Electronic Supplementary Material

Strong enhancement of the twisting frequency of achiral orthorhombic lamellae in poly(ε-caprolactone) banded spherulites via evaporative crystallization

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Fig. S1 The comparison of (A) PCL$_{10k}$ nonbirefringent, (B) birefringent concentric-ringed spherulites and (C) PCL$_{84.4k}$ extinction banded spherulites elucidating that the extinction banding in PCL$_{84.4k}$ banded spherulites possesses the nature of the periodic twisting of radial lamellae rather than the rhythmic-crystallization-induced periodic variation of thickness. The data exhibited in part (A) and (B) were published in Macromolecules 2007, 40, 4381, and Macromolecules 2008, 41, 7584, respectively.
Fig. S2 POM images unveiling the influence of initial solution concentrations upon band spacing in PCL₈₄.₄₆ extinction banded spherulites. The initial solution concentrations are (a) 5, (b) 10, (c) 20, (d) 50, and (e) 100 mg mL⁻¹, and the corresponding radial band intervals in central zones are ca. 7.4, 8.5, 9.9, 11.0 and 12.1 μm respectively. Here the smaller band periods in (a-c) further indicate the strong twisting of PCL lamellae.

Fig. S3 In situ OM photographs displaying the growth process of the PCL₈₄.₄₆ classical banded spherulites from 10 mg mL⁻¹ solution. The plot of radius with time along the arrow direction is demonstrated in (d), indicating a slight increase of the radial growth rate of spherulites.
Fig. S4 POM photos displaying the morphological change during the shift of the drying environments from that of Fig. 7a (the slow drying) to the case in Fig. 7c (fast free evaporation). The immediately morphological transition from extinction banded spherulites to common Maltese spherulites indicates that it is the solvent evaporation and desorption rather than the supersaturation that is essential for the strong intensifying of the twisting frequency of achiral orthorhombic PCL lamellar crystals.

Fig. S5 POM, AFM phase and TEM images of the PCL\textsubscript{42.5k} spherulites developed under the same evaporation environment as that employed in Fig. 7a from a 10 mg mL\textsuperscript{-1} solution-cast film. The inset in (c) is the corresponding SAED pattern of the circle region. It is depicted that the PCL\textsubscript{42.5k} spherulites possess the nonbirefringent feature resulting from the nature of consisting of uniform flat-on lamellae, while under which PCL\textsubscript{84.4k} spherulites exhibit the extinction banded morphology with twisted lamellae. The feature implicates that the more seriously unequal solvent evaporation is necessary for triggering the twisting of PCL lamellae in the lower molecular weight sample, further confirming that the proposed intensifying mechanism for the twisting of achiral orthorhombic PCL lamellar crystals.