

Density Fluctuations during the Early Stage of Polymer Crystallization

Takashi KONISHI

Graduate School of Human and Environmental Studies, Kyoto University, Kyoto

konishi.takashi.8c@kyoto-u.ac.jp

Polymer crystallization mechanism has been studied for a long time. The classical nucleation theory has explained the crystal nucleation and growth mechanism[1], while the existence of density fluctuations with the formation of precursor domains during the initial stage of crystallization has been discussed using experimental[2], simulation[3] and theoretical studies[4]. Recently, the density fluctuations during the induction period of crystallization for poly(trimethylene terephthalate) (PTT) from the glassy state has been reported[4].

In order to clarify the density fluctuations, we have investigated the crystallization processes of PTT using X-ray techniques. The isothermal crystallization from the melt state of poly(trimethylene terephthalate) (PTT) has been studied by wide-angle X-ray diffraction (WAXD), small-angle X-ray scattering (SAXS) and ultra-small-angle X-ray scattering (USAXS). Large scattering intensity in the low- q region $I_L(q)$ has been observed by SAXS and USAXS during the early stage of crystallizations. $I_L(q)$ increases with time, reaches a maximum, and decreases. On the other hand, the scattering intensity in the high- q region ($I_H(q)$) has a peak around $q = 0.08 \text{ \AA}^{-1}$, and monotonically increases with t_c . We have quantitatively analyzed the X-ray results using the scattering equations which can simultaneously deal with the hierarchical structures consisting of the crystallites and their aggregates. The results revealed the crystallization mechanism in which the crystalline nodules cover the entire sample with the aggregation regions[6]. The conclusion quantitatively showed that the large SAXS intensity is due to the correlations among the heterogeneous aggregation regions of the nodules.

- [1] J. D. Hoffman, G. T. Davis, and J. I. Lauritzen, in Treatise on Solid State Chemistry, edited by N. B. Hannay (Plenum, New York, 1976), Vol. 3, p. 497.
- [2] K. Kaji et al., Adv. Polym. Sci. 191, 187 (2005).
- [3] P. D. Olmsted et al., Phys. Rev. Lett. 81, 373 (1998).
- [4] M. Muthukumar, Phil. Trans. R. Soc. Lond. A 361, 539 (2003).
- [5] W. T. Chuang et al., Macromolecules 44, 1140 (2011).
- [6] T. Konishi et al., Phys. Rev. Materials 2, 105602 (2018).