Supplementary Information:

Optical Imaging of Large Gyroid Grains in Block Copolymer Templates by Confined Crystallization

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Melting and Recrystallization Experiments

Figure S1: Variation of birefringent textures of solvent-annealed ISO thin films with temperature. (a) At room temperature, after solvent vapor annealing and before heating, extended domains of uniform birefringence are visible. (b) At 55°C, the birefringent texture disappears. The residual non-uniformity in the image is caused by the surface roughness of the terpolymer film. (c) The birefringence gradually reappears upon cooling at ≈ 40 °C. Birefringent features are visible and increase in density upon further cooling to 36°C. (d) The initial birefringent texture reappears at 26°C with a pattern nearly identical to the one shown in (a). The domains exhibit an increased defect density, which is likely due to incomplete crystallization. The crossed arrows indicate the orientation of the polarizers. Scale bars: 500 µm.

To confirm the crystalline nature of the extended domains of uniform birefringence (Figure 1b) and to confirm that the birefringence is the result of the semicrystalline PEO and not any underlying structural anisotropy, heating experiments were carried out (Figure S1). A heating chamber with transparent windows allowed the in situ observation of the birefringent textures by polarizing optical microscopy (see Experimental Section for details). Samples exhibiting extended domains of uniform birefringence (Figure S1a) were heated at a rate of 15°C/min and the birefringent texture disappeared at 55°C (Figure S1b). This temperature
is consistent with the melting temperature of PEO as determined by DSC ($T_{m}^{\text{PEO}} \approx 55^\circ\text{C}$; Figure S2). The samples were kept at 55$^\circ\text{C}$ for 1 min, after which they were allowed to cool. At a temperature of $\approx 40^\circ\text{C}$, the birefringence began to reappear, becoming increasingly clear as the temperature decreased (Figure S1c). Below $\approx 26^\circ\text{C}$, no further changes were observed (Figure S1d). Figure panels S1a and S1d show nearly identical birefringent textures and patterns.

Figure S1c provides evidence for macroscopically aligned individual crystallites. Upon cooling from the melt, individual extended crystalline assemblies are discernible, which have the same alignment within each extended domain. Progressive crystallization causes these crystallites to coalesce and form the homogeneous birefringent texture (Figure S1d).

**Differential Scanning Calorimetry**

![DSC graphs](image)

Figure S2: **Differential scanning calorimetry (DSC) of the ISO triblock terpolymer.** (a) The melting and crystallization peaks are clearly visible at 55$^\circ\text{C}$ and 30$^\circ\text{C}$, respectively. (b) A magnification of the region between 40$^\circ\text{C}$ and 120$^\circ\text{C}$ shows the glass transition of polystyrene at $\approx 87^\circ\text{C}$ and $\approx 90^\circ\text{C}$ (half-step temperatures) during cooling and heating, respectively.

As the crystallization behavior of the ISO triblock terpolymer depends on the glass transition temperature of the amorphous PS block ($T_{g}^{\text{PS}}$), and the melting and crystallization
temperatures of the semicrystalline PEO block ($T_{m}^{\text{PEO}}$ and $T_{c}^{\text{PEO}}$, respectively), differential scanning calorimetry (DSC) was performed to determine these key parameters (Figure S2). The peaks at 55°C during heating and 30°C during cooling are consistent with values previously reported for the melting and crystallization temperatures of PEO (Figure S2(a)).\(^1\) A shallow $T_{g}^{\text{PS}}$ can be seen at $\approx 87$°C (Figure S2(b)), determined by the 50% heat capacity change during vitrification. The corresponding $T_{g}^{\text{PS}}$ during heating is $\approx 90$°C and thus slightly higher than during cooling. The higher $T_{g}^{\text{PS}}$ during heating is probably related to its proximity to the PEO melting peak in the heating curves. The “true” liquid base line is expected to be less steep and any error in its identification shifts both the onset and half-step temperatures to higher values (i.e. away from the $T_{g}^{\text{PS}}$ measured during cooling).

### Grazing-Incidence Wide-Angle X-Ray Scattering

![Grazing-Incidence Wide-Angle X-Ray Scattering](image)

Figure S3: **Grazing-incidence wide-angle X-ray scattering (GIWAXS) of as-spun and solvent-annealed terpolymer thin films.** Azimuthally-averaged GIWAXS data for as-spun (black dots) and solvent-annealed (red dots) samples. The blue line is the curve fitted to the as-spun data using two peaks (red lines). The gray line indicates the expected (120) crystallite peak for uniaxially-oriented PEO (homopolymers) after stretching and melt quenching.\(^2\)
References

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(2) Takahashi, Y.; Tadokoro, H. Structural Studies of Polyethers, -(CH2)m-O)-n. X. Crystal Structure of Poly(ethylene oxide). *Macromolecules* 1973, *6*, 672–675.