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Heat Capacity Relaxation during Annealing of Poly(ethylene oxide) Crystals

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Time dependence of the heat capacity of poly(ethylene oxide) crystals during isothermal annealing has been measured with TM-DSC operated in the quasi-isothermal mode. It was found that the relaxation of the heat capacity was composed of two components, that is, fast and slow components. The relaxation time of the slow component was five to ten times as long as that of the slow component. These two components were attributed to melting of thin crystals and lateral growth of the lamella crystals.

Keywords: Heat capacity relaxation, Temperature modulated DSC, Annealing, Poly(ethylene oxide)

1. Introduction

Annealing effects on polymer crystals have been studied by many researchers for a long time [1]. Since the annealing is the thermodynamically irreversible process, thermodynamic viewpoint is important in the studies. Heat capacity is a typical thermodynamic property of materials, but the heat capacity change accompanying the annealing has not been studied extensively. Heat capacity measurement of polymers has been carried out mainly with differential scanning calorimeter (DSC). However, DSC is not applicable to measure the heat capacity change with time during the isothermal annealing because DSC signal is proportional to the heating rate which is equal to zero during the isothermal annealing. The temperature modulated DSC (TM-DSC) [2,3] solved this problem. TM-DSC enabled the quasi-isothermal measurement in which the heat capacity was calculated from the modulation component measured with a fixed average temperature ($\bar{T}$). The sample temperature stays within the temperature range from $\bar{T} - T_{amp}$ to $\bar{T} + T_{amp}$ where T_{amp} is the amplitude of the temperature modulation. If T_{amp} is small enough the measured value of the heat capacity can be regarded as the value at $\bar{T}$. The quasi-isothermal measurement technique is applied to polyethylene crystals and the isothermal annealing effects are investigated [4]. In this work the quasi-isothermal measurement technique was applied to a study of annealing effects on poly(ethylene oxide) (PEO) crystals. Time dependence of the hat capacity was measured at various annealing temperatures and the time dependence was analyzed in detail.

2. Experimental

Sample film was made from PEO powder (Aldrich Chemical Co., $M_w = 2 \times 10^5$). The PEO powder was melted in a vacuum oven and pressed at 85 °C. PEO film with the thickness of 0.16 mm was obtained. A disk shaped sample was cut from the film and put in an aluminum crucible. The sample mass was 3mg and the melting temperature (T_m) was 62 °C. Before measurement the sample was melted at 95 °C in the DSC furnace. The molten sample was taken out of the furnace then quenched on an aluminum plate cooled in iced water. The crucible was lightly pressed against the aluminum plate for good thermal contact.

All measurements were made with the temperature modulated differential scanning calorimeter (TM-DSC) (TA Instruments, MDSC2920). The quenched sample was heated from the room temperature to the annealing temperature (T_a) at 5 K/min without temperature modulation. Time dependence of the heat capacity during the annealing was measured in the quasi-isothermal mode. Period and amplitude of the temperature modulation were 30 s and 0.5 K, respectively. After the annealing, the sample was cooled to 0 °C and then conventional DSC measurement was made on the heating process to 95 °C. The molten sample was quenched with the method explained above. These measurements were repeated with a different T_a in each repeating cycle. T_a's investigated were 48.6, 50.6, 52.6, 54.5, 56.6, 58.5 and 60.5 °C and the annealing time was 6 hours. For comparison standard TM-DSC measurement of a quenched sample at the underlying heating rate of 2 K/min was done from -15 to 75 °C without annealing. The underlying heating rate, the modulation period and the modulation amplitude were 2 K/min, 30 s and 0.5 K, respectively.

3. Results and Discussion

Conventional DSC traces on the heating process after the annealing are shown in Fig.1. It is clearly seen that the endothermic peak accompanying the melting shifted to the higher temperature side and the heat of fusion became larger as T_a became higher. These results show that the thickening of the lamella crystals and increase in the crystallinity occurred during the annealing. The onset temperature of the endothermic peak was higher than T_a. This suggested that the thin crystals with the melting temperatures (T_m) lower than T_a melted during the

annealing and thick crystals with T_m higher than T_a grew. These are typical behaviors observed in the conventional DSC studies on the annealing effects. However, as described in the first section, time dependence of the annealing process cannot be analyzed with this type of experiments.
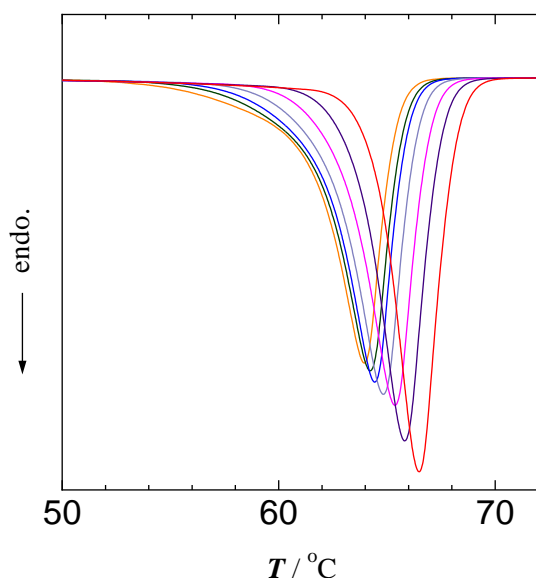

Fig.1 Conventional DSC traces on the heating process after the annealing. The annealing temperatures of the curves from right to left were 48.6, 50.6, 52.6, 54.5, 56.6, 58.5 and 60.5 °C.
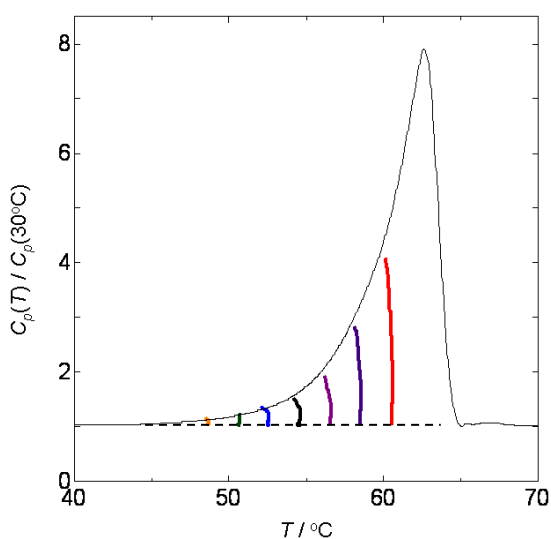

Fig.2 Heat capacity traces during the isothermal annealing and on the hating process with the underlying heating rate of 2K/min. The heat capacity was calculated from the modulation component and scaled to the value at 30 °C. The broken line is the extrapolated line from the crystalline state before starting of the melting peak.

In Fig.2 the almost vertical curves show the heat capacity during the isothermal annealing and the curve with a peak is the heat capacity calculated from the modulation component measured on the heating process with the underlying heating rate of 2 K/min. The heat capacity during the isothermal annealing started from the top of each curve and decreased with time. It

should be noted that the end points of the annealing are almost on the line extrapolated from the crystalline state. Figure 3 shows time dependence of the heat capacity during the annealing. The heat capacity decreased with time at all T_a's. It was found that the time dependence of the heat capacity $C(t)$ could be expressed sufficiently well with the next mathematical form.

$$C(t) = C_f \exp\left(-\frac{t}{\tau_f}\right) + C_s \exp\left(-\frac{t}{\tau_s}\right) + C_\infty \tag{1}$$

In eq. (1) C_f and τ_f are the relaxation strength and the relaxation time of the fast component, respectively. C_s and τ_s are those of the slow component. C_∞ is the asymptotic value of $C(t)$. Calculated curves using eq.(1) are shown in Fig.3. C_f, τ_f, C_s and τ_s are plotted against T_a in Fig. 4.
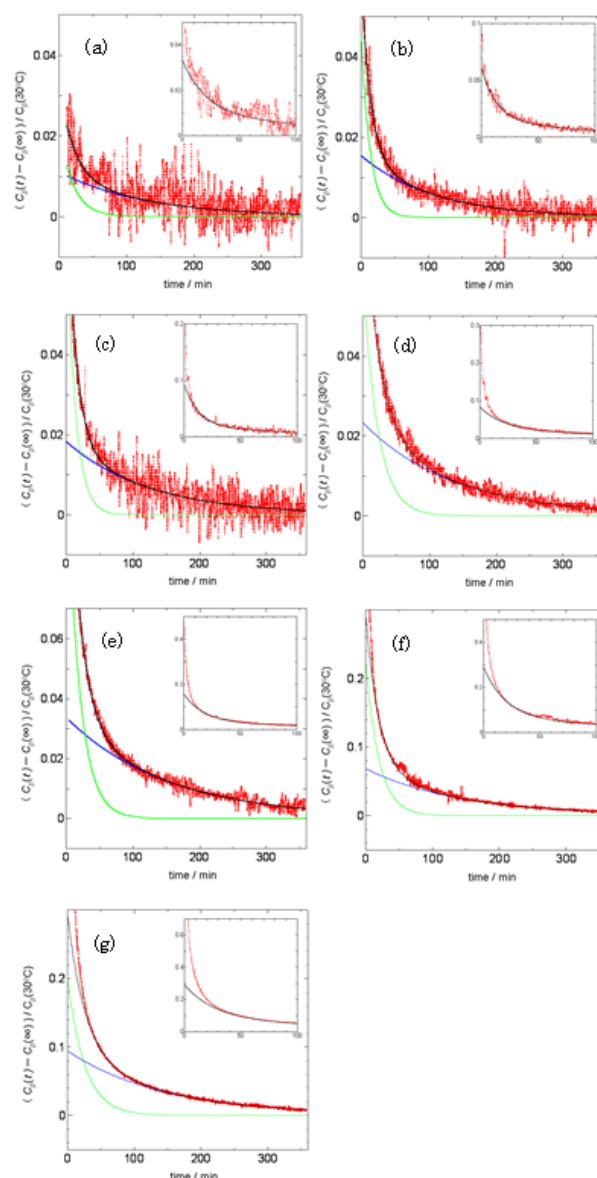

Fig.3 Time dependence of the heat capacity during the annealing at (a) 48.6, (b) 50.6, (c) 52.6, (d) 54.5, (e) 56.6, (f) 58.5 and (g) 60.5 °C. Red circles show the measured heat capacity. The fitted curve calculated with eq.(1) is shown by the black curve together with the fast (green) and slow (blue) components on the right hand side of eq. (1). Extensions of the initial 100min are shown in the insertions.
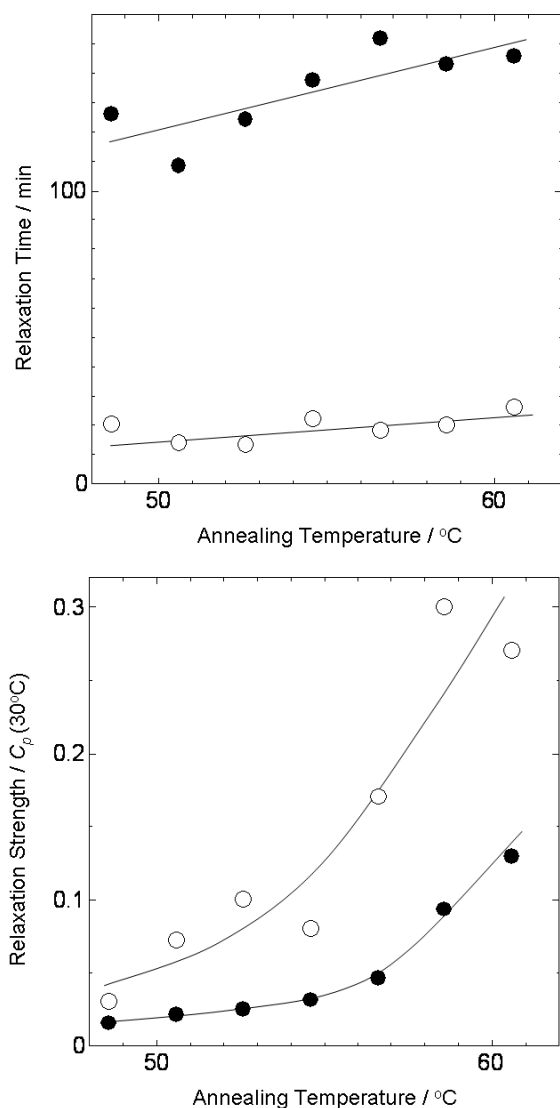
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Fig.4 The relaxation time and the relaxation strength of the fast and slow components of eq.(1) plotted against the annealing temperature. Curves are drawn for eye guide.

Three possible origins for the time dependence of the heat capacity can be considered. The first one is the latent heat of the thin crystals. Contribution from the latent heat to the heat capacity obtained from the modulation component depends on the modulation frequency [5]. The modulation frequency used in this work was not high enough to exclude the latent heat from the heat capacity. The second one is difference between the heat capacities of the crystalline state and the molten state. Since the crystalline state has excess heat capacity as explained below, the heat capacity decreases as melting progresses. The third one is structural change of thick crystals. Since the sample was quenched from the molten state, the lateral dimension of the lamella crystals was considered to be small at the beginning of the annealing. This means that the total area of the side surface of the crystals is large. At the side surface reversible crystallization/melting takes place [6]. Since the reversible crystallization/melting occurs quickly, the emission/absorption of the latent heat is observed as excess heat capacity. As the annealing time becomes longer the crystals merges together and lateral dimension of the lamella crystals becomes larger. This leads to decrease in the total area of the side surface of the crystals, that is, decrease in the heat capacity.

As the temperature increases towards T_a the thin crystals melt. The first origin makes the heat capacity larger and the second one makes it smaller. Since the effect of the first origin is much larger than that of the second one, the total heat capacity becomes larger. This explained the increase in the heat capacity seen in the standard TM-DSC trace in Fig.2. The effect of the third origin was negligible at this stage because the structural change of the crystal needs much longer time. After starting of the isothermal annealing the number of thin crystals undergoing melting decreased because the number of the crystals with T_m lower than the sample temperature did not increase anymore. This leaded to decrease in the heat capacity with time, which corresponded to the fast component of eq. (1). Heat capacity decrease due to the third origin continues for long time and is observed as the slow component of eq. (1). As can be seen in Fig.4 the relaxation time of the slow component is five to ten times as long as the fast component. Notable increase in the relaxation strength is consistent with the above model. As pointed out the heat capacity are almost on the line extrapolated from the crystalline state at the end of the annealing (Fig.2). This suggests that the crystals with T_m lower than T_a are almost completely melted and the lateral growth of the crystals finished. Ordering of the crystal structure occurs with the lateral growth and the reversible crystallization/melting decayed.

4. Conclusion

Time dependence of the heat capacity of poly(ethylene oxide) crystals during isothermal annealing has been successfully measured with TM-DSC operated in the quasi-isothermal mode. It was found that the relaxation of the heat capacity composed of two components, that is, fast and slow components. Three origins for the heat capacity relaxation were proposed and discussed in detail. The fast component was attributed to melting of thin crystals with the melting temperature lower than the annealing temperature. The slow component was attributed to decay of the reversible crystallization/melting at the side surface of the crystals.

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