Three-Dimensional Interior Analyses on Periodically Banded Spherulites of Poly(dodecamethylene terephthalate)

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Original submission:

CrysEngComm RSC

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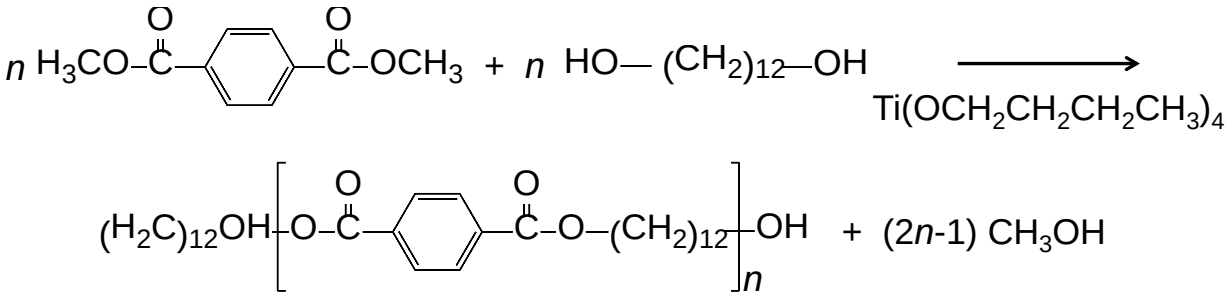
Supporting information

Synthesize Procedures of Poly(dodecamethylene terephthalate)

Poly(dodecamethylene terephthalate) (P12T) was prepared by transesterification and polycondensation (two-step) involving dimethyl terephthalate (DMT) and 50% excess 1,12-dodecanediol with 0.1% butyl titanate as a catalyst. The processes were carried out in a three-neck flask equipped with stirrer, nitrogen inlet to remove the volatile materials (methanol), and vacuum pump. The flask was swept with a slow stream of nitrogen, stirred, and heated to 200^{o}C and kept for 2 hours. After 2 hours of alcoholysis, the temperature was slowly increased to 270^{o}C (2^{o}C.min^{-1}). At 270^{o}C, the nitrogen inlet was closed and vacuum pump was applied until the pressure of the system less than 0.5 mmHg. Stirring and heating under reduced pressure were continued for an hour. The flask was then cooled down under reduced pressure. After cooling, the polymer was collected from the flask.

Reactions:



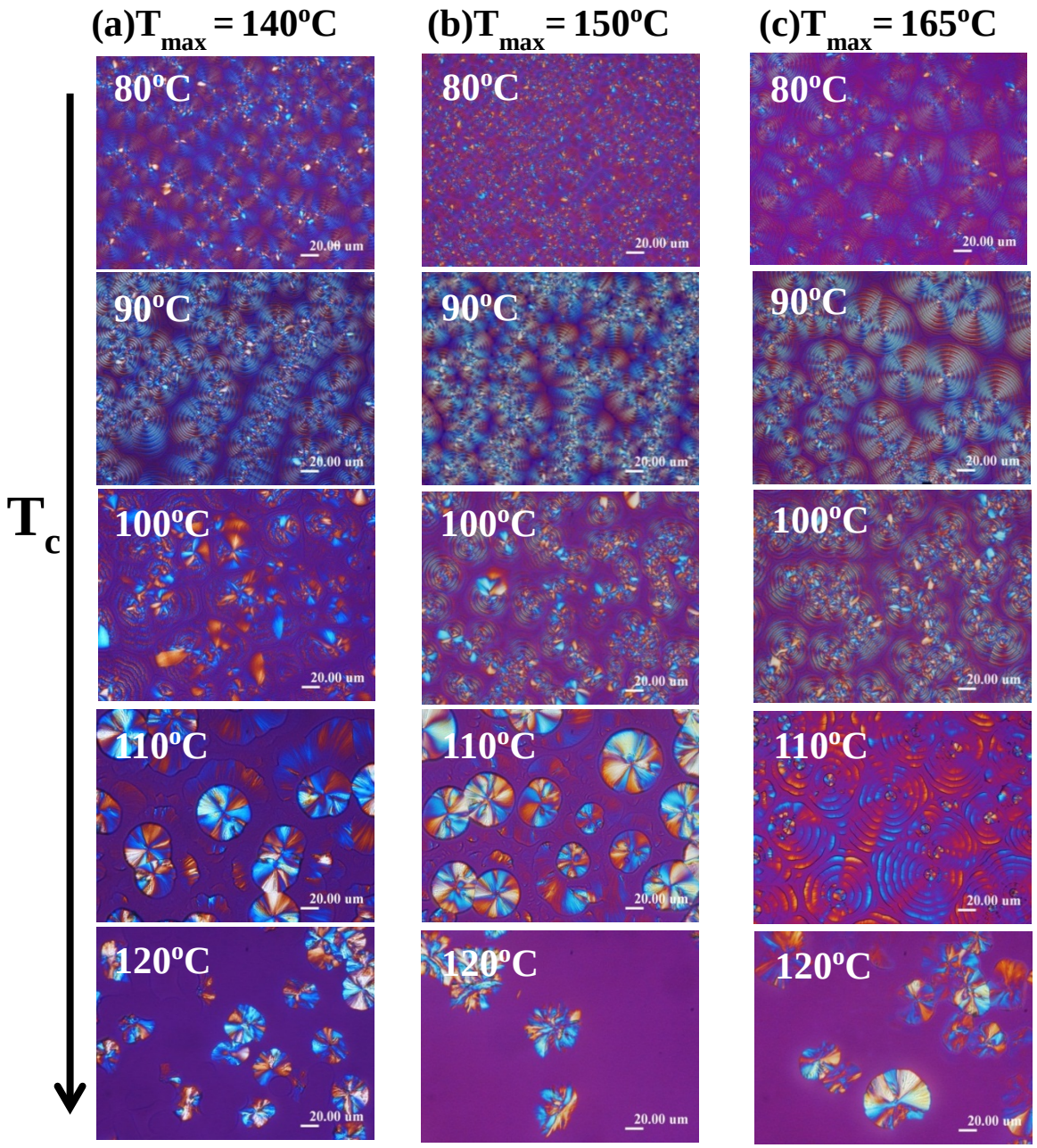


Figure S1. Effect of T_{max}: P12T spherulites melted at various T_{max} : (a) 140°C, (b) 150°C and (c) 165°C, to be followed by isothermally crystallization at 80-120°C (T_c=80, 90, 100, 110, 120°C) for 30 min.

Melt exposure of samples at a temperature above the melting temperature of P12T (T_m=121°C) might influence the crystallization morphology. Effects of melt exposure at T_{max} on the ring patterns in P12T crystallized at various T_c's were examined, with the temperature of melting the polymer prior to crystallization being fixed at a specific T_{max}. **Figure S1** shows the spherulite patterns of P12T crystallized T_c=80, 90, 100, 110, and 120°C after being melted at three different T_{max}=140, 150, 165°C. The increasing of T_{max} decreases the nuclei density of the films; thus, larger

spherulites could be achieved. Although all spherulites are periodically banded, the spherulitic patterns undergo a systematic change from double ring-banded (with small spacing) at lower T_c's (below 100^{o}C) into petal-like extinction-banded (with wider spacing) at higher T_c's (above 100^{o}C). At the transition ($T_c \approx 100^oC$), both patterns (single-ring and double-ring) are co-existing together. The fact that they differ in shape and optical properties implies that the double-ring-banded spherulites (grown at lower T_c's) and the petal-like extinction banded spherulites (grown at higher T_c's) differ in their self-assembly nature.

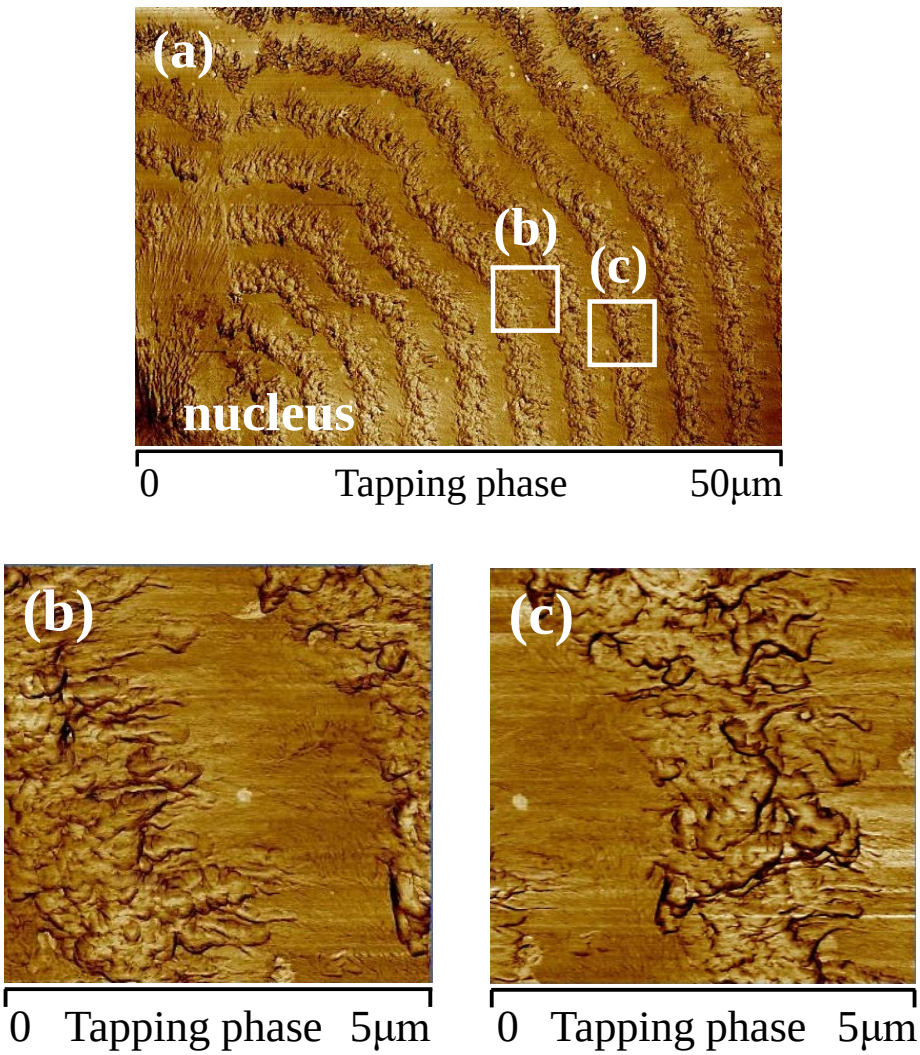


Figure S2. AFM phase images of P12T spherulite melt-crystallized at 96°C: (a) showing the periodic ridges and valleys; (b,c) zoom-in images showing contrasts between the valley and ridge, respectively.

Two specific spots (5 × 5 μm^2) covering both ridge and valley of the spherulite were compared to ensure that the morphology details of these banding patterns were not sporadic or incidental but truly reproducible within the spherulite. The topology in top-surface morphology is reproducible in spots A and B. The top surface morphology of P12T spherulites is quite similar to that reported earlier in Type-2 banded spherulites (with alternating blue/orange birefringent bands) of PNT (thin films at T_c = 75°C).[26] In summary, on the top surface of the ridge-bands, one sees only fibrous crystals aggregate on the ridge-band and gradually taper to needle-like ends, all pointing in the radial directions; the valley-band is generally flat but there are thin fiber-like crystals going in the transverse direction along the circular valley. However, other than the topological morphology of the top surface showing apparent ring bands, nothing about the crystal assembly underneath the top surface could be unveiled using AFM.

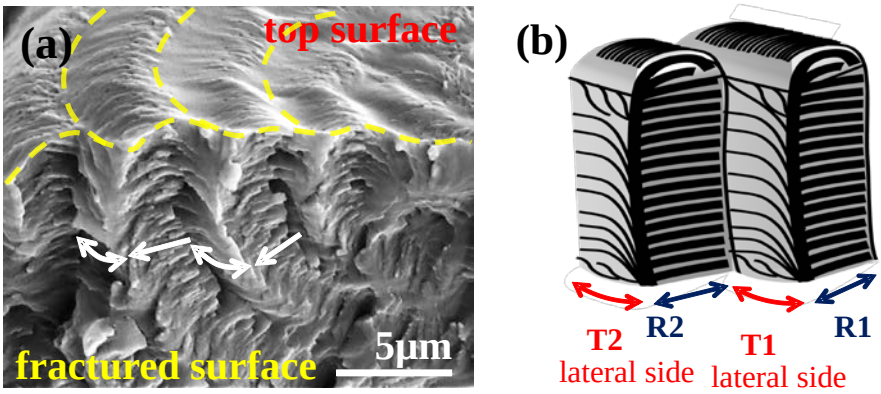


Figure S3. (a) SEM graph (b) and scheme for two adjacent layers of medially and laterally fractured P12T spherulite (obtained from 30-40 μm film crystallized at 96ºC) displaying the interior lamellae as the layer-like crystals growing away from nuclei center.

For greater magnifications of lamellar assembly, specific spots of the interior were zoomed in for better views. **Figure S3** shows SEM zoom-in images of fractured surface displaying interior lamellae of ring-band spherulites in bulk-form P12T melt-crystallized at 96ºC and simplified schemes that illustrate the phenomena. Similarly corrugated layers (composed of radial and tangential lamellae) are apparent in all spots chosen for zoom-in, suggesting the layered structures are not incidental or sporadic, but generally ordered in all 3D spherulite interior. Each layer is composed of a thin sub-layer of tangential lamellae and a thicker sub-layer of radial lamellae. Although some lamellae continuously bend/twist 90º angle from tangential to radial, the general trend is that there exists a distinct discontinuous interface between successive layers. The inter-layer interface (confined in region of less than 2 μm) between subsequent layers is a thin region populated mainly with tangentially grown lamellae (indicated by straight white arrows in SEM graphs), and the thicker sub-layer is filled mainly with radially grown lamellae (indicated by white arc-shaped white arrows in graphs).

Scheme is made to illustrate the growth of lamellae within the spherulite. Apparently, some of the tangential lamellae bend 90º to form radial lamellae in the subsequent layer; others of the tangential lamellae go upward and directly to the top surface, then bend 90º to the radial direction. As the tangential lamellae surface upward to the top, and they also immediately bend 90º angle, forming a periodically convex ridge. Simultaneously, they bend 90º in the radial direction, from the original tangential direction while they are in the interior layer. The bent lamellae initially convex up to form a ridge on the top topology; then, gradually precipitate downward and taper down to become fibrous needle-like lamellae, and eventually submerge and bend 90º angle again into a circumferential direction into the valley region. Thus, the periodic convex protrusion from tangential lamellae and corresponding 90º bends together forming the up-and-down ring bands on the top surface. Underneath the convex ridge, the corrugated structure of alternating tangential/radial layers are hidden and masked below the top surface bands.

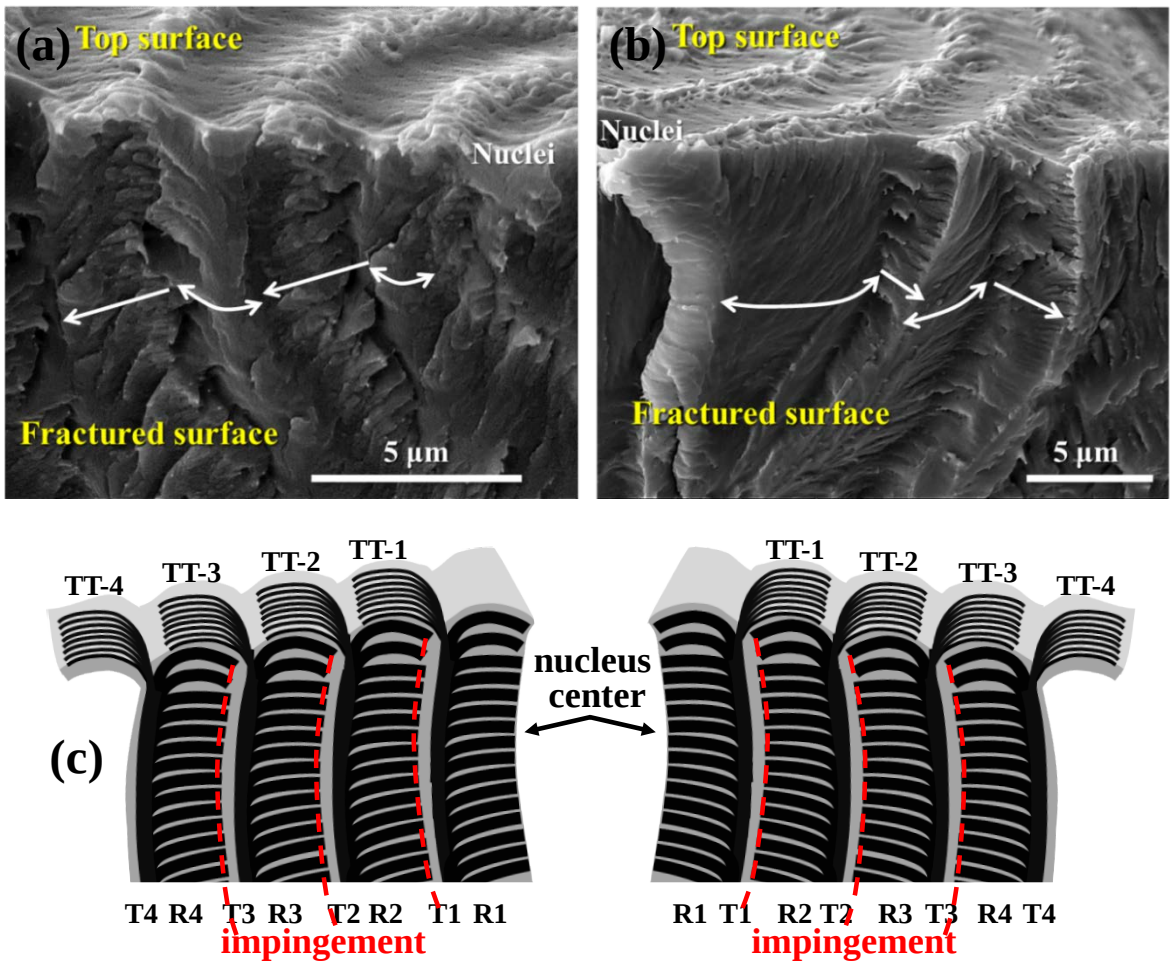


Figure S4. SEM micrographs of two randomly fractured vertical surfaces of P12T bulk spherulites, displaying interior lamellae at surfaces that: (a) laterally fractured across, (b) tangentially fractured along the interface of the adjacent bands, and (c) schemes that illustrate the lamellar assembly on fractured surface in correlation to that on top surface.

For further demonstrating that there exists distinct discontinuity between the successive bands (perpendicular intersection between the tangential and radial crystals), a portion of the fractured 3D spherulite (T_c=96°C) was zoomed in for clearer views. The SEM graph and corresponding scheme in **Figure S4** (a,b) shows clearly the interior crystal assembly and top-surface of ring bands, and a very interesting correlation between the crystals on the top surface and interior assembly. The radial lamellae (branches) account for ~3 μm, and the tangential lamellae are thinner at ca. ~2 μm, which together compose one band (band width = tangential+radial crystals = ~5 μm). Each of the layers is composed of radial lamellae (or bundles) and tangential lamellae (or bundles), with the tangential lamellae of the first layer impinging with the radial lamellae from next layer. Furthermore, owing to the impingement and discontinuity between two different species of crystals (tangential shish to radial kebab lamellae), the interface between layers tends to be easily separated.

Although the subsequent layers may be still connected by a small portion of continuous fibrous lamellae, most of the interfacial regions are detached.

The tangential crystals in general fan out from the bottom, and tend to grow side branches in the perpendicularly radial directions. The radial crystals are mostly "flat-on" platelets, which actually are branches evolving from the tangential crystals and bend at ca. 90^{o} pointing to the radial direction. By contrast, the tangential crystals are fibrous lamellae pointing vertically upward (perpendicular to the top surface of the 3D spherulites). For a better appreciation of the corrugate-board layers in 3D ring-banded P12T spherulites, a scheming plot is shown in Fig. S4-c, where a staggered layer-like structure depicts the exposed portions of the interior concentric spherical (or hemispherical) shells mutually wrapped/stacked as a rounded onion. The layer-like assembly is labeled as Layers#1, 2, 3, 4, etc., starting from the first layer closest to the nuclei center in the radial direction to the periphery. The radial and tangential lamellae in layer#1 are labeled as R1 and T1, respectively; and the radial and tangential lamellae in layer#2 are labeled as R2 and T2, respectively, and so forth, from nuclei to the periphery. Taking Layer#1 in the scheme as an example, one should note that the radial lamellae R1 always grow backward though in line with the radial direction, while the tangential lamellae grow upward in directions perpendicular to the radial one. The tangential crystals in general fan out from the bottom, and tend to grow branches in reverse radial directions. The tangential lamellae of Layer#1 then impinge with the backward-growing radial lamellae from Layer#2, creating a distinct interface of discontinuity between the subsequent layers (marked as the red dash lines in the scheme). The layer structure of radial+tangential lamellae repeats itself into a periodic repetition of stacked corrugate-board until the periphery impinges with neighboring spherulites. Then, let us direct attention to the top surface where ring bands are present. Another feature worthy of noting here is that as the tangential crystals emerge upward to the top surface, the fibrous tangential crystals bend and curve in a convex shape toward the radial direction. These bend/curved tangential crystals then become the "ridge-band" on the on top-surface topology. It should be emphasized nevertheless that the ridge-bands actually are situated on top of radial crystals that evolve from the next tangential crystals. Direct correlation between the top-surface ring bands and interior lamellae crystals is a key approach to the understanding of ring bands formation.