evidence lends another critical hint that analysis of banding mechanisms and phenomena in ring-banded spherulites cannot be based solely on top-surface analysis using AFM or micro-beam X-ray analysis by assumption that lamellae are monotonous and continuous spirals single-crystal-like lamellae, as the real situations in banded spherulites are likely much more diversified. The cases in PA banded spherulites demonstrate that they are stacked by many polycrystals with statistical distributions and variations between the periodically alternating ridges and ridges in bending, orientation, inclinations, and perhaps some irregular and localized twisting, through the thickness as well as across the radial directions.

More insights have been advanced that the crystal assembly in PA banded spherulites with sufficient film thickness and higher temperature of casting (80 °C), as viewed from lateral surface and top surface, reveals an imbricate structure of discrete crystals assembly of two alternating directions. When cast at relatively low temperatures near the room temperature (25°C), the lamellae in banded PA spherulites may display features of twisting as reported in earlier investigations in the literature.[3,4] However, for PA spherulites cast at higher temperatures (60–110 °C), the ring bands apparently are composed of discrete crystals that are perpendicularly oriented in the ridge vs. valley bands.

Conclusions

Ring-banded spherulites in low-M_w compound phthalic acid (PA), with two COOH groups in the meta-position of benzene, were analyzed in details using various microscopic techniques into the internal and top views for lamellar assembly that accounted for the ring formations. Conventional views that lamellar plates being continuously and periodically twisted up (edge-on) and down (flat-on) to form the ring bands may need adjustment. Phthalic acid (PA) dissolved in ethanol/water (20/80) (or virtually any other ratios), which upon casting onto substrates at a wide range of T_c = 28–110 °C, could easily form ring-banded spherulites with alternating bright/dark rings. Lamellae, either in ridge or valley, are packed like pieces of roof-shingle plates with each of single crystals measured as 2–3 µm in width and 5–10 µm in length.

For the PA banded spherulites grown at lower T_c (28 °C), as the lamellae grow outward from radii center, they continuously branch out to fill the ever-expanding larger spherulites, with each branching plates measured roughly the same (2–3 µm in width and 5–10 µm in length). The growth of PA at lower Tc (ambient) may be closer to the conventional model of twisting and branching periodically.

By contrast, the ring bands in PA crystallized at higher T_c = 50–110 °C (above ambient) are more regularly ordered, which have never been reported or discussed before. For PA banded spherulites grown at higher T_c's (50–110 °C), the lamellae are denser and increasingly more compact, but each pieces of crystal plates still measured the same (2–3 µm in width and 5–10 µm in length) as those crystallized at lower T_c's. In the ridge region, the crystal bundles (sheet-like crystal lamellae) point to the radial direction (long axis of crystals in radial direction); by contrast, in the valley region, the crystal bundles point to the tangential direction (long axis in the transverse direction). Althogh the current results still could not rule out possibility of lamellae being twist continuously from ridge to valley; we think the cyrstal assembly for a more ordered ring band may likely take a different mechanim, which is that they are discretely packed and differ in ways of packing in the ridge vs. valley regions of the banded spherulites. Further work is needed to more evidently construct a model for PA ring bands crystallized at a wide range of temperatures.

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