

Review

Morphological Control of Polymer Spherulites via Manipulating Radial Lamellar Organization upon Evaporative Crystallization: A Mini Review

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Abstract: Various spherulites or spherulitic crystals are widely encountered in polymeric materials when crystallized from viscous melts or concentrated solutions. However, the microstructures and growth processes are quite complicated and remain unclear and, thus, the formation mechanisms are rather elusive. Here, diverse kinds of spherulitic growths and patterns of typical polyesters via evaporative crystallization of solution-cast thin films are delineated after detailed investigating the microstructures and in situ following the developing processes. The spherulitic crystals produced under different evaporation conditions reflect variously optical features, such as the usual Maltese Cross, non-birefringent or half-birefringent concentric-rings, extinction spiral banding, and even a nested ring-banded pattern. Polymer spherulites are composed of stacks of radial fibrillar lamellae, and the diversity of bewitchingly spherulitic morphologies is dominated by the arrangement and organization of radial lamellae, which is predicted to be tunable by modulating the evaporative crystallization processes. The emergence of various types of spherulitic morphologies of the same polymer is attributed to a precise manipulation of the radial lamellar organization by a coupling of structural features and specific crystal evolving courses under confined evaporation environments. The present findings improve dramatically the understanding of the structural development and crystallization mechanism for emergence of diverse polymer spherulitic morphologies.

Keywords: polymer spherulite; ringed or banded morphology; lamellar organization or assembly; periodic twisting; rhythmic crystal growth; evaporative crystallization

1. Introduction

Since the first observation of ordered crystals in high polymers there has been a vast amount of scientific activity and longstanding interest in the study of polymer crystallization and morphology, for which not only is it a basic and significant research field in polymer physics but it also exerts profound influence on material properties and performances [1–4]. Spherulites or spherulitic structures, as the most common and representative morphologies of crystalline polymers, can be encountered when crystallized from disordered melts or concentrated solutions [4–8]. Specifically, the ring-banded spherulites or spherulitic crystals have attracted massive interest because of their inherent beauty, intriguing complexity, and morphological diversity [8–10]. Despite the extensive number and variety of experiments and explorations over the past decades, the understanding and explanations for the structural formation and pertinent crystallization mechanisms of variably spherulitic morphologies in polymeric materials have been rather elusive [7–9].

Owing to the discovery and establishment of chain folding [11], it is now generally recognized that polymer crystalline aggregates exhibit a unique structural feature of being comprised of a large number of folded-chain lamellae that are arranged and organized together [12], and the schematic example of the multilevel architecture of a polymer spherulite is illustrated in Figure 1. This feature is common to, at least, all flexible polymers despite their diversely chemical compositions, widely differing stereochemical and chain architectures, as well as various crystal structures and patterns. It is, therefore, possible to explore the crystallization and morphology of crystalline polymers from a unified standpoint that encompasses the formation and distortion of lamellae with different shapes and sizes, and the lamellar arrangement and organization [9,12–17]. Despite polymer crystals displaying ordering at a variety of dimensional levels from interatomic spacings to macroscopic measures (as shown in Figure 1), the characteristic optical, physical, and mechanical properties, and the variably morphological features possessed by polymer aggregate crystals can be explained, to some extent, by the arrangement and assembly of a large amount of individual lamellae. For the case of polymer spherulitic morphologies that generally exhibit the radial symmetry, it is apparent that numerous fibrils that are usually composed of lathlike or ribbon-like lamellae elongate in the radial direction synchronously [4–8], implicating that their optical properties, as well as morphological features, are dominated by the radial lamellar organizations. This cognizance can motivate one to understand and interpret the structural formation and the underline crystallization mechanisms of diverse polymer spherulites. Woo and coworkers have performed a series of excellent works upon this topic, and the majority have been summarized in a recent review published in 2015 [9]. Moreover, the subsequently intensive studies are still in progress [18–24].

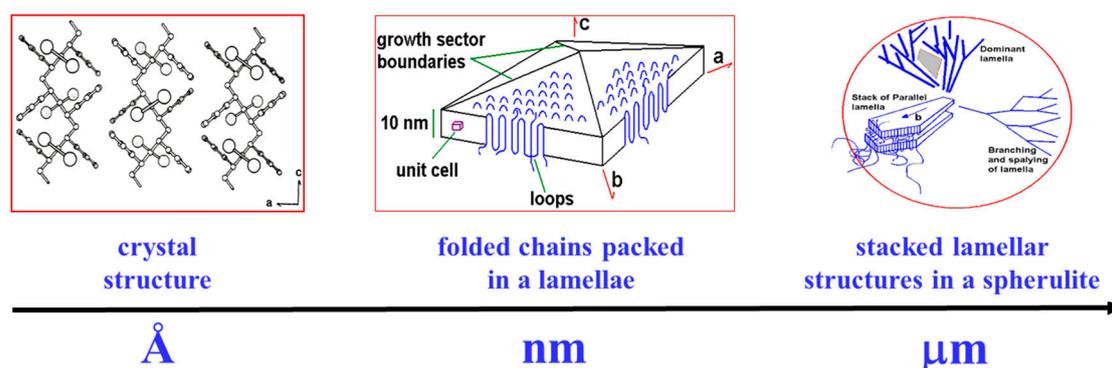


Figure 1. Schematic illustration unveiling the multilevel ordering structures and the organization of folded-chain lamellae in a polymer spherulite.

Thin films with thickness ranges from dozens of nanometers to several micrometers are often employed to explore spherulites or spherulitic crystals of crystalline polymers [6,7,25–27]. Based on the viewpoint of lamellar assembly, one can simply divide the radial lamellar organization of two dimensional (2D) polymer spherulites produced in thin films into two situations, the distortion or orientation and the stacking or packing mode of lamellae. In other words, the characteristics of spherulites and spherulitic growths encountered in polymer thin films are expected to be controlled by the radial lamellar orientation and stacking. The orientations of radial lamellae might be uniform, random, or periodically twisted, and two cases of the radial packing of lamellae, continuous and discrete, can be roughly separated. As a result, with the alteration of radial lamellar organizations, six kinds of spherulitic growths or morphologies can be fabricated in thin films of the same polymer, independent of its chemical, chain, and crystal structures, the radial crystallographic axis, and the crystallization medium, etc. The possible radial lamellar organizations and corresponding optical features of the simplest case, i.e., the uniaxial crystal growing along an invariant crystallographic axis, are demonstrated in Figure 2, and four spherulites can exhibit the intriguingly ring-banded

morphologies [28]. Taking multilevel ordering structures of polymer crystals (as depicted in Figure 1), various growth environments and crystallization media into account, it can then be predicted that diversely spherulitic patterns possessing more complex lamellar organizations should be found under appropriate conditions using the same polymer as crystallizable species. For examples, Woo et al. reported the emergence of three kinds of banded spherulites in the blends of poly(L-lactic acid) (PLLA) and poly(1,4-butylene adipate) with differing lamellar assemblies [16]. They also found that a phase separation induced lamellar reassembly leads to a birefringence reversion of poly(hydroxyl butyrate) (PHB) spherulites [29]. Meanwhile, a novel ring-banded morphology was produced in the poly(1,6-hexamethylene adipate) spherulites by a step-crystallization-induced discrete packing of positive and negative birefringence lamellae [24]. Furthermore, the change of growth axis resulted in quite a complex pattern in the poly[(R)-3-hydroxyvalerate] (P3HV) banded spherulites [30].

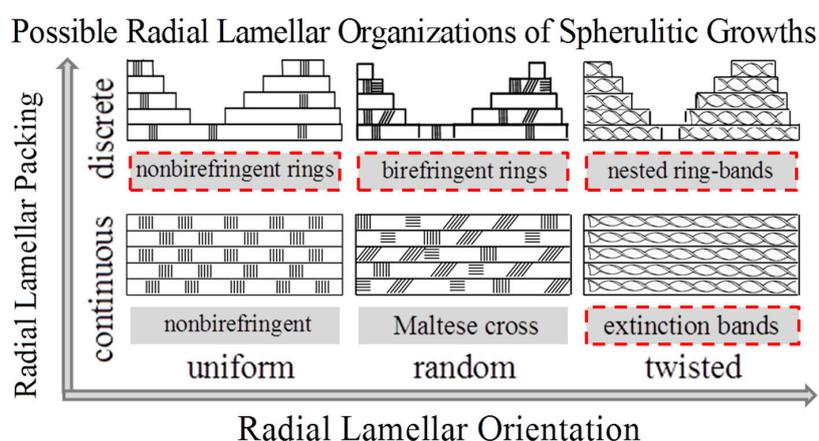


Figure 2. Schematic representation of the possibility of cross-sectional radial lamellar organizations for 2D polymer spherulites developed in thin films. Reprinted with permission from [28]. Copyright (2014) American Chemical Society.

Essentially, for the 2D ring-banded spherulites formed in polymer thin films, it is evident from Figure 2 that there are two different underlying origins, i.e., the periodic change of orientation (e.g., lamellar twisting) and the rhythmic variation of packing mode of radial lamellae [28]. In the former situation, so-called classical extinction-banded spherulites (CEBS), the extinction bands are widely observed under polarized light, but are poorly discernible in unpolarized light [8]. In the latter case, one can now be named as non-classically concentric ringed spherulites, the concentric rings often possess a clearer contrast in non-polarized light and exhibit a rhythmic variation of the radial thickness [31–33]. Figure 3 give the typical examples to display the optical features and corresponding radial lamellar organizations of the two different types of polymer ring-banded morphologies, where Figure 3a,b are the CEBS of poly(trimethylene terephthalate) (PTT) and the non-birefringent concentric-ringed spherulites (ZBCRS) of isotactic polystyrene (iPS), respectively [33,34]. It should be noted that some extinction banded spherulites of polymer blends also possess an origin of the structural discontinuity deriving from an alternative stacking of lamellar crystals and the blended amorphous materials [35–37]. Unexpectedly, the two different kinds of ring-banded morphologies were seldom encountered in the same polymer as the crystallizable object.

Inspired by the feature of being composed of lamellae, we believe that it is feasible to construct and modulate the morphological behavior of polymer spherulitic growths from a unified standpoint of manipulating the lamellar organization and arrangement along the radial growth direction during the structural developing process. It is well known that the crystal morphology of crystalline polymers is determined not only by the chain and crystal structures (the internal features), but also by the crystallization condition and the process of that growth (the external factors). For the situation of spherulitic growths, it is generally believed that the resulting crystal morphology is controlled by the

balance between the driving force for the spherulite growth and the diffusion of chain [38]. Yet, when polymers crystallize from a melt, the mass transfer is difficult due to the high viscosity, and the only tunable factor is the crystallization temperature, so quite limited spherulites are often encountered. Solvent vapor annealing is a facile technique for varying the aggregated microstructures of polymer materials [39]. Shao et al. found a polymorphic transition of polybutene-1 via chloroform and water vapor annealing [40]. Using a similar PLLA film–chloroform system, an unusually-banded pattern that is distinct from that of melt crystallization was also produced [41,42]. More spherulites of the same crystallizable object were observed via an evaporative crystallization procedure [43]. With respect to traditional melt crystallization, it is expected that crystal morphology grown from solution media should be more variable and can be controlled more conveniently.

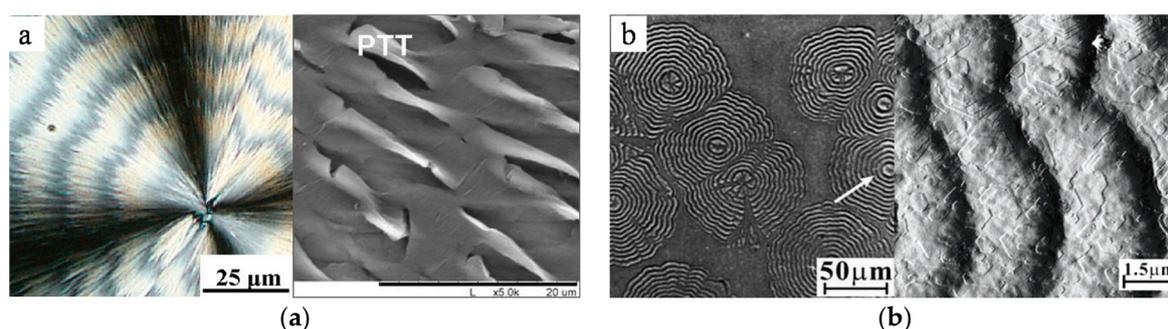


Figure 3. (a) Polarized optical microscopy (POM) and scanning electron microscopy (SEM) and (b) optical microscopy (OM) and atomic force microscopy (AFM) phase images exhibiting the representative features and lamellar organizations for the two kinds of ring-banded patterns in 2D polymer spherulites having the origins of (a) periodic twisting and (b) discrete packing of radial lamellae. Reprinted with permission from [33,34]. Copyright (2011) and (2004) American Chemical Society.

For the topic concerning polymer spherulites, several reviews have been published [8–10]. Lotz and Cheng extensively analyzed the possible cause(s) for periodic twisting of lamellar crystals [10]. Woo et al. focused on the origins for emergence of ring-banded patterns in polymer spherulites [9]. Recently, a critical review contributed by Crist and Schultz involved the structure and development, formation kinetics, formation cause of lathlike crystals, space filling, effects of molecular parameter, effects of film thickness and substrates, and the banding and twist [8]. In this article, the pertinent studies of the subject of manipulating radial lamellar organization to construct the occurrence and modulate the development and evolution of diverse spherulites are reviewed mainly on the basis of our current works on evaporative crystallization of polymer solution-cast thin films by coupling the changes of structural feature and crystallization condition. The solutions and structural features of polymers employed for this theme are listed in Table 1. In Section 2, the various spherulitic morphologies and microstructures of poly(ϵ -caprolactone) (PCL) with varied molecular weight are described from the standpoint of tuning the packing and orientation of radial lamellae, respectively, and the key factors to determine the radial lamellar packing and orientation behavior are analyzed. Section 3 emphasizes the spherulitic growths and transitions of the same crystallizable polymer, poly(ϵ -caprolactone)-*b*-poly(ethylene oxide) diblock copolymer (PCL-*b*-PEO), to further illustrate the morphological manipulation and the dominant roles for controlling radial lamellar organization. On the basis of the analysis in Sections 2 and 3 of the inconsistency of condition dependencies of the lamellar packing and orientation, Section 4 is devoted to the morphological control via cooperative tuning of the radial lamellar packing and orientation to produce the nested ring-banded spherulites of poly(ethylene adipate) (PEA). In Section 5, the structural evolution processes and pertinent growth dynamics of diversely spherulitic growths in evaporating polymer solution-cast films are depicted based on in situ optical observations to enhance the understanding of the structural formation and

morphological control of polymer spherulites. Section 6 outlines, respectively, the underlying origins and pertinent crystallization mechanisms for the occurrence of rhythmic growth and the periodic twisting of radial lamellae during the evaporative crystallization process with the emphasis on the unique effects of the solvent and its evaporation. We complete this review in Section 7 with a summary of the main conclusions and an outlook towards key issues of potential developments in this field.

Table 1. The solutions and structural features of polyesters employed for modulating the spherulitic morphologies of 2D polymer spherulites via evaporative crystallization of solution-cast thin films.

Solutions	M_n (kg·mol ⁻¹)	Structural Feature of Polymer
PCL _{11.3k} ¹ /toluene	11.3	Orthorhombic, low M_n
PCL _{42.5k} /toluene	42.5	Orthorhombic, middle M_n
PCL _{84.4k} /toluene	84.4	Orthorhombic, high M_n
PCL _{24.5k} - <i>b</i> -PEO _{5.0k} /toluene	CL: 24.5 EO: 5.0	Orthorhombic, introducing a small amount of the second block
PEA _{10.0k} /tetrahydrofuran	10.0	Monoclinic: chain tilt

¹ The subscript in each polymer abbreviation indicates its number average molecular weight.

2. Morphological Control of Various Spherulites of Achiral Orthorhombic PCL

2.1. Manipulating the Stacking of Radial Lamellae to Prepare Concentric Ringed Spherulites

Generally, polymer spherulitic crystals exhibit a continuous structure of fibrillar lamellae along the radial growth direction [6–8]. Although this seldom happened, the non-traditional concentric-ringed morphology with a rhythmic change of radial thickness stemming from a discrete packing of radial lamellae can be occasionally observed in 2D spherulites when polymers crystallized from thin films. Typical examples are the observations of non-birefringent concentric ringed crystals in both iPS and poly(bisphenol A hexane ether) (BA-C6) thin films [31–33]. The morphological features and lamellar organizations of the case of iPS are displayed in Figure 3b [33]. It is illustrated that such periodically spherulitic structures derive from a rhythmic crystallization-induced discrete packing of multilayer flat-on lamellae, and which can merely be formed under limited thicknesses and temperature ranges.

By employing a good solvent, toluene, to dissolve the low molecular weight PCL_{11.3k} and then controlling slow solvent evaporation to decrease the spherulitic radial growth rate in solution-cast films, Wang and coworkers have produced concentric-ringed spherulites of PCL_{11.3k} under an extremely slow average evaporation rate of ca. 1.50×10^{-4} mL·h⁻¹ at 20 °C [44,45]. Both the non-birefringent and birefringent concentric ringed morphologies, as exhibited in Figure 4, were observed by changing the initial concentration of the casting solution. The coupling of the evident concentric rings appeared under non-polarized light and the height differences comparable to film thickness (Figure 4) indicates that such periodic patterns possess the origin of the discrete stacking of radial lamellae induced by rhythmic crystallization. It is obvious that the birefringent property depends on the initial solution concentration, for which determines the thickness of the resultant films. The lower initial solution concentration leads to the thinner film, in which the spherulites are composed of almost uniform flat-on lamellae because of the combination of a strong polymer-substrate interplay and the slow spherulite radial growth, so a non-birefringent pattern is observable in the uniaxial PCL spherulites with the radial and tangential directions along the fixed crystallographic *b*- and *a*-axis, respectively (Figure 5a) [44]. As the films thicken with increasing initial solution concentration, the lamellae orientations change from the uniform flat-on case near the substrate to become gradually tilted and, eventually, edge-on situations toward the top layers of the ridges (Figure 5b) [45]. As a result, the tangential directions alter gradually from the *a*-axis on the valleys to even the *c*-axis upon the peak of ridges, leading to the appearance of the continuously-enhanced birefringence with the increase of ridge height [46]. In the valleys of both spherulites, there are a few flat-on lamellae that again show the non-birefringent feature. Hence, the two cases in Figure 4 are actually non-birefringent and half-birefringent concentric ringed spherulites (abbreviated as NBCRS and HBCRS), respectively.

The occurrence of non-traditional concentric rings in PCL spherulites is first dependent on the average solvent evaporation rate. They can merely be developed upon slow evaporation, and rapid drying, such as free evaporation, gives rise to the emergence of the usual Maltese Cross spherulites (MCS) with continued packing of randomly oriented, radial lamellae [45–47]. By tuning a gradually accelerated solvent withdrawal that drives the successive increasing in crystal growth rate, Li et al. have observed that the concentric rings became gradually narrowed and eventually disappeared, leading to a band-to-non-band transition and, consequently, the emergence of a novel PCL crystal pattern, as depicted in Figure 6 [48]. The bands consist of discrete stacks of uniform flat-on lamellae, while the non-banded section possesses a continuously-radiating texture with mainly tilted, or even edge-on lamellae (Figure 6). In other words, the packing of radial lamellae can be controlled to shift from a discrete mode to a continuous manner by modulating the evaporative crystallization process.

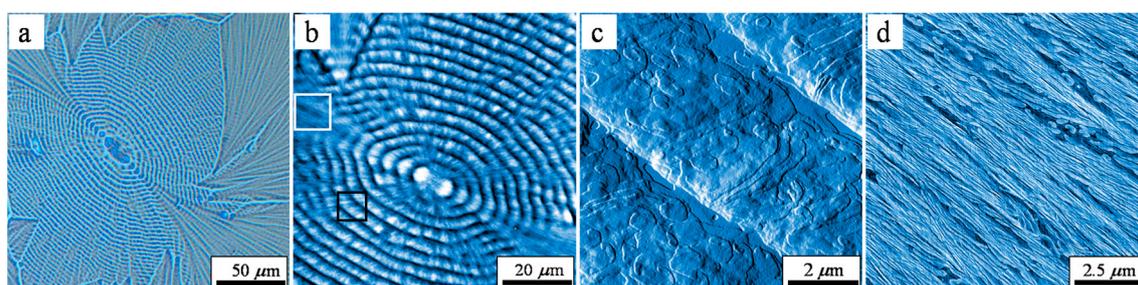


Figure 6. OM (a); AFM topography (b); and phase images (c,d) displaying the band-to-non-band transition originating from the discrete packing of flat-on lamellae to continuous fibrils with tilted or edge-on lamellae. Zones (c,d) are indicated by the dark and white squares in (b), respectively. Reprinted with permission from [48]. Copyright (2012) American Chemical Society.

The average molecular weight also has a profound influence on the morphological behavior of PCL spherulites. Under the same evaporation condition as that resulting in the formation of PCL_{11.3k} concentric-ringed spherulites, non-birefringent compact spherulites were produced in the moderate molecular mass PCL_{42.5k} thin film from 10 mg mL⁻¹ solution [47]. Not unexpectedly, the spherulites exhibit the successive stacking of uniform flat-on lamellae along the radius, as depicted in Figure 7.

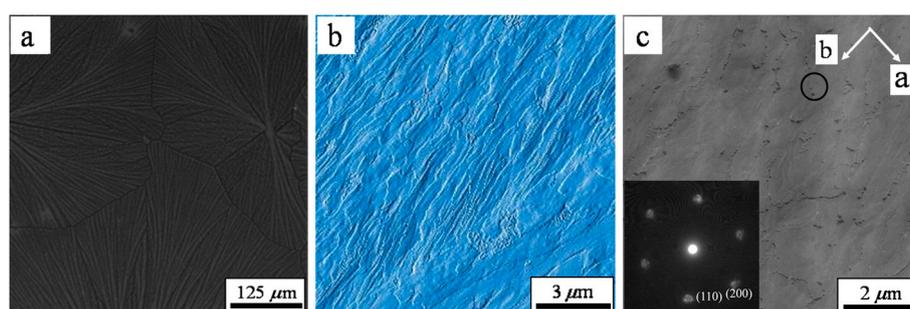


Figure 7. (a) POM; (b) AFM phase; (c) TEM images and SEAD pattern displaying the morphological features and pertinent lamellar organization of PCL_{42.5k} nonbirefringent compact spherulites. Reproduced from [47,49] with permission from Elsevier and the Royal Society of Chemistry.

The discrete packing of radial lamellae is a result of rhythmic crystal growth. The occurrence of rhythmic crystallization demands the rearrangement of the crystallizable component during the crystal growth process. That is, the material depletion caused long-range transport of crystallizable species should take place ahead of the growing spherulite front. In the crystallization process of polymer thin films, the lower specific volume of the crystal phase is the prerequisite for the generation

of the material deficit. However, the occurrence of a long-range material transport also requires that the crystallization medium possesses the good mobility and the system can offer a suitable timescale [47]. In molten thin films, owing to the small volume contraction, the rapid spherulite growth, and the rather poor mobility of long-chain polymer molecules, rhythmic crystallization is difficult to occur. Consequently, non-classically concentric ringed morphology can only be observed in iPS and BA-C6 molten thin films, which have extremely slow crystallization rates [31–33]. For the situation of evaporative crystallization of solution-cast thin films, the existence of solvent not only enhances the medium mobility, but also increases the material deficit caused by volume contraction during the crystallization process. Meanwhile, the fastest solvent withdrawing ahead of the growing crystal front is a benefit for inducing the emergence of a radial evaporative convection, which can carry the solute to crystal face to feed its further propagation. Furthermore, the evolution time can be controlled by altering the solvent evaporation rate [47]. Hence, rhythmic crystallization is predicted to occur more easily. Even so, non-traditionally concentric-ringed spherulites can also be found merely under slow evaporation [44–47]. Obviously, when polymers crystallize from solutions, the supersaturation is the basic requirement. In the crystallization process of PCL_{11.3k}/toluene solution-cast films, the coupling of the low molecular mass and good solvent ensures a good mobility of supersaturated solution, the slow solvent escaping affords enough time for the occurrence of slow crystal evolution and long-range transport of solutes to the growing crystal front, so the rhythmic crystallization can happen, resulting in the emergence of concentric-ringed spherulites with the discrete stacks of radial lamellae [47]. Once accelerating the drying rate or increasing PCL molecular weight, a discrete to continuous transition of the lamellar packing along radial direction occurs, leading to the generation of common compact spherulites [47]. The former narrows the evolution time and the latter reduces the liquid mobility.

Actually, by controlling slow evaporative crystallization of solution-cast thin films of the low molecular mass PCL_{24.5k-b}-PEO_{5.0k} and PEA_{10.0k}, non-traditionally concentric-ringed spherulites were also formed [28,50], as discussed in the following. Moreover, a solvent vapor annealing is predicted to also enhance the ability of polymer transport. Meanwhile, PLLA has quite a slow spherulite growth. As expected, the similar periodic patterns were reported recently in low molecular weight PLLA thin films both from melt-crystallization and vapor-assisted crystallization [27,41,42]. It can, therefore, be concluded from the above findings that it is the crystallization condition rather than the structural feature that is important to determine the stacking mode of radial lamellae in polymer spherulites. In other words, the competition between the material transport to growing crystal front and the spherulite radial growth dominates the occurrence of rhythmic crystallization. The authors reckon that by manipulating a proper matching relationship between material transport and crystal growth, non-traditionally concentric-ringed spherulites comprising of the discrete stacks of radial lamellae can be produced in the most crystallizable polymers under appropriate conditions.

2.2. Modulating the Periodic Orientation of Radial Lamellae to Produce PCL Extinction-Banded Spherulites

In Section 2.1, by changing solvent evaporation to control spherulitic growth processes of PCL, four kinds of spherulitic morphologies, NBCRS, HBCRS, MCS, and uninterruptedly non-birefringent pattern, were successfully prepared. The former two spherulites exhibit a discrete packing of radial lamellae. Instead, the radial extending is successive in the latter two cases. Clearly, it is the change of the orientations of the radial lamellae that can be attributed to the emergence of non-birefringent and birefringent features. As has been presented, the spherulitic morphology relies on a combination of the stacking and orientation manners of radial lamellae. The authors had tried to manipulate the orientation behavior of radial lamellae in PCL_{11.3k} spherulites by changing the evaporative crystallization process. Excepting the successful manipulation between uniform flat-on and random orientations, the periodic variation of radial lamellar orientation, e.g., lamellar twisting, cannot happen. For the origins of periodic twisting of polymer lamellae, the most acceptable model should belong to that advocated by Keith and Padden [51–53]. They suggested that the periodic twisting is a

consequence of the unbalanced stresses on opposite fold surfaces originating from the significantly different overcrowding and inefficient packing in the fast-growing lamellae [51]. According to this theory, it is reasonable that the disorder can be intensified with the increase of both the molecular weight and crystallization rate which is, therefore, expected to promote the twisting of lamellae [53].

By choosing a high molecular weight PCL_{84.4k} and employing a rapid drying simultaneously, Li et al. have prepared classical extinction-banded spherulites (CEBS) upon a faster evaporation rate of $9.70 \times 10^{-3} \text{ mL}\cdot\text{h}^{-1}$ at 0 °C [49]. The PCL_{84.4k} spherulites show quite a clear appearance of both Maltese Cross and the extinction bands under polarized light, but the banding becomes poorly observable in non-polarized light, as revealed in Figure 8. While it can be discernible again, the amplitude of the surface fluctuation is rather small relative to film thickness, and both AFM and TEM measurements verify that PCL_{84.4k} extinction-banded spherulites possess the nature of being composed of periodically-twisted lamellae along the radial direction [49]. Meanwhile, a comparison of in situ observations of the evolution processes of PCL_{11.3k} concentric-ringed crystals and PCL_{84.4k} extinction-banded spherulites demonstrates that the spherulite radial growth rate of the latter case is much faster than the former situation. For example, the radial growth rates of the two kinds of ring-banded spherulites formed in the films of $20 \text{ mg}\cdot\text{mL}^{-1}$ solution are ca. 615 and 65 $\text{nm}\cdot\text{s}^{-1}$ respectively [47,49]. It is, therefore, convincing that it is effective in modulating the orientations of the radial lamellae in polymer spherulites by the combination of increasing the molecular weight and accelerating the spherulite growth velocity. As the evaporation decelerates the twisting frequency of radial lamellae gradually decreases and, thus, the banding becomes successively widened and eventually disappears, giving rise to the occurrence of Maltese Cross spherulites (MCS) and non-birefringent spherulites consisting of randomly-oriented and flat-on lamellae in the thinner and thicker films, respectively [49]. More importantly, the strong twisting (i.e., band spacing less than 10 μm) of achiral orthorhombic PCL lamellae was observed for the first time [49]. Thus far, besides the special case of nested ring-banded patterns, the five kinds of spherulite morphologies, the usual Maltese Cross, non-birefringent compact pattern, non-birefringent and birefringent concentric-rings, and extinction banding, that have been predicted in Figure 2 from radial lamellar organizations, were all produced from the solution-cast films of PCL uniaxial crystal with an unvaried radial direction of the crystallographic *b*-axis by controlling the crystal developing process. Furthermore, the associated lamellar organizations are also consistent with expectations.

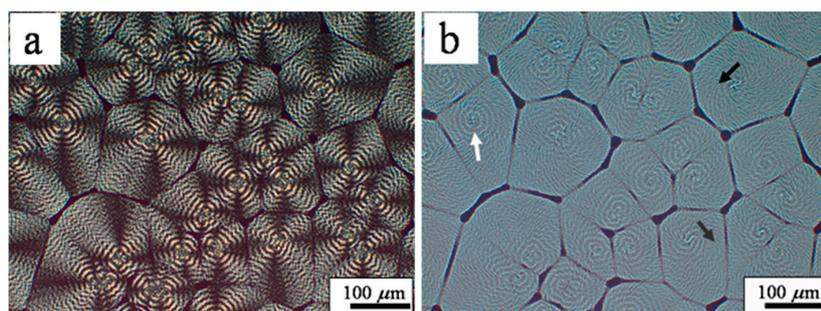


Figure 8. POM (a) and OM (b) micrographs of PCL_{84.4k} CEBS formed from a $50 \text{ mg}\cdot\text{mL}^{-1}$ solution-cast film. Reproduced from [49] with permission from the Royal Society of Chemistry.

3. Tuning Radial Lamellar Organization to Construct Diverse PCL_{24.5k}-*b*-PEO_{5.0k} Spherulites

For polymers that are difficult to form CEBS, introducing a second block or a blend component is generally believed to intensify the unequal stresses upon opposite lamellar surfaces that are benefit for the occurrence of periodic twisting of radial lamellae and then emergence of CEBS [8,10]. Spherulitic morphologies of a low molecular weight PCL_{24.5k}-*b*-PEO_{5.0k} diblock copolymer can also be modulated by controlling the solvent evaporation rate during evaporative crystallization of its solution-cast films, and the structural evolution with enhancing solvent evaporation was

basically similar to those of PCL [28]. Four distinct types of spherulites with variedly optical features, i.e., ZBCRS, HBCRS, CEBS, and MCS, were again encountered, as exhibited in Figure 9. Likewise, three kinds of spherulites possess the intriguingly ring-banded morphologies. Concentric rings showing the non-birefringent and half-birefringent features were again formed at the quite slow evaporation velocity of $1.50 \times 10^{-4} \text{ mL h}^{-1}$ from the thinner and thicker films (Figure 9a,b), respectively. With respect to PCL_{11.3k}, it is apparent that the birefringence in PCL_{24.5k}-*b*-PEO_{5.0k} spherulites appears in a thinner film, implicating that the introduction of the second PEO segments favors the controlling of the lamellar orientation. This point can be strongly supported by the generation of CEBS via increasing solvent evaporation rate to $4.68 \times 10^{-3} \text{ mL} \cdot \text{h}^{-1}$ (Figure 9c). The morphological alteration is accentuated with further enlarging solvent withdrawing, and usual MCS were yielded at a more intensified free drying (Figure 9d). The four different kinds of spherulites with three possessing the periodically ring-banded morphology were observed for the first time in the same polymer, and never been reported in other crystallizable polymers under various crystallization conditions.

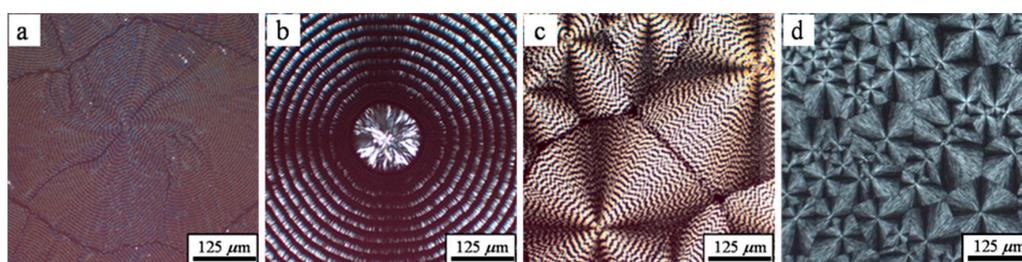


Figure 9. POM images exhibiting the morphological features of diverse PCL_{24.5k}-*b*-PEO_{5.0k} spherulites, i.e., (a) NBCRS; (b) HBCRS; (c) CEBS; and (d) MCS, observed in solution films evaporated from varied conditions. Reprinted with permission from [28]. Copyright (2014) American Chemical Society.

Meanwhile, by varying the evaporative crystallization conditions, Li et al. have performed the morphological transitions among the four kinds of PCL_{24.5k}-*b*-PEO_{5.0k} spherulitic crystals [28]. Firstly, the shift of the birefringent property in concentric ringed spherulites can be controlled by changing the film thickness, and slanting the substrate is sufficient (Figure 10a,b). Second, the change of the stacking of radial lamellae from a discrete manner to a continuous mode can be achieved by enhancing the drying rate (Figure 10c). Finally, the transformation of the lamellar orientation to a periodic twisting can be realized by a coupling of lowering the crystallization temperature and accelerating the solvent extraction (Figure 10d). The morphological evolutions and pertinent variations of lamellar organizations along the radial direction of the spherulites are schematically demonstrated in Figure 10e.

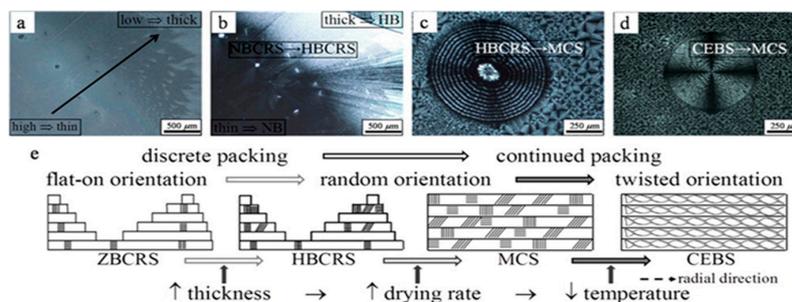


Figure 10. OM (a) and POM (b–d) micrographs depicting the morphological transition behavior among diverse PCL_{24.5k}-*b*-PEO_{5.0k} spherulites: (a,b) NBCRS→HBCRS; (c) HBCRS→MCS; and (d) CEBS→MCS; (e) The schematic illustration of radial lamellar organizations for the four different spherulites and the corresponding conditions for morphological transition. Reprinted with permission from [28]. Copyright (2014) American Chemical Society.

In the PCL_{24.5k}-*b*-PEO_{5.0k} solution system, on one hand, the low molecular weights of both PCL and PEO blocks ensure the good movability of growth medium upon slow evaporative crystallization. Hence, concentric-ringed spherulites that are composed of discrete stacks of radial lamellae can be generated. On the other hand, the small amount of PEO segments that are dangled on the surfaces of PCL lamellae enhance the unbalanced surface stresses and, subsequently, drive the periodically-twisted orientation of radial lamellae, resulting in the formation of extinction-banded spherulites [28]. The results of PCL_{24.5k}-*b*-PEO_{5.0k} further demonstrate the primary role of structural factor for tuning lamellar twisting and the effectivity of controlling crystallization process to modulate the packing of radial lamellae. Likewise, it is the majority PCL blocks, rather than the minority PEO segments, that dominate the crystallization processes and consequently the emergences of the four different kinds of PCL_{24.5k}-*b*-PEO_{5.0k} spherulitic morphologies upon above conditions [28]. That is, they again possess the radial direction of the crystallographic *b*-axis of orthorhombic PCL crystals [28].

4. Collaborative Tuning of Lamellar Packing and Orientation to Yield a Nested Ring-Banded Pattern

As analyzed above, the lamellar packing and lamellar orientation along the radial direction of spherulites possess different influential factors. It is reasonable to modulate the periodic twisting of the lamellae in ridges of non-classically concentric-ringed spherulites. In other words, the discrete packing and periodic twisting of radial lamellae can coexist in the same spherulite, resulting in the emergence of a nested ring-banded morphology. Obviously, the premise for successfully building such nested ring-banded spherulites is that the twisting period should be much narrower than the interval of rhythmic crystallization. It is known that when crystallizing from the melt, PEA can form double-banded spherulites with the quite narrow band spacing under a wide temperature range, and the twisting frequency of PEA lamellae is quite insensitive to the crystallization temperature [54]. By selecting a slow evaporation of PEA/tetrahydrofuran solution-cast films, Li and colleagues have successfully fabricated a nested ring-banded structure of the low molecular weight PEA_{10.0k} [50]. It is apparent that the spherulites exhibit the wider concentric-rings and the narrower double-banding nested in the bright rings (Figure 11). As expected, the large concentric rings show similar optical features of PCL_{11.3k} and PCL_{24.5k}-*b*-PEO_{5.0k} concentric-ringed crystals, and the inner double-bands are identical with those of traditional extinction-banded spherulites of polymers showing a biaxial crystal structure. The lamellar microstructures and organizations illustrate that the large concentric rings stem from a rhythmic change of thickness caused by a discrete packing of radial lamellae, and the double banding is an optical phenomenon of periodic twisting of biaxial lamellae (Figure 12).

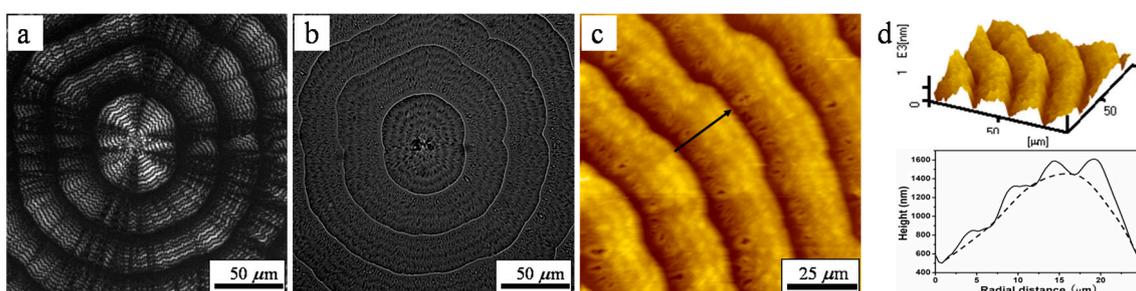


Figure 11. (a) POM; (b) OM; (c) AFM height; and (d) 3D pictures and height profiles revealing the morphological features of nested ring-banded spherulites observed in the PEA_{10.0k} solution-cast film via slow solvent evaporation. Reprinted with permission from [50]. Copyright (2012) American Chemical Society.

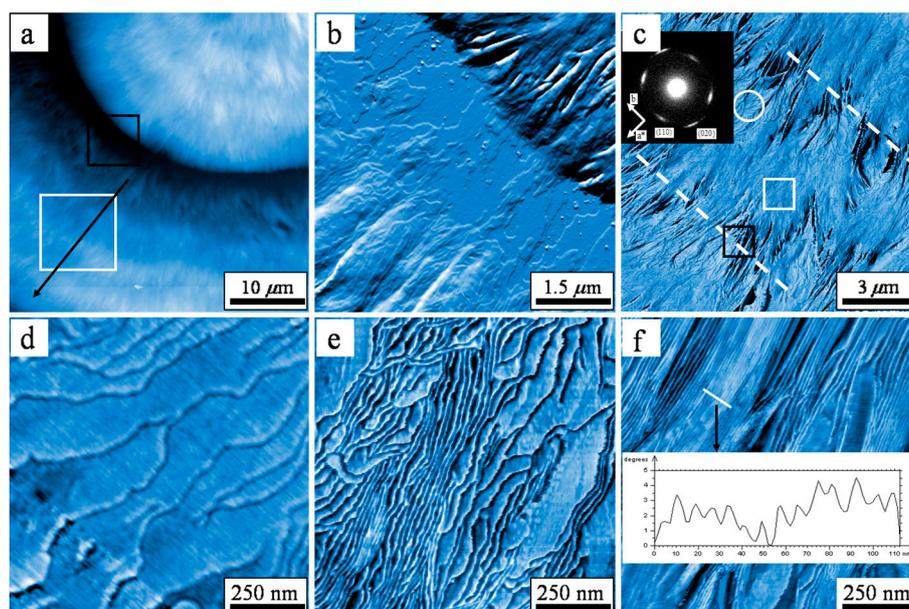


Figure 12. AFM height (a) and gradually enlarged phase images (b–f) demonstrating the radial lamellar microstructure and organization of PEA_{10.0k} nested ring-banded spherulites. Reprinted with permission from [50]. Copyright (2012) American Chemical Society.

On one hand, the coupling of a low molecular weight and a good solvent endows the excellent mobility of the PEA supersaturation solution, and slow solvent evaporation offers enough time to allow the generation of long-range transport. Consequently, the spherulites grow in a rhythmic manner, giving rise to the discrete stacking of radial lamellae. On the other hand, PEA crystallizes as the monoclinic crystal structure, i.e., the chain tilt is a common presence in PEA unit cells. This feature can cause the severely uneven stresses upon the opposite lamellar surfaces that trigger the powerful twisting of radial lamellae, leading to the appearance of narrow extinction bands. The conjunction of the two aspects is attributed for the concomitance of discrete packing and periodic twisting and, consequently, the emergence of a nested ring-banded morphology in PEA spherulites [50]. It is now obvious that the six differing kinds of spherulitic morphologies of crystalline polymers that have been predicted from the viewpoint of changing radial lamellar organizations (see Figure 2) were all produced by controlling the evaporation crystallization processes of solution-cast thin films.

The dependence of the initial solution concentration on PEA nested ring-banded spherulites was also examined. As the increase of initial concentration and actually film thickness, the separation of the large concentric rings originating from discrete lamellar packing enlarges, while the inner double bands hold an approximately invariant band spacing, further supporting the essential roles of the evolution condition and the structural factor for the occurrence of rhythmic crystallization and lamellar twisting, respectively [28]. Likewise, by accelerating the drying rate and slowing the crystallization temperature, the common Maltese Cross and classical double-banded spherulites of PEA can also be obtained, further confirming the operability of controlling spherulitic morphologies of crystalline polymers from the standpoint of manipulating radial lamellar organizations.

5. Structural Evolution and Dynamic of Ring-Banded Spherulites via Evaporative Crystallization

To understand the structural formation, the detailed crystal evolving processes and pertinent growth dynamics are quite informative. Li et al. have employed an optical microscope to real-time monitor the whole crystal developing processes of the spherulitic growths during the evaporative crystallization of solution-cast thin films, which uncovered the important and interesting insights to the structural formation and morphological evolution of diverse polymer spherulites.

5.1. Nontraditionally-Concentric Ringed Spherulites

For concentric ringed spherulites, it has been shown that the crystal-growing front progresses with a typical repetitive manner along the radial direction [47]. In other words, the developing process of each period is nearly identical, and the radial extension is linear when one chooses each period as the object of examination (Figure 13a). However, once the valleys and ridges were considered separately, the nonlinear behavior, i.e., the slow formation of ridges and the fast occurrence of valleys, is evident (Figure 13b). Actually, even within one period, the developing processes of both the crystal growing face and the region ahead of the growing crystal front are periodically changed. As shown by a series of in situ OM pictures displayed in Figure 13c–i, after the fast generation of a valley, there is an induction time, e.g., ca. 15 s in this case, before the growing of the next ridge. More specifically, the development of the ridges exhibits a slow-rapid-slow fashion [47], while during the induction time a melt-like ultrathin film crystal growth behavior takes place in valleys [46]. This situation is different from the rhythmic crystallization that occurred in the melt-crystallization of homopolymers, but resemble the cases of some polymer blends. For example, Duan et al. have illustrated that in the growth process of concentric ringed patterns from iPS thin films, the bottommost lamella extends at a constant velocity [32]. Yet, it has been reported that the growth rate of the rhythmic crystallization induced ringed spherulites in the blends of PCL/poly(styrene-co-acrylonitrile) under isothermal crystallization is varied [55].

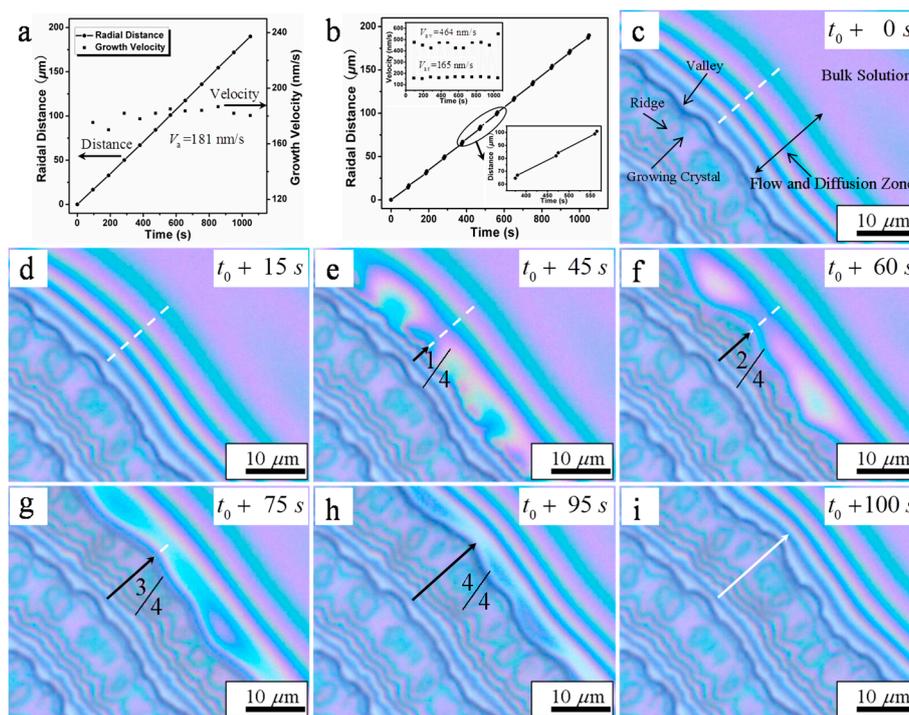


Figure 13. Plots of the changes of radial length and growth rate against time (a,b) and in situ OM images of the evolution of one period (c–i) illustrating the growth dynamic and structural formation of PCL_{11.3k} concentric ringed spherulites. The time intervals are times consumed for (a) each period, (b) each valley and ridge, respectively. Insets in (b): upper left is the plot of the velocity in time for each valley and ridge, and the lower right is the magnified distance–time variation. Reproduced from [47] with permission from Elsevier.

It has been illustrated that a long-range mass transfer is necessary for rhythmic crystallization. It is evident from in situ OM images (e.g., Figure 13c–i) that the repetitively-altered Newton interference rings ahead of the growing crystal front that are indicative of the generation of evaporative

convection are a common presence for the formation of concentric ringed spherulites from evaporative crystallization of solution-cast films [47]. The two key factors that ensure the emergence of such evaporative flow are the suitable timescale of the system and the good mobility of the crystallization medium. Accelerating the solvent evaporation reduces the evolution time, and increases the molecular weight while depressing the mobility of the supersaturation solution. They both result in the absence of such evaporative flow and, concomitantly, the disappearance of the concentric-ringed spherulites (Figure 14). It is, therefore, reasonable that it is the evaporative-flow that carries nutrient materials to the crystal-growing face to feed its further propagation, realizing the long-range transport of crystallizable solutes during the rhythmic crystallization process of evaporating polymer solution-cast films [47].

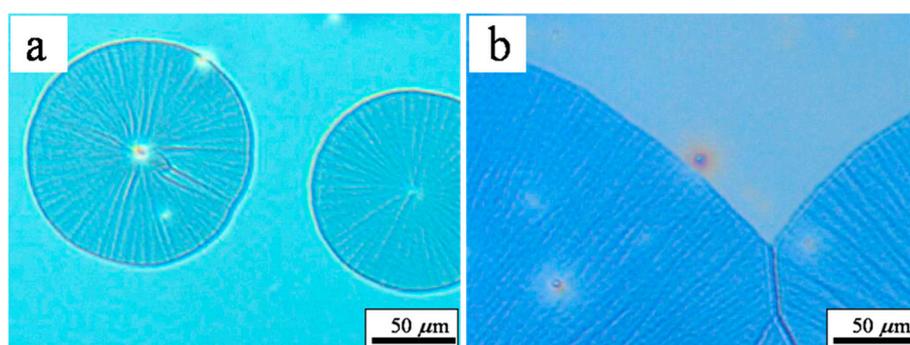


Figure 14. In situ OM images illustrating that enlarging drying rate from 1.50×10^{-4} to 3.50×10^{-2} mL·h $^{-1}$ (a) and increasing molecular weight from 10.0 to 42.5 kg·mol $^{-1}$ (b) both can induce the absence of evaporative-flow and then the disappearance of concentric ringed spherulites. Reproduced from [47] with permission from Elsevier.

5.2. Classical Extinction Banded Spherulites

Whereas both the spherulitic evolving process and radial growth dynamic of CEBS follow different fashions [49], as demonstrated in Figure 15, the spherulite also propagates with a periodic fashion in the radial direction, while the region ahead of the growing face is unvaried. Meanwhile, the radial extending within one period is quite uniform. This shows that the extinction-banded spherulites possess an identically-continuous feature of radial lamellar packing behavior with those of common compact polymer spherulites, e.g., the situations illustrated in Figure 14, so the uniform spherulite radial growth results. This point is similar to the cases of melt-crystallization [56].

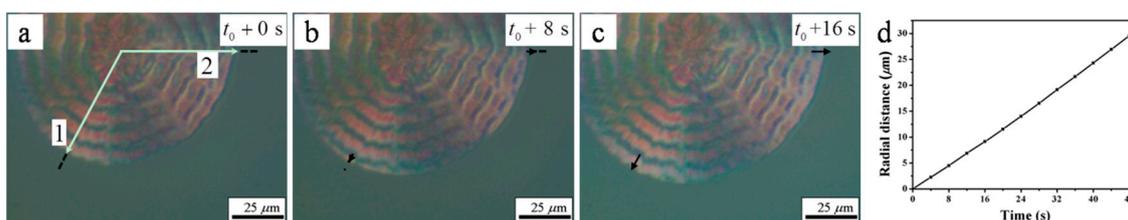


Figure 15. Real-time POM photos (a–c) showing the evolution process of one period in a PCL_{84.4k} extinction-banded spherulite and the plot of the temporal change of radial distance against time (d). Reproduced from [49] with permission from the Royal Society of Chemistry.

The most interesting feature of the spherulitic growth behavior in the evaporative crystallization of polymer solution-cast films is the thickness dependence of radial growth velocity. It is generally reported that when polymer spherulites are generated from the molten films, the radial growth rate first increases with increasing film thickness and then holds a constant value [56]. However, the cases

in the evaporative crystallization are directly opposite. As shown in Table 2, the average radial growth of both PCL_{11.3k} and PCL_{24.5k}-*b*-PEO_{5.0k} concentric-ringed spherulites formed under the identical slow evaporation conditions are depressed with enlarging the used initial solution concentration [28,47]. Furthermore, the radial velocities of PCL_{84.4k} extinction-banded spherulites follow a similar feature even upon the rapid drying conditions [49]. It is obvious that the thickness of solution-cast films is nearly proportional to the initial solution concentration [46]. In other words, the spherulite radial growth rate decreases with increasing film thickness during the evaporative crystallization process. This point can be attributed to the crystal growth of solutes via evaporative crystallization being dominated by solvent withdrawal [47,49]. It is evident that the thicker films contain more solvent when the nucleation occurred, so the same evaporation rate demands the longer time to eject the residual solvent, resulting in the reduction of radial extension of spherulitic growth.

Table 2. The thickness dependences of average radial growth rate of different polymer spherulites formed from evaporative crystallization of solution-cast films. Reproduced from [28,47,49] with permission from the American Chemical Society and Royal Society of Chemistry.

Initial Solution Concentration (mg·mL ⁻¹) ¹	Average Radial Growth Rate (nm·s ⁻¹)		
	Concentric Ringed Spherulites		Extinction Banded Spherulites
	PCL _{11.3k}	PCL _{24.5k} - <i>b</i> -PEO _{5.0k}	PCL _{84.4k}
5	266	107	0.95 × 10 ³
10	181	66	0.83 × 10 ³
20	65	30	0.72 × 10 ³
40(50 for PCL _{84.4k})	44	-	0.61 × 10 ³
100	-	-	0.56 × 10 ³

¹ The film thickness is nearly proportional to the initial solution concentration [46].

6. Crystallization Mechanisms of Different Ring-Banded Spherulites upon Solution Evaporation

Both the underlying origins and formation mechanisms of rhythmic crystallization and periodic twisting for generation of ring-banded morphologies of polymer spherulites from melts have been extensively discussed [8–10]. Owing to the presence of solvent, the cases must be different to some extent. Here, we outline the pertinent crystallization mechanisms for the occurrence of the rhythmic growth and periodic twisting of radial lamellae during the evaporative crystallization process with the emphasis on the unique effects of the solvent and its evaporation.

6.1. Rhythmic Crystal Growth Mechanism under Evaporative Crystallization

Based on the above observations and analyses, the formation of the non-classically concentric ringed morphology during the evaporative crystallization process is attributed to the discrete packing of lamellar crystals along the radial direction of spherulites. The connection is rhythmic crystal growth that is induced by a suitable combination of the volume-contraction-driven nutrient deficiency and the long-range material transport in spherulite developing course. When the transport process of polymer chains dominates the crystal development, the concentration gradient around the growing face becomes essential for the resulting crystal morphology. In other words, the matching relationship between the nutrient consumption of crystal growth and the crystallizable material supplied by long-range transport is important. The rhythmic crystallization in evaporative crystallization of solution-cast films can be elucidated as follows (Figure 16) [47]. Once the nucleation happens, the crystal growth exhausts the surrounding polymer chains, giving rise to a concentration gradient that triggers the solution flow and solute diffusion to growing face. The volume contraction induced by the crystal height increase leads to a decrease of liquid level (Figure 16a). The combination of the volume contraction and crystal height increase results in the emergence of a three-phase contact line, as shown in Figure 16b, at which the most rapid solvent evaporation drives the generation of a

long-range evaporative-convection that carries the crystallizable solutes nearby to the growing crystal face to feed its further propagation. However, owing to the coupling of the lower special volume of crystal and the disability of transport of enough solutes, the crystal cannot proceed with its original height; concomitantly a dimple appears ahead of the growth front (Figure 16c). Under the concave surface, the large interfacial curvature difference creates a capillary pressure gradient that drives an opposite drainage flow (Figure 16d). The coupling of the inside evaporative-convection and outside drainage flow accelerates the decrease of solution surface and eventually the rupture of the dimple, which causes the occurrence of a new contact line and the transition of the concave of dimple to a convex surface (Figure 16e), again resulting in the generation of a new evaporative-flux (Figure 16f). The periodic emergence of evaporative-flow and dimple rupture is responsible for the rhythmic growth into discrete concentric ringed crystals. Meanwhile, the nonlinear radial growth can be elucidated by a combination of solvent evaporation and solute crystallization [47].

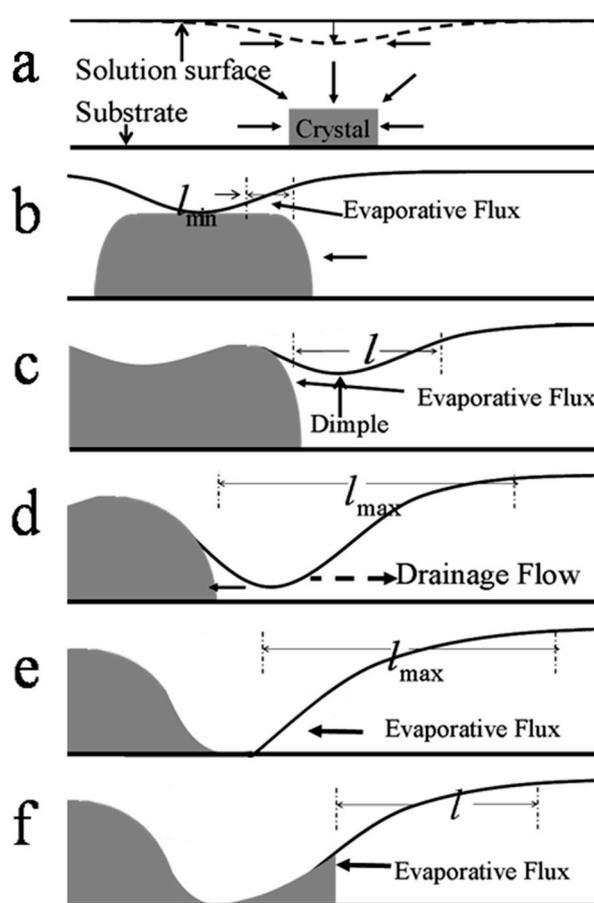


Figure 16. Schematic representations of the different developing stages (a–f) to elucidate the rhythmic growth model in the evaporative crystallization process of solution-cast films. Reproduced from [49] with permission from Elsevier.

6.2. Solvent Evaporation Assisted Enhancing Model for Lamellar Twisting

As reported by Li et al., by tuning fast evaporative crystallization of PCL_{84.4k} solution-cast films, a strong enhancement of twisting frequency of achiral orthorhombic PCL lamellae was encountered, leading to the emergence of extinction banded spherulites with the smallest band spacing less than 10 μm [49]. They have proposed a solvent evaporation assisted intensifying mechanism to explain such vigorous twisting of PCL lamellae, as demonstrated in Figure 17. Owing to the existence of a slightly asymmetric structural feature from the disposition of the ester groups within PCL unit

cell, a weak disorder is expected to exist upon the opposite lamellar surfaces [57,58]. This point is supported by the quite easy formation of extinction-banded spherulites from its block copolymers and blends [8], in which this disorder can be magnified by the adsorption of the second components. In contrast to such symmetrical adsorption effect on opposite surfaces, the authors have claimed that the dramatically uneven solvent evaporation and desorption on the upper and under surfaces can strongly enhance the original disorder of structural feature in such evaporative crystallization process. Consequently, the narrow-spaced PCL_{84.4k} extinction-banded spherulites were produced. Meanwhile, by introducing a small amount of PEO segments, extinction bands can be spotted in spherulites of the low molecular weight PCL_{24.5k}-*b*-PEO_{5.0k} [28]. Finally, the inner chain tilt makes the easy generation of traditional extinction banding in PEA_{0.0k} spherulites [50].

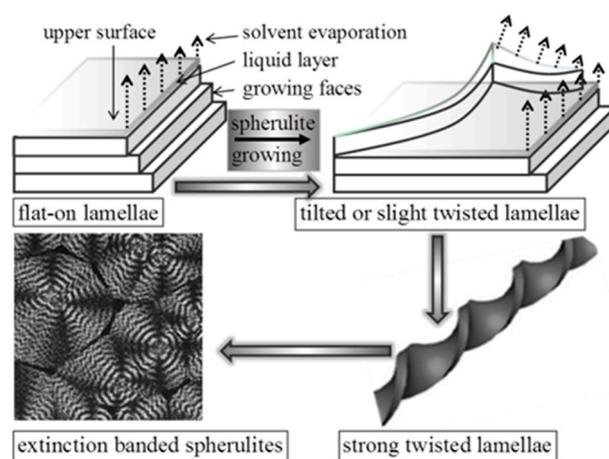


Figure 17. Schematic illustration explaining the possible enhancing mechanism for strong twisting of achiral orthorhombic PCL lamellae in the evaporative crystallization process. Reproduced from [49] with permission from the Royal Society of Chemistry.

7. Conclusions and Outlooks

In summary, polymer spherulites possess the unique structural feature of being composed of a large amount of lamellar crystals that elongate in the radial direction synchronously, and diverse spherulitic morphologies of PCL, PCL-*b*-PEO, and PEA were successfully produced by controlling the evaporative crystallization of solution-cast films under various environments and conditions. It was demonstrated that polymer spherulites can display the common Maltese Cross, non-birefringent compact pattern, extinction banding, non-birefringent or birefringent concentric-rings, and even a nested ring-banded structure. On one hand, the compact spherulitic architectures are indicative of the uninterrupted extending of radial lamellae, i.e., the successive stacking of radial lamellae, and the concentric ringed morphologies that show the periodic variation of radial thickness deriving from a rhythmic-crystallization-induced discrete packing of lamellae along the radius of the spherulites. On the other hand, the alterations in the orientations of radial lamellae are responsible for the change of birefringent properties of polymer spherulites. The uniform flat-on oriented lamellae leads to the absence of birefringence, random orientation gives rise to the appearance of both the Maltese Cross and bright rings under polarized light, and a periodic twisting of radial lamellae induces the formation of classical extinction banded spherulites. Finally, the emergence of nested ring-banded structures is attributed to the perfect coupling of discrete packing and periodic twisting of radial lamellae.

A combination of in situ observations of crystal growth process and the condition dependencies of structural transition illustrates that the essence for the formation of concentric ringed spherulites is the generation of material deficit-induced long-range transport of crystallizable species. The major role of the coupling of a low molecular weight and slow evaporation is to ensure the occurrence of

an evaporative flow towards the growing crystal face that realizes the long-range transport and then the rhythmic crystallization, resulting in the discrete packing of radial lamellae. The cooperation of a weakly asymmetrical structural feature of the disposition of ester groups and a strikingly magnified effect of unbalanced solvent evaporation on opposite lamellar surfaces should be responsible for the strong twisting of achiral orthorhombic PCL lamellae and, consequently, the emergence of narrow extinction banded spherulites. The successful construction of concentric ringed spherulites with a rhythmic alteration of radial thickness and other uninterrupted spherulites of all selected polymers demonstrates that it is the crystallization process that is important for manipulating the stacking mode of radial lamellae in polymer spherulitic crystals. Meanwhile, by enlarging the molecular mass, introducing a minority second block, and adding the chain tilt to gradually intensify the degree of disorder on opposite lamellar surfaces, the lamellar orientation and band spacing can be controlled, fully convincing that it is the internal structural factor that dominates the twisting issue of polymer lamellae. Meanwhile, the external crystallization condition can enhance or weaken the lamellar twisting frequency. In a word, by slightly changing the nanoscale chain structures, combined with a tuning of the crystal developing process to control the microscale lamellar organizations, one can successfully fabricate the mesoscale or even macroscale polymer spherulites. The present findings first enrich the spherulitic morphogenesis of polymer crystallization, then deepen the understanding of the occurrence of different ring-banded polymer spherulites and, finally, provide a unique perspective to elucidate and prepare the fixed crystal morphology for expected material properties and performance.

Although extensively investigated and analyzed, fully understanding the structural evolutions and crystallization mechanisms of the formation of diverse morphologies in polymer spherulites remains a long lasting and severe challenge in the field of polymer crystallization and morphology. Firstly, how are numerous individual lamellae organized and arranged into spherulites during the crystal growth process? This question is quite obscure and difficult to examine. Secondly, the precise relationship between the chain diffusion and the spherulite growth for the occurrence of rhythmic crystallization is difficult to determine. Further, the underlining origin for periodic twisting of polymer lamellae, especially in achiral cases, is not well understood, and the accurate measurement of unequal stresses on lamellar surface is near impossible. Finally, the mismatching of the results of different researchers also restrains the proceeding to approach the essence. These become the potential development aspects in the field of polymer spherulites and spherulitic growths.

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