

Formation of lamellar structure of poly(ethylene terephthalate) as a function of time at constant heating temperatures

Yumiko NAKANO¹, Kumiko TSUDA¹, Yanling LUO¹, Yuezhen BIN¹,
Masafumi HARADA¹, Kenji SAIJO² and Masaru MATSUO*¹

¹Department of Clothing Environmental Science, Faculty of Human Life and Environment,
Nara Women's University, Nara 630-8506, Japan

²Department of Polymer Chemistry, Graduate School of Engineering,
Kyoto University, Kyoto 606-8501, Japan

Introduction

Extensive studies have been performed on the morphology of crystalline polymers obtained by annealing amorphous films or by cooling melt films^{1,2}. The growth of polymer crystals has been well established in literature, and there are reliable theories to predict the kinetics of crystallization. Most of these studies have been concentrated on the observation of crystal growth processes, while little information exists about how nucleation proceeds from the disordered amorphous state. The initiation of crystallization or nucleation step remains somewhat of a mystery. The thermal behavior of amorphous PET film by rapid-jump of temperature was investigated in terms of the density fluctuation of amorphous chains by using depolarized light scattering techniques. The logarithm of scattered intensity from amorphous PET film increased linearly with time in the initial stage (stage II) of the density fluctuation when the specimen was annealed immediately at a constant temperature^{1,2}. This phenomenon could be analyzed within the framework of the linear theory of SD proposed by Cahn. Namely, the amorphous chains at elevated temperature are thermodynamically unstable and tend to incur density fluctuation. This concept provided the definition of a sort of spinodal temperature. During the annealing process, compact molecular aggregates may be formed and these connect to the heterogeneous continuous region (high density amorphous phase). For the undrawn sample, in spite of the ordering of molecules in the high density phase, the behavior was independent of crystallization. To clear this concept, SAXS intensity distribution was measured as a function of time after the specimen was put into the hot tube maintained at a constant temperature.

Experimental

The PET used in this study was furnished by Toyobo Industries, Inc. The density of the PET film is ca. 1.335 g cm⁻³, which agrees with the value reported for amorphous PET. The film thickness is about 76 μm. SAXS distribution for the PET film was performed by the synchrotron radiation dynamic small-angle X-ray scattering (SR-DSAXS) apparatus at BL-15A. The scattering data was collected by a position sensitive proportional counter (PSPC). The wavelength (λ) of

incident X-ray was 0.15 nm, and the spectral distribution was $\Delta\lambda/\lambda = 10^{-3}$.

Results and Discussion

Figure 1 shows SAXS intensity against time measured for the specimens at two temperatures. The specimen was put into the tube maintained at the indicated temperature. As shown in Figure 1, the scattered peak was not observed before 40 min, when the specimen was put into the tube maintained at 100°C. At 110°C, the peak appeared 5.5 min. This indicates that the lamellar formation time became faster as temperature increased. The lamellar thickness is ca. 7 nm. Interestingly, the lamellar formation became significant at 110°C and this is probably thought to be due to the thermal crystallization. This phenomenon is in good agreement with FTIR spectra showing rapid transition from gauche to trans conformation of PET chains at 110°C.

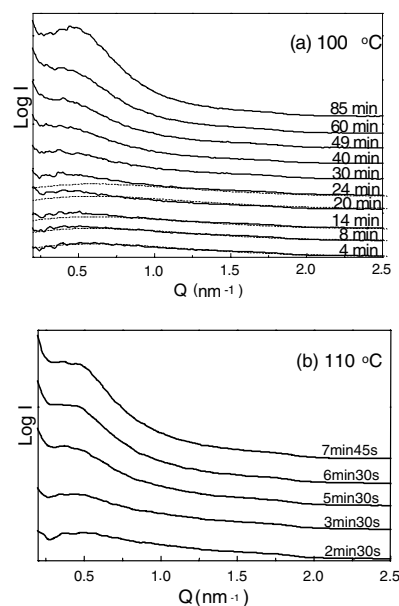


Fig. 1. SAXS intensity against time measured for the PET films at (a) 100 °C and (b) 110 °C.

References

- [1] X. Tong et al. *Macromolecules* **37** 6985-6993 (2004)
- [2] X. Tong et al. *Phys. Rev. B* **71** 75204-75213 (2005)

*m-matsuo @cc.nara-wu.ac.jp