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Simultaneous Measurement of SAXS and Heat Capacity During Isothermal Annealing of Semicrystalline Poly(ethylene oxide)

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Introduction

Semicrystalline polymers are known to exhibit notable change in SAXS pattern during isothermal annealing just below the melting temperature. This change is attributed to irreversible thickening of the lamellar crystals. Time resolved SAXS studies have been carried out by many researchers mainly using synchrotron radiation.

It is known that the heat capacity decreases during the isothermal annealing. Comparison between the time resolved SAXS results and the time dependence of the heat capacity is expected to give useful information about the annealing effects.

Combined measurement of the X-ray diffraction and the differential scanning calorimetry (DSC) has been applied to phase transitions. However, DSC can not measure time dependence of the heat capacity during isothermal annealing. Ac calorimetry is a technique to measure the heat capacity using small temperature modulation around a constant temperature. This technique can measure the heat capacity with the quasi-isothermal condition. Since the amplitude of the temperature modulation is very small (less than 0.5K) disturbance of the annealing condition is negligible. In this study an instrument for simultaneous measurement of SAXS and ac calorimetry has been developed and applied to the annealing effects on the semicrystalline poly(ethylene oxide).

Experimental

Poly(ethylene oxide) (PEO) (M_w = 200,000) was used. The sample film with the thickness of 280μm was quenched from the molten state at 85°C. Thin aluminum film was fixed on the both surfaces of the sample as the heater for temperature modulation. The sample was set in a temperature controlled cell. Period and amplitude of the temperature modulation were 100s and 0.47K, respectively.

Results

Preliminary results are shown below. Fig.1 shows the SAXS pattern obtained during annealing at 53.5°C. The non-annealed curve (t_a=0min) was measured just after the annealing temperature was reached. The curves for t_a = 10, 20, 30, 40, 50, 60 and 70min are shown as well. As the annealing time increases the curves shifted upwards. The broad peaks around 1/d = 0.01 are atributed to the lamella crystals. The peak position shifted to the left direction corresponding to the lamella thickening. It can be seen that the shift of the peak position is faster at the beginning of the annealing. Figure 2 shows time dependence of the heat capacity measured simultaneously with the data of Fig.1. Decrease in the heat capacity was clearly observed. The decreasing rate was larger at the beginning of the annealing similarly to the lamellar thickening.

These results show that the simultaneous measurement of the SAXS and the heat capacity was successful. Results of detailed data analysis will be reported elsewhere.

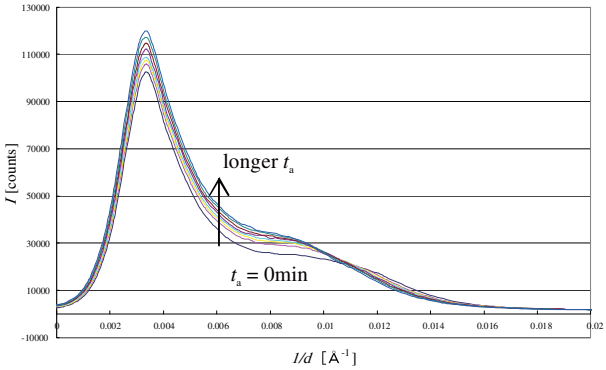

Fig.1 The scattering intensity plotted against the inverse of the d spacing.

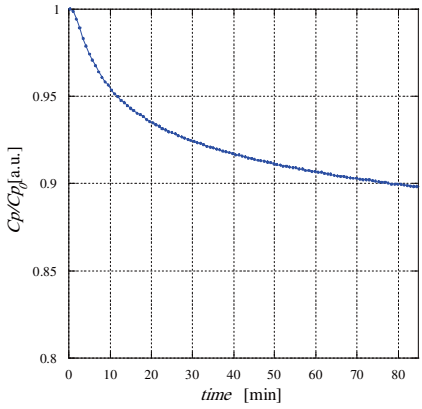

Fig.2 The heat capacity relative to the value at the beginning of the annealing at 53.5°C.

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