molecular length). The bulk AWC array developed in this work provides comparable water permeability at transport length of hundreds of μm (**Fig. 1(e)**), showing that, with a great control in the mesoscale structures, the synthetic molecule is able to transfer their molecular functions hierarchically into useful material properties.

Water plays important roles in physiological functions of living matter. Through dynamically interacting with biomolecules, water assists them to switch quickly between different physical states under ambient conditions. Combining suitable molecular designs and profound structural characterizations at the NSRRC, the study turns the role of water in the supramolecular chemistry of the synthetic molecule from passive to active. The WISA process allows water to govern the self-assembly and function of the synthetic molecule as it does to biomolecules. The quick physical transformation resulting from the dynamic interaction with water is highly desirable for the development of condensed-phase soft materials and might inspire more innovation in the development of self-assembled functional materials. (Reported by Chien-Lung Wang, National Yang Ming Chiao Tung University)

This report features the work of Chien-Lung Wang, Wei-Tusng Chuang and their collaborators published in ACS Nano ***15****, 14885 (2021).*

TLS 23A1 Small/Wide Angle X-ray Scattering
TLS 01C2 X-ray Powder Diffraction
TLS 17A1 X-ray Powder Diffraction

- SAXS, WAXS, GI XRD, *In-situ* SAXS
- Supramolecular Chemistry, Artificial Water Channels, Materials Science, Condensed-matter Physics

Reference

1. H. Y. Chang, K. Y. Wu, W. C. Chen, J. T. Weng, C. Y. Chen, A. Raj, H. O. Hamaguchi, W. T. Chuang, X. Wang, C. L.Wang, ACS Nano **15**, 14885 (2021).

Application of Synchrotron Microbeam X-rays to Mechanisms of Periodic Assembly of Polymeric Ring-Banded Spherulites

Periodic patterns are commonly seen in nature, and spontaneously form on nanometer molecular to macro-cosmic scales, as illustrated in Fig. 1.

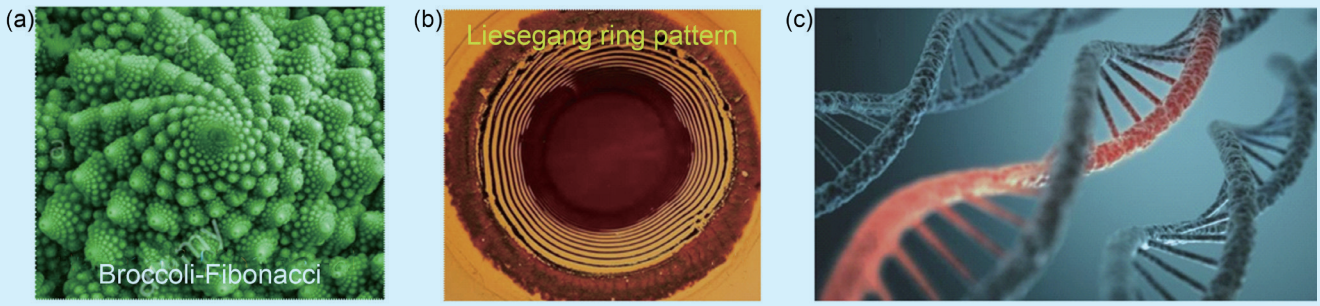

Fig. 1: (a) Broccoli flower with fractal pattern in a Fibonacci sequence, (b) Liesegan ring pattern on dropping a crystal of silver nitrate onto a thin gel layer containing potassium dichromate, and (c) DNA double-helices in genes. [Images all adapted from free sources, Wikipedia].

One of the most fascinating phenomena in crystallization is self-assembly in the periodic repetition of the same circular-ringed patterns. All crystalline spherulites, including ring-banded spherulites (RBS), of polymers or small-molecule compounds are packed in an anisotropic fashion. Polymeric spherulites are highly isotropic with lamellar crystals highly aggregates of all kinds, and a standard table-top X-ray instrument has wide X-ray beams and inherent limitations and can perform analysis results only as a cumulative average of multiple lamellae of varied morphology or orientation, *etc*. A specific location of crystal size and orientation can be precisely measured only *via* microbeam X-ray analysis. A limitation of the surface morphology is that it is unable to predict how to explore the mechanism of 3D lamellar assembly in polymeric RBS. Polymeric RBS are constructed with periodic rings with alternate valleys and ridges in 3D space, not just 2D films. Self-assembled lamellar architectures of RBS can be examined in two ways, *via* destructive and non-destructive methods. In

the non-destructive method, microbeam X-ray analysis is the most powerful tool to determine the micro-architectures of a lamellar distribution in a specific location of micrometres. So we specifically chose a poly(β-hydroxy butyrate) (PHB) spherulite with band spacing > 20 μm (in PHB/poly(ethylene oxide) (PEO)) crystallized at T_c = 50 °C, band spacing ~25 μm).

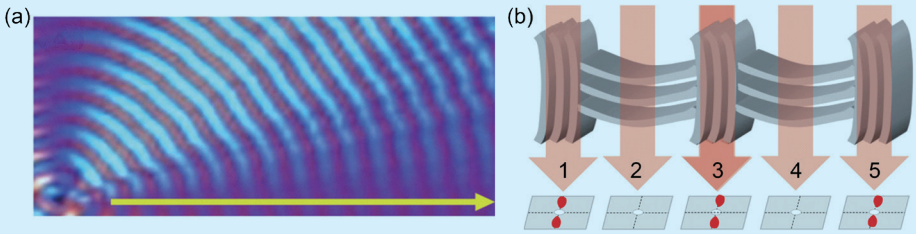

Fig. 2: (a) POM graph showing alternate colored rings, and (b) expected 2D-SAXS pattern variation with respect to a microbeam moving position along the radial direction at five spots: tangential (edge-on) lamellae 1, radial (flat-on) lamellae 2, back to tangential (edge-on) lamellae in next cycle 3, radial (flat-on) lamellae 4, back to tangential (edge-on) lamellae in next cycle 5. [Reproduced from Ref. 1]

A mechanism of 3D-grating structure assembly of RBS is positively proven with synchrotron microbeam small-angle X-ray scattering (SAXS) and various microscopic techniques. This grating structure in the banded PHB resembles many of nature's iridescent crystals and is further proved by photonic reflection results as a critical novel finding. The powerful synchrotron microbeam of small-angle X-ray scattering is ~15 μm available at **TPS 25A** of the NSRRC, where the microbeam facility was recently made possible by a group of experts led by Wei-Tsung Chuang, and his collaborator Yi-Wei Tsai (NSRRC)..

The morphological microstructures of a PHB ring-band spherulite were examined with microscopic techniques and powerful synchrotron microbeam SAXS by a research team led by Eamor M. Woo (National Cheng Kung University), assisted and supported by Chuang and Tsai of the NSRRC. The microbeam analysis was recorded through two sets of alternate valleys and ridges. In the periodic ring, the statistical-average lamellae orientation across the film thickness ata specific location of alternate valley/ridge periodicity was investigated withsynchrotron microbeam SAXS. **Figure 2** shows (a) a banded pattern of PHB across which a microbeam moved, and (b) expected SAXS 2D patterns as the beam moved in a radial direction on five separate spots (A–E). The POM-banded pattern of a typical PHB-banded spherulite is exemplified; a yellow arrow is marked from its nucleus center to a periphery to guide the movement of the microbeam. The interior lamellar construction of periodic rings with respect to alternate ridge and valley is given in **Fig. 2(b)**. When the microbeam was passed through a ridge, the feasible 2D-SAXS signals are showcased in **Fig. 2(b)** for conceptual understanding. As the lamellar plates are vertically aligned in a ridge, the contrast of electron density between the amorphous and crystalline phases of a lamellae plate can be deduced in the X-ray pattern. In the valley, lamellar plates are arranged in a horizontal direction, so the microbeam X-rays cannot reduce the phase contrast of electron density, resulting in no signal in a 2D-SAXS pattern. Note that one should not be misled by the top surface morphology, as the X-ray beam would actually penetrate the interior lamellae in much greater path length (*ca.* ~20 μm) than the thin top surface (< 1 μm). This effect is to hint that the resulting X-ray signal is built not by the thin top surface layer, but mostly by the interior bulk lamellae and their assembly patterns (crystal orientation relative to the X-ray beams *etc.*). The scheme in **Fig. 2(b)** shows that, as the X-ray microbeam is stepwisely moved along the radial direction of a PHB banded spherulite from its central nucleus to the outer periphery, the interior crystal orientation traverses from tangential to radial orientations in a repetitive periodic cycle.

The general universality of such periodicity with cross-hatch grating architectures can be demonstrated, which tends to be ubiquitous in periodically banded crystals or crystal aggregates. In earlier work on another polymer system, Nagarajan and Woo[2] analysed 2D- Wide Angle X-ray Diffraction (WAXD)/SAXS microbeam data of poly(ethylene adipate) (PEA)-banded spherulites to provide evidence for a corrugate-grating lamellae assembly, using similar synchrotron microbeam SAXS and WAXD analyses, with a 1-μm microbeam at the SPring-8 facility, Japan, in collaboration with Kohji Tashiro. The analysis of the PEA banded spherulite has proved that SAXS/WAXD signals indicate that alternate strut-to-rib crystal plates in PEA are interfaced with a discontinuity; abruptly changed orientations from the ridge to valley bands account for the periodic optical birefringence (band spacing = 6.5 μm).

Using NSRRC microbeam SAXS, an analysis of the interior assembly of the PHB-banded spherulite was performed. Although the available beam size in this work is a bit large, the band spacing in PHB is much larger (15–30 μm) than that in PEA. Considering the constraint of the large beam size, we specifically chose a PHB spherulite with band spacing > 20 μm (in PHB/PEO crystallized at T_c = 50 °C) as a model for such analysis. The X-ray beam was directed to travel stepwise along the radial direction originating from the nucleus of the banded PHB spherulites; signals were collected in each intermittent step-move. The results are shown in **Fig. 3(a)** (see next page). The beam size covers a fixed area *ca.* ~177 μm^2; the signal is thus a statistical average of crystals distributed in this region and crystal plates across the entire film thickness. **Figure 3(b)** shows 2D signals for each spot marked on **Fig. 2(a)**,

Spots 1–4. The SAXS pattern indicates that, in Spots 2 and 4, there are signs with respect to electron densitycontrast between crystalline and amorphousphasesin the vertical lamellae in a ridge as shown earlier in **Fig. 2(c)**. As signals of Spots 1 and 3 are weak, these signals can be regarded as no signal, indicating that the lamellae on Spots 1 and 3, respectively, are mostly normal to the X-ray beam (thus horizontal to the substrate). The periodic morphology and optical changes in the ring bands are caused not by the thickness of individual lamellae in ridge versus valley bands but result from crystal assembly and orientation. The valley region is dominated with flat-on crystals; the ridge region is packed mainly with edge-on crystals. Similarly, in SAXS, a X-ray beam perpendicular to the lamellae results in a poor contrast of electron density between amorphous and crystalline regions; so there is no, or only weak, signal observed in Spots 1 and 3. Thicker films produce more intense birefringence patterns due to more pronounced anisotropic crystals in varied orientations. In this work, the film thickness of PHB was kept at ≈20 ± 2μm, so alternate blue and orange birefringence rings are respectively associated with the ridge and valley bands seen in POM. In the ridges, the lamellae are oriented perpendicularly to the micro-beam X-rays as well as to the optical axis in POM. This perpendicular arrangement of the lamellae induces signals on Spots 2 and 4. Furthermore, SAXS maximum azimuthal angles 145°and 290° confirm that the edge-on lamellae in ridges are mostly mono-axially oriented in **Fig. 2(c)**.

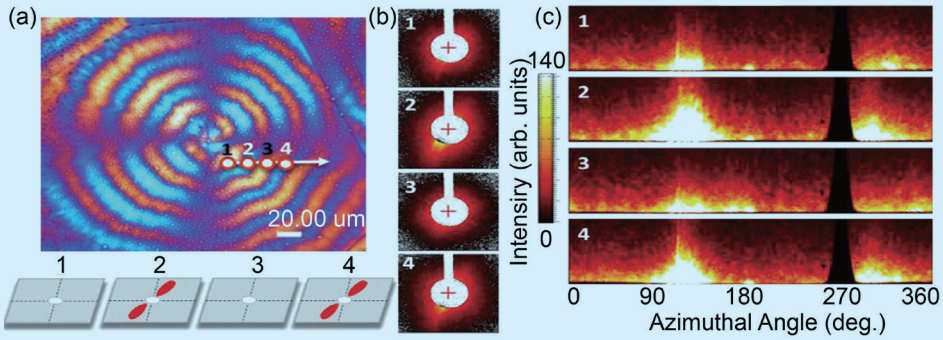

Fig. 3: Microbeam SAXS analysis along several radial-direction spots of a PHB spherulite crystallized from PHB/PEO (75/25) at T_c = 50 °C (band spacing ≈ 27 μm): (a) POM image, (b) 2D-SAXS patterns, and (c) intensity profiles at various positions (1, 2, 3, 4) in PHB/PEO spherulite. [Reproduced from Ref. 1]

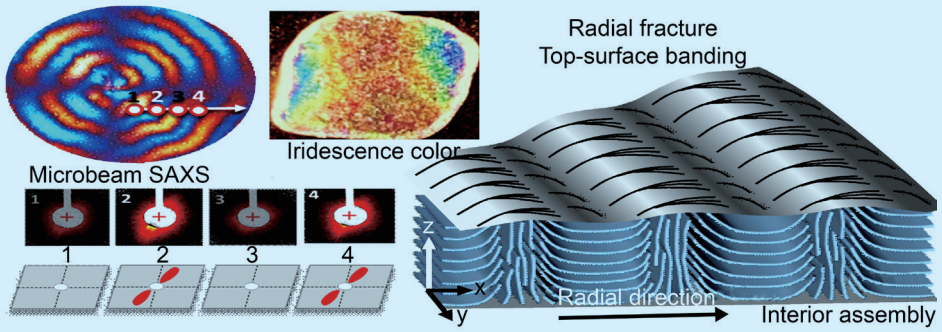

Fig. 4: Summary of POM, SEM, microbeam X-ray SAXS results, and a schematic for grating structure for periodic banded PHB. [Reproduced from Ref. 1]

In summary, **Fig. 4** shows that a detailed 3D assembly in the periodic ring PHB crystal aggregates is proved by delicate microscopic techniques, assisted with synchrotron X-ray analysis and supported by direct evidence of morphology dissection; the grating architecture of the periodic PHB aggregates possesses a novel property of photonic-crystal iridescence, which was never reported or discovered before for such polymeric crystals.

NSRRC synchrotron microbeam SAXS sources and various microscopic techniques were used to analyze the PHB crystal aggregates on specific spots of the banded spherulites. Through X-ray microbeam 2D-SAXS, this critical proof reinforces that the lamellar assembly in the PHB-banded periodic architectures are such that the optical-blue bands are packed mainly by grating normally oriented strut-crystals periodically interfaced with horizontally oriented rib-crystals. The grating structure with alternate strut-rib assembly in the banded PHB resembles many natural iridescent crystals, and is further proved with striking photonic reflections as a critical novel finding. (Reported by Eamor Woo, National Cheng Kung University)

This report features the work of Eamor Woo and his collaborators published in Macromol. Rapid Commun. ***42****, 2100281 (2021).*

TPS 25A Coherent X-ray Scattering

- XPS, NEXAFS, UPS
- Materials Science, Chemistry, Surface, Interface and Thin-film Chemistry, Condensed-matter Physics

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