Origin of ringed polymer spherulites

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高分子結晶が作る球晶に同心円状のリングパターンがみられる場合がある(図1)。球晶内の微結晶が成長方向を軸として捩れ相関を持つことが原因であるが、捩れの機構については未だ明らかでない。今回、成長界面の Mullins-Sekerka 不安定性と結晶に内在するキラルな歪みの結合により、リング周期が決定される機構を提案し、ポリエチレンのリング球晶について検証した(図2, 3)。

Polymer spherulite is a higher order structure formed by lamellar crystallites of folded polymer chains. Due to twisting correlation of the crystallites along the radial direction, spherulites of a variety of polymers develop periodic ring patterns (Fig. 1). We examined the determination mechanism of the ring period in polymer spherulites. From the microscopic observations by OM and SPM (Fig. 2), we have experimentally confirmed the morphological instability of Mullins-Sekerka type. We propose a new type of three-dimensional pattern formation by the coupling of the instability and intrinsic growth strain of polymer crystallites, which leads to the periodic branching and periodic twisting as the consequence (Fig. 3).

Based on the modeling, we expect the following relationship among the ring period, P, crystal growth rate, V, and the width of the tip splitting, λ,

$$P \propto \lambda \propto (D/V)^{0.5}$$

where D represents the mass diffusion coefficient. By the microscopic observations of spherulites and single crystals, we have successfully confirmed the above relationship in polyethylene ringed spherulites.

[Reference]

A. Keller: Nature **169** 913 (1952).

B. Lotz and S.Z.D. Cheng: Polymer **46** 577 (2005).

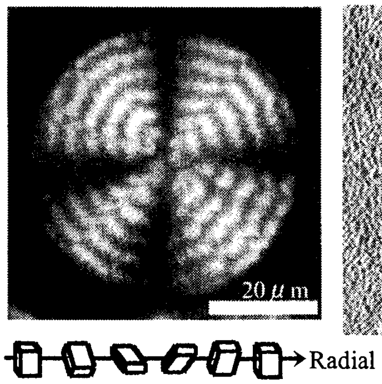

Fig. 1 polarizing optical micrograph of a ringed spherulite of polyethylene.

Fig. 2 AFM image of a polyethylene single crystal grown from the melt with tip splitting at a certain wavelength.

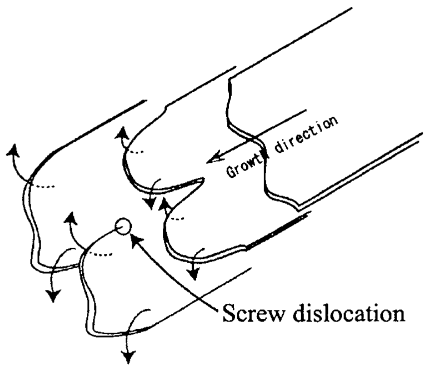

Fig. 3 Schematic illustration of the formation of branches by the coupling of the morphological instability and inherent growth strain.

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