Transformation from Heterogeneous to Homogeneous Nucleation in 2D Confinement

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In this experiment, a diblock copolymer system, poly(4-vinylpyridine)-b-poly(ε-caprolactone) (P4VP-PCL) was used to create cylindrical morphology to study the crystallization behavior of polymer chain under nanoconfinement. It is known that the final morphology of block copolymer is depended on two factors: the segregation strength and the crystallization temperature. Segregation strength is expressed through the product of χN, where χ is the Flory-Huggins segmental interaction parameter, inversely related to temperature, and N is the degree of polymerization. For phase separation to occur, the crystallization must be performed below T_{ODT} (the order-disorder transition temperature). According to the crystallization temperature in relation to the glass transition temperature of the amorphous block, there are two kinds of confinements, hard ($T_{ODT} > T_g^a > T_c^c$) and soft ($T_{ODT} > T_c^c > T_g^a$).

With the self-assembled P4VP-PCL cylinder morphology, the PCL crystalline orientation is thus restricted within cylindrical contour under hard confinement. To study the crystallization behavior under 2D confinement, the crystallographic details within the confined MDs should be investigated. In other words, it is necessary to clarify the crystalline orientation of crystallites grown within the cylinder phase.

TEM and simultaneous 2D SAXS/WAXD experiments were carried out to explore the evolution with respect to the transformation in crystallization kinetics (Figure 1). While confined size is larger than 10nm, as shown in Figure 1 (a), the crystal growth starting from the heterogeneous nucleus can spread over few tens micrometers along the cylindrical MDs. By contrast, the single slab PCL crystals (Figure 1 (e)) displays discrete granules, which may imply the occurrence of homogeneous nucleation. The morphology demonstrates that the crystal growth starting from the heterogeneous nucleus, which is in line with the interpretation based on the sigmoidal crystallization kinetics. In addition, as evidenced by X-ray results, crystalline PCL stems were perpendicularly oriented with respect to the cylindrical axis for the crystal growth of heterogeneous nucleation (Figure 1 (b) ~ (c)) whereas random orientation to the cylindrical axis was found (Figure 1 (f) ~ (g)) for that of homogeneous nucleation. The observed WAXD reflections were indexed by an orthorhombic unit cell with dimensions a= 0.7096 nm, b= 0.4974 nm and c= 1.7297 nm.

On the basis of the orthorhombic lattice structure of PCL crystals, the observed reflections could be indexed as (110) and (200) reflections as shown in Figure 1 (c). The WAXD pattern shows that the maximum diffraction intensity of the (110) reflection is located at the azimuthal angles, Φ = 53, 125, 231 and 300°; that of the (200) reflection is at Φ = 0 and 180°. According to the corresponding SAXS and WAXD patterns, the scattering patterns suggest that an anisotropic orientation can be found in the VP/CL 90/38 samples crystallized at high temperatures. A preferred growth direction along *b*-axis parallel to central axes of the cylinders can thus be proved. The preferred crystalline orientation induced by confinement is referred to the restriction of the confined MD, the level of nucleation density and the type of crystalline growth. In the case of large confined size (i.e., ~14.7 nm), it is intuitive to suggest that the crystal growth direction may selectively follow the unrestricted pathway to reach the fast growth as the primary concern for the crystalline growth (Figure 1 (d)); that is, indicating that the crystalline growth under confinement is indeed directed by confined contour for polymeric crystallization. When the confined size decreased below a certain size (i.e., 10 nm), the crystal orientation altered from the specific preferential orientation to random orientation (Figure 1 (h)). Hence, the specific crystal growth direction under 2D confinement was observed.

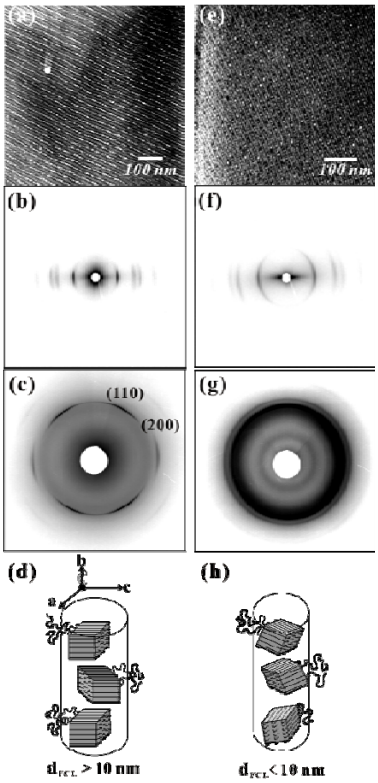

Figure 1. VP/CL 90/38 System: (a) TEM image (T_C= 10 °C), (b) 2D anisotropic SAXS, (c) fiber-like WAXD patterns with incident X-ray beams along the gradient-direction and (d) the schematic presentations of chains orientation under confinement. VP/CL 85/23 System: (e) TEM image (T_C= -50 °C), (f) 2D anisotropic SAXS and (g) ring-like WAXD patterns with incident X-ray beams along the gradient-direction and (h) the schematic presentations of chains orientation under confinement.