Crystallinity Development in PFO: From Nanograins to Crystalline Lamellae as Revealed by In-Situ SAXS/WAXS/DSC

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With in-situ small-angle and wide-angle X-ray scattering and differential scanning calorimetry (SAXS/WAXS/DSC), we have studied the structural evolution during the cold crystallization process of Poly(9,9-di-n-octyl-2,7-fluorene) (PFO). The SAXS data (Figure 1) indicates clearly the formation and growth of nanograins, from ~8 nm in globular shape to ~15 nm in disk-like shape, during the temperature elevation to 140 °C for isothermal crystallization (Figure 2). The simultaneously recorded WAXS and DSC consistently reveal an accompanied crystallization, at the time when a lamellar packing order of the nanograins appears in the in-site SAXS spectra. Few minutes after the isothermal crystallization at 145 °C, we found that PFO already reaches a thermal equilibrium structure, with an α crystalline structure in the lamellar ordered domains of a lamellar spacing of 50 nm. SEM images (Figure 3) taken in the isothermal crystallization show the consistent nanograin size and lamellar spacing. Instead of the classical scenario of stem-by-stem folding on the crystal front, we found that structural evolution observed during reheating of quenched PFO is better described by a sequence of intragrain nucleation, intragrain growth, followed by nanograin re-orientatation and coalescence at elevated temperatures.

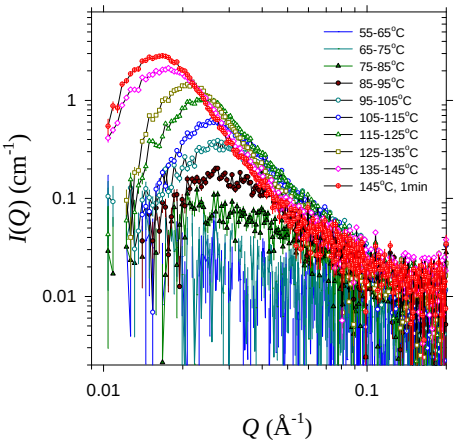

Figure 1. Temperature dependent SAXS data after the subtraction of the SAXS from fractal-like density fluctuations.

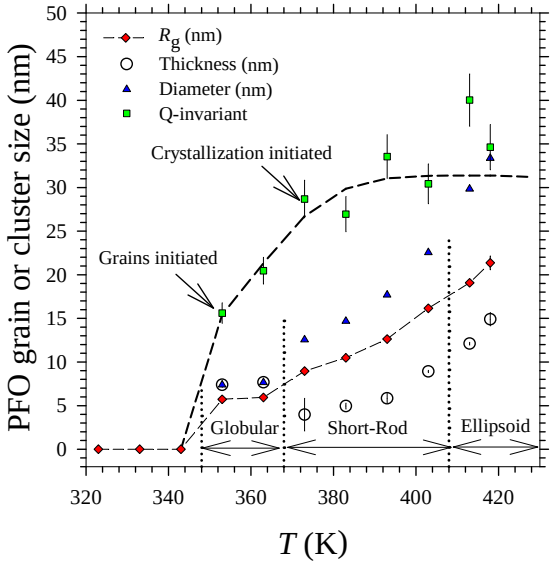

Figure 2. The temperature evolution of PFO grain size and shape.

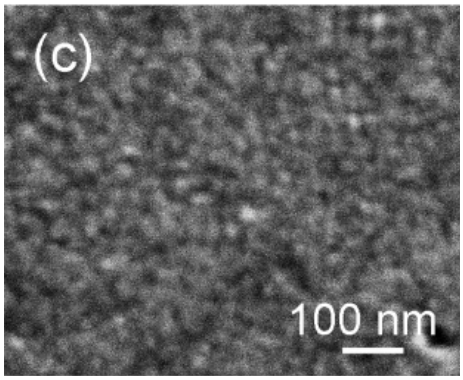

Figure 3. Representative SEIs of cold-crystallized PFO films, suggesting local alignment of nanograins with increasing t_{cc} or T_{cc}: quenched after t_{cc}= 1 h,

Based on the micro-Brownian motion model, we propose that the PFO crystallization proceeds by, first, molecular nucleation into nanometer-sized globules, then, a subsequent coalescence of nanoglobules or nanograins via Brownian motion, in a manner similar to siliceous nanograins. More importantly, the nanograins appear to play a fundamental role in the morphological development of several polymer films, such as PFO and sPS we observed.