Supplementary Text: Details of the experimental set-up for carrying out the SR- μ -XRD experiments at the beamline BL-4A of the synchrotron radiation facility Photon Factory (PF) at the High-Energy Accelerator Research Organization (KEK) in Tsukuba (Japan). Information obtained from S. Ueno, T. Nishida and K. Sato, *Cryst. Growth Des.*, 2008, **8** (3), 751.

The sample set was placed in a temperature-controlled furnace, Linkam LK-600. Using an Olympus CX31 microscope system, polarized optical-microscope observations and SR- μ B-XRD measurements were carried out. The SR- μ B-XRD measurement was performed at beamline 4A of the Photon Factory, the synchrotron radiation facility of the High-Energy Accelerator Research Organization (KEK), Tsukuba, Japan. A microbeam was prepared by reflecting a synchrotron X-ray beam onto a K-B mirror and focusing the reflected beam on the sample position. The wavelength of the X-ray microbeam was 0.11 nm, and the focused beam size was $5 \times 5 \mu$ m. The position of the microbeam was detected by moving a wire (40 μ m diameter) perpendicular to beam direction, and always pointed on a monitor image on which the sample subjected to microbeam diffraction was shown using an optical microscope (magnification 100 to 200×). The sample was moved by an x-y-z stepping motor (1 μ m step) while being observed by the optical microscope. The length between the sample and the detector was around 110 cm. Because of the difficulty in simultaneous measurements of the small-angle and wide-angle X-ray scattering, we only observed the small-angle X-ray scattering (SAXS) in the SR-µB-XRD experiments.



Fig. S1 Scanning SR- μ -XRD patterns taken at the all positions of a spherulite of the mixture of 25POP:75OPO grown from neat liquid (a) at 9 °C and (b) at 6° C

(a)



(b)

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Fig. S2 Scanning SR- μ -XRD patterns of a spherulite of the mixture of 75POP:25OPO grown from n-dodecane solution at 7 °C

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Fig. S3 Scanning SR- μ -XRD patterns of a spherulite of 25POP:75OPO grown from n-dodecane solution at 2 °C



Fig. S4 Scanning SR-µ-XRD patterns through the horizontal direction over many small spherulites of 25POP:75OPO mixture grown from neat liquid (a) at 6 °C and (b) at 9 °C.