Precursors of Shish-kebab in Isotactic and Syndiotactic Polystyrene Induced by Shear Flow

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It is well known that when semi-crystalline polymers are crystallized under shear or elongational flow, crystallization rate is enhanced and the so-called "shish-kebab" structure is formed. It is considered that shish-kebabs consist of extended chain crystals (shish) and fold chain lamellar crystals (kebab) grow periodically around shish.[1] Recent researches have focused on the formation mechanism of shish-kebab and revealed the existence of precursors of shish-kebab.[2] However, the precursors formed before shish-kebab is still an unsolved problem regardless the illuminating results.

In this study, we have investigated formation and relaxation of precursors of shish-kebab in isotactic polystyrene (iPS) after applying a pulse shear flow at temperatures above the nominal melting temperature T_m (=223 ℃). Using polarized optical microscope (POM) and small-angle X-ray scattering (SAXS), it was found that string-like objects which were thought to be precursors of shish-kebab are formed in micrometer even above the nominal melting temperature, but up to ~285 ℃ , which was very close to the equilibrium melting temperature T_m^0 (=289 ℃), they were molten entirely. When quench string-like objects to an isothermal crystallization temperature of 210 ℃, a spot scattering developed with time was detected by in-situ SAXS which is attributed to the formation and growth of kebab.(Fig 1) On the other hand, when anneal string-like objects above T_m (Fig 2, at 250 ˚C) there was no anisotropic scattering observed during time evolution regardless the persistence of string-like objects observed by POM. The volume fraction of string-like objects is extremely low (e.g. ~0.3% at 265 ˚C) which makes the signals of string-like objects undetected.

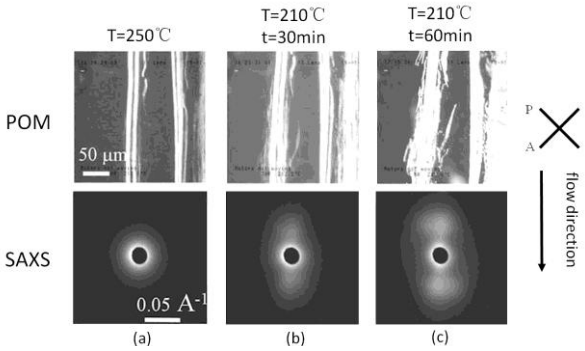

Figure 1. Formation and crystallization of string-like objects induced by a pulse shear flow in isotactic polystyrene. (a) formation of string-like objects at a shear temperature of 250 ℃ (T_m =223 ℃)*;* (b)and (c) time evolution of isothermal crystallization at 210 ℃.

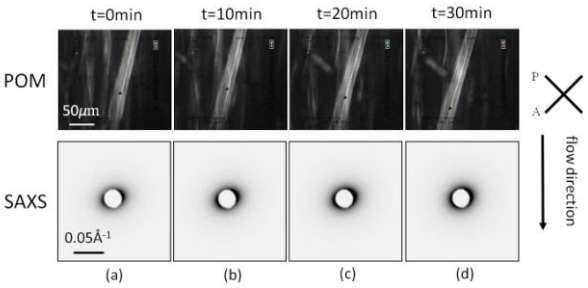

Figure 2. Time evolution of string-like objects at a shear temperature of 250 ℃ and a annealing temperature of 250 ℃ in isotactic polystyrene.

Our recent topic is about the distinctness between isotactic and syndiotactic polystyrene after applying a pulse shear flow.

1) Keller, A; Kolnaar, J. W. H. *In Processing Polymers*; Meijer, H. E. H. Ed.; VCH: New York, **1997**; pp 189-268
2) Balzano, L.; Kukalyekar, N.; Rastogi, S.; Peters, G. W. M.; Chadwick, J. C. *Phys. Rev. Lett*. **2008**, *100*, 042302-1-042302-4