6A/2010G007

Shear-Induced Crystallization Process of Syndiotactic Polystyrene

Yunfeng ZHAO, Go MATSUBA* and Hiroshi ITO
Yamagata University, Yonezawa 992-8510, Japan

1 Introduction

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 in the simplest case. The formation mechanism of shish-kebabs is still an unsolved problem about polymer physics and properties regardless the considerable works. Especially, it is very significant to understand shear-induced crystallization and to control polymer properties. In this study, we have focused on shear-induced crystallization process of a crystalline polymer with x-ray scattering measurements.

2 Experiment

We used syndiotactic polystyrene (sPS) with molecular weight M_w = 300,000 and polydispersity of M_w/M_n = 3.9 purchased from Scientific Polymer Products Inc. The nominal melting temperature T_m of sPS determined in DSC measurements with a heating rate of 5 °C /min is 270 °C. A Linkam CSS-450 high temperature shear cell was used to control the temperature of the sample and the shear conditions. Time-resolved small-angle X-ray scattering (SAXS) measurements were carried out by using an apparatus installed at a beam BL15A/6A in a synchrotron radiation X-ray scattering facility, Photon Factory, KEK, in Tsukuba, Japan. A two dimension (2D) CCD camera (C7300: Hamamatsu Photonics K.K.) with an image intensifier was used as the X-Ray detector. The wavelength λ of the X-ray beam was 1.54 Å, and the camera length was 2.3 m for SAXS measurements. The q range in the SAXS measurements was 8 x 10^{-3} - 1.5 x10^{-1} Å^{-1} where q is the scattering vector, $q=4\pi\sin\theta/n\lambda$ (2θ and n are the scattering angle and the refractive index, respectively).

3 Results and Discussion

We observed isothermal crystallization process sPS after applying a steady shear flow with a constant shear rate and various shear strains below the nominal melting temperature T_m by using time-resolved SAXS. The shear temperature T_{shear} was 260 °C and the isothermal crystallization temperature T_c was 250 °C. The shear rate was 60 s^{-1} and the shear stain was 0 to 360,000 %. Fig 1 showed crystallization time evolution of SAXS profiles in various shear strains. It was found that crystallization was accelerated after cessation of shear flow (b, c, d) compared with the quiescent state (a). Especially, it is obvious that crystallization had been progressed in the case of (c, d) at the onset of measurements (t = 0) while no crystalline scattering feature was observed in (a) at the same time.

On increasing shear strain, the meridian scattering features respect to the flow direction became stronger and the 2D scattering patterns became more heterogeneous. Meanwhile, only homogeneous 2D scattering patterns were observed in the quiescent state, which indicated the spherulitic morphology. The anisotropic scattering features can be attributed to the scattering features of oriented (stacked) lamella crystals in size dimension in the case of flow-induced crystallization. Usually, the equatorial streaks with respect to flow direction are thought to be the scattering features of shishs while the meridian spots are thought to be the scattering features of kebabs. The meridian scattering features were found during isothermal crystallization but the equatorial streaks were absent at these shear conditions. As the intensity scattered by SAXS measurements is insensitive to low concentration or low electron density contrast, we cannot deny the existence of shish entity at above shear conditions.

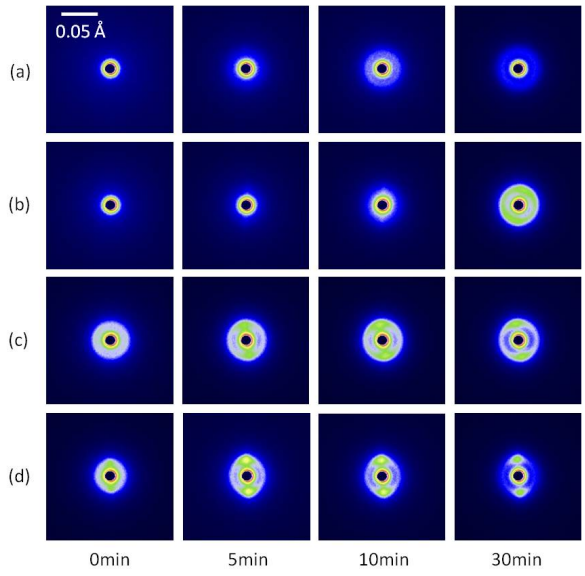

Fig. 1: Crystallization time evolutions of 2D SAXS patterns of sPS at 250 °C. (a): at quiescent state; (b), (c), (d): after applying a steady shear flow with a constant shear rate = 60 s^{-1} and various shear strains ε at 260 °C. (b): ε = 48,000 %; (c): ε = 180,000 %; (d): ε= 360,000 %.

*gmatsuba@yz.yamagata-u.ac.jp