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Effect of structural relaxation of glassy PET on crystallization process observed by the simultaneous DSC–XRD and DSC–FTIR

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Abstract

The effect of structural relaxation of the glassy poly(ethylene terephtalate) (PET) caused by annealing below its glass transition temperature (T_g) on the cold-crystallization observed was investigated by the simultaneous DSC–FTIR and DSC–XRD methods. The nucleation and the conformational ordering processes proceeded faster by annealing. From the relationship between the absorbance change and the exothermic heat during the cold-crystallization, the heat of cold-crystallization for the unannealed PET was caused mainly by the conformational ordering. For the annealed PET, the long range ordering contributed to the heat of crystallization in the late stage of cold-crystallization, which was also confirmed by the DSC–XRD method.

Keywords: Poly(ethylene terephtalate) (PET); Enthalpy relaxation; Nucleation; Cold-crystallization; Conformation

1. Introduction

Ordering of poly(ethylene terephtalate) (PET) from the glassy state in the heating process proceeds as: (1) the nucleation immediately after glass transition, (2) the crystal growth and the formation of metastable crystals (cold-crystallization) and (3) the ordering of metastable crystals just before the melting (re-organization). These structural changes can be observed in the temperature range of about 150° between the glass transition temperature (T_g) and the melting temperature (T_m). As the glassy state is non-equilibrium state, the relaxation of thermodynamic quantities occurs toward the equilibrium state. This relaxation phenomenon in the glassy state is known as volume and enthalpy relaxations [1–3]. The enthalpy relaxation, one of the thermodynamic quantities, occurs by annealing below T_g and it is attributed to the internal main chain rotation resulting in the structural relaxation of polymeric glass [4,5]. It is well known as "physical aging" that the physical properties of polymeric glass are influenced by the enthalpy relaxation [6]. The ordering processes of PET are expected to be influenced by the structural relaxation occurring by annealing at temperature below T_g.

The conformational and structural changes of polymeric materials during various thermal events are observed on real time by the simultaneous DSC–FTIR and DSC–XRD method [7–9]. Especially for the crystallization, we can evaluate the conformational change and transition heat at the same time by DSC–FTIR. In this study, we will discuss about the effect of structural relaxation on the cold-crystallization using the degree of enthalpy relaxation as the order-parameter of glassy state.

2. Experimental

PET (Mn = 25,000, Mw/Mn = 2.5) supplied from Toyobo Co. Ltd., Japan, was used for the experiments. The unannealing PET was obtained by quenching the sample from

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the molten state to ice water (quenched PET). The quenched PET was annealed for various periods at 60 °C in DSC (annealed PET).

DSC measurement was carried out to obtain the relaxation enthalpy (ΔH_r). Each annealed sample was measured from room temperature to 300 °C at a heating rate of 10 K min^{-1}. The sample was quenched from 300 °C to room temperature immediately after heating, and then was heated again to 200 °C under the same condition.

The simultaneous DSC–FTIR measurement was carried out by setting the simultaneous DSC instrument [10] on the JASCO FTIR 620 with mercury cadmium telluride (MCT) detector in the wavelength range between 4000 and 650 cm^{-1}. A PET sample about 2 mg was put between thin KBr disks and clamped in an aluminum DSC vessel. The accumulation of one spectrum and the wave number resolution were 32 times and 2 cm^{-1}, respectively. Under this condition, the time resolution was 15 s. The scanning rate of DSC was 8 K min^{-1}.

The simultaneous DSC–XRD measurement was carried out by setting the simultaneous DSC instrument on the X-ray scattering optics at BL-10C of Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Japan. The monochromatic synchrotron radiation X-ray filtered by double Si crystals was used for the DSC–XRD measurement. The wavelength of the X-ray was 0.1448 nm. The scattering vector $q = \frac{4\pi \sin\ \theta}{\lambda}$ range of XRD was between 0.08 and 0.3 nm^{-1}, where 2θ and λ are the scattering angle and the X-ray wavelength, respectively. A PET sample of about 7 mg was clamped in an aluminum DSC vessel. Time resolution of XRD was 30 s. The scanning rate of DSC was 2 K min^{-1}.

3. Results and discussion

Fig. 1 shows the DSC curves of the quenched PET and the annealed PET ($\Delta H_r = 5.7$ J g^{-1}, ΔH_{ris} shown below). As seen in Fig. 1, for the quenched PET (left) the heat flow jump at glass transition and the endothermic peak in the glass transition region ($T_g = 76.2$ °C) were observed, and for the annealed PET at 60 °C for 200 h (right) an endothermic peak appeared in the glass transition regions and the exothermic peak due to cold-crystallization ($T_{cc} \approx 118$ °C) sharpened.

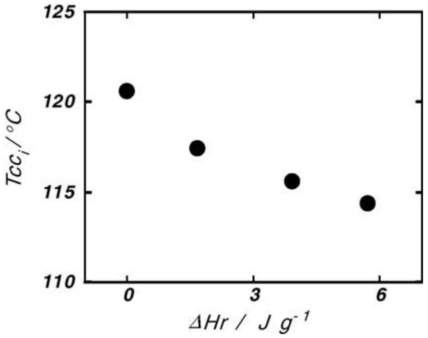

Fig. 2. Relationship between onset temperature of cold-crystallization and relaxation enthalpy.

The relaxation enthalpy (ΔH_r) was obtained from the subtraction of DSC curves using the following equation:

$$\Delta H_r = \int_{T_a}^{200\ ^\circ\mathrm{C}} C_{p_a} - \int_{T_a}^{200\ ^\circ\mathrm{C}} C_{p_q}\ \mathrm{d}T \qquad (1)$$

where, C_{p_a} and C_{p_q} are the heat capacities of annealed PET and quenched PET, respectively, provided that ΔH_r for the quenched PET is assumed to be 0.0 J g^{-1}. The relaxation time (τ) was obtained from Kohlrausch–Williams–Watts (KWW) function [11].

$$\Delta H_t = \Delta C_p(T_g - T_a) \exp\left\{-\left(\frac{t}{\tau}\right)^{\beta}\right\} \qquad (2)$$

where $\Delta H_t (= \Delta C_p(T_g - T_a) - \Delta H_r)$ is excess enthalpy, ΔC_p is the C_p jump at T_g, T_a is the annealing temperature ($T_a < T_g$) and β is a parameter corresponding to the relaxation time distribution ($\beta < 1$). ΔH_r of samples for DSC–FTIR measurement were 0.0, 1.7, 3.8 and 5.7 J g^{-1}. τ was 78.1 h at 60 °C, provided that $\beta = 0.6$ [12]. Fig. 2 shows the onset temperature of cold-crystallization as a function of ΔH_r. The onset temperature of cold-crystallization decreased with the increase

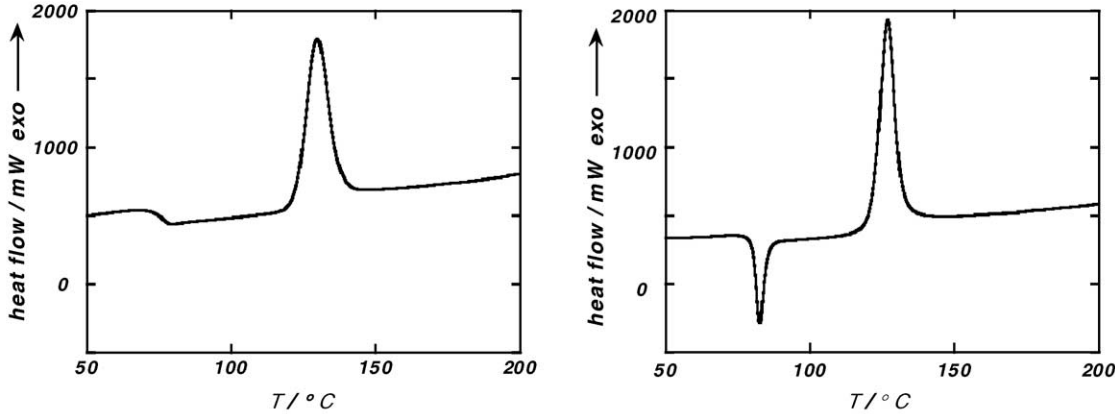

Fig. 1. DSC curves of quenched PET (left) and annealed PET (right) on heating at 10 K min^{-1}.

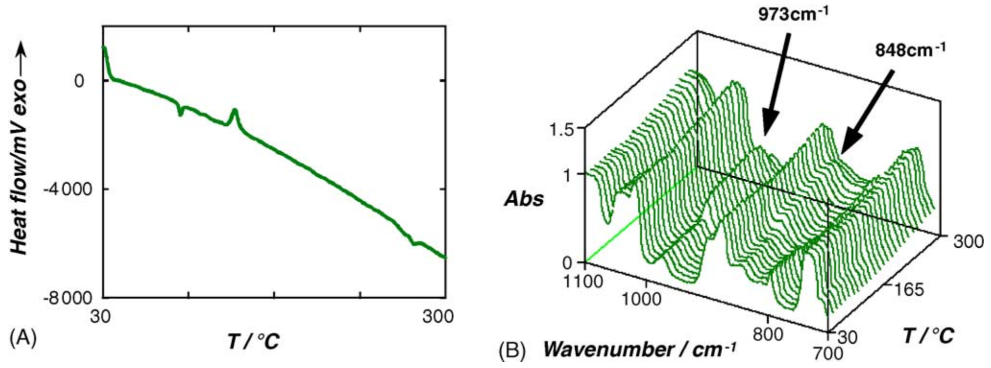

Fig. 3. Raw DSC result (A) and stacked FTIR spectra (B) for PET annealed for 220 h at 60 °C observed by the simultaneous DSC–FTIR method on heating at 8 K min^{-1}.

of ΔH_r suggesting that the nucleation was accelerated by annealing below T_g.

The simultaneous DSC–FTIR result for annealed PET (ΔH_r = 5.7 J g^{-1}) on heating at 8 K min^{-1} is shown in Fig. 3. In this temperature range from 30 to 300 °C, the glass transition, the cold-crystallization and the melting were observed at around 75, 110 and 240 °C, respectively. In the wave number range between 1100 and 700 cm^{-1}, the rocking vibration modes of methyl units (gauche, 896 cm^{-1}; trans, 848 cm^{-1}) and the stretching vibration mode of ether unit (gauche, 1042 cm^{-1}; trans, 973 cm^{-1}) are related to conformation of ethylene units [13]. Originally, these bands are considered to assign to the conformation of methyl units. However, the vibration mode direction of ether unit is parallel to the direction of in-plane vibration mode of aromatic unit. Therefore, the band at 973 cm^{-1} seems to be affected by the ordering of aromatic units. We paid attention to the bands correspond to trans conformation, which increased in absorbance at the cold-crystallization. The absorbance values of bands mentioned here were normalized by the absorbance at 795 cm^{-1} (C=O rocking vibration mode + CCO scissoring vibration mode).

Fig. 4 shows the absorbance change at 848 and 973 cm^{-1} during the cold-crystallization. Comparing the absorbance change at 848 cm^{-1} with 973 cm^{-1} in the cold-crystallization region, the increment at 973 cm^{-1} was faster than that of 848 cm^{-1}. This fact indicated that the ordering of aromatic units occurred faster than the conformational ordering of ethylene units during the nucleation and the initial stage of crystallization. Comparing the absorbance change of quenched PET and annealed PET, the absorbance of annealed PET starts to increase at a lower temperature than that of quenched PET. It indicated that the conformational ordering of annealed PET occurred faster than that of quenched PET. This corresponds to the decreasing of the onset temperature of cold-crystallization obtained by DSC shown in Fig. 2. The increasing rate (shown as slopes of lines in Fig. 2) of the absorbance at 973 cm^{-1} during the cold-crystallization is greater for the annealed PET. The same tendency was also observed at 848 cm^{-1}, but the difference between quenched and annealed PETs was small. These data indicated that the crystalline growth rate became faster for the annealed PET than the quenched PET. It is equivalent to the sharpening of DSC exothermic peak for the annealed PET (see Fig. 1).

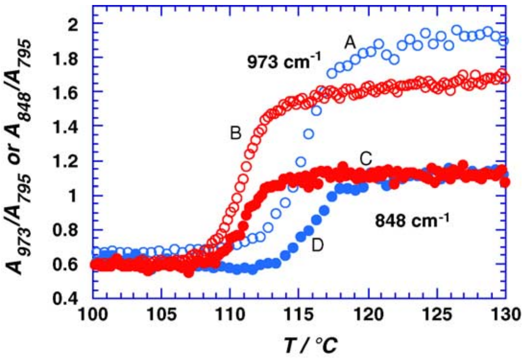

Fig. 4. Absorbance changes at 848 and 973 cm^{-1} normalized by the absorbance at 795 cm^{-1} at the cold-crystallization region observed by the simultaneous DSC–FTIR method on heating at 8 K min^{-1} for the quenched PET (ΔH_r = 0.0 J g^{-1}; A, 973 cm^{-1}; D, 848 cm^{-1}) and the annealed PET (ΔH_r = 0.0 J g^{-1}; B, 973 cm^{-1}; C, 848 cm^{-1}).

Fig. 5 shows the relationship between the increase of absorbance obtained by FTIR method, which reflects the degree of conformational ordering and the exothermic heat obtained at the same time from DSC during the cold-crystallization. The plots are on the straight line up to 90% for quenched PET suggesting that the exothermic heat observed at the cold-crystallization is almost due to the conformational ordering of PET, while it is to 60% for the annealed PET (shown as broken lines).

The exothermic heat of the crystallization (ΔH_{crys}) consists of three ordering factors: as conformational ordering (ΔH_{conf}), positional ordering of molecular chain (ΔH_{pos}) and orientation of molecular chain (ΔH_{ori}) [14] (see Eq. (3)).

$$\Delta H_{\mathrm{crys}} = \Delta H_{\mathrm{conf}} + \Delta H_{\mathrm{pos}} + \Delta H_{\mathrm{ori}} \qquad (3)$$

Last two factors of long range ordering begin to occur in the late stage of cold-crystallization, when the DSC exothermic peak approaches to the base line and continues to the reorganization just before melting [15]. It is considered that the conformational orderings occur mainly for the quenched PET

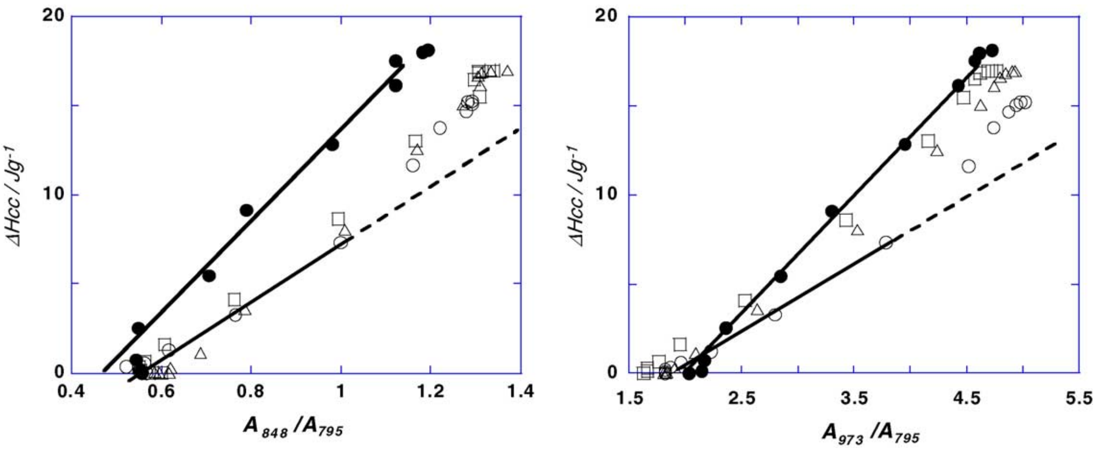

Fig. 5. Relationship between the absorbance change at 848cm^{-1} (left) and 973cm^{-1} (right) and the exothermic heat (ΔH_r; (●): 0.0 (△): 1.7 (□): 3.8 (○) 5.7 J g^{-1}).

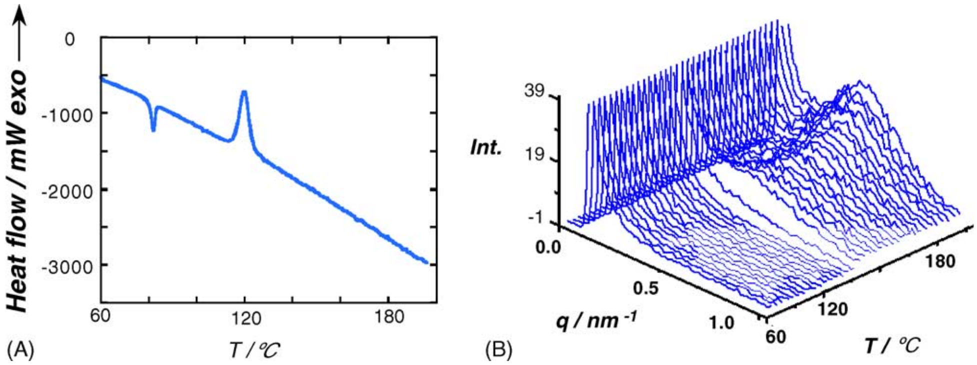

Fig. 6. The raw DSC curve (A) and stacked XRD profile (B) for PET annealed for 170 h at 60 °C observed by the simultaneous DSC–XRD method on heating at 2 K min^{-1}.

during the temperature range of the DSC exothermic peak, while other two factors occur in addition for the annealed PET.

To examine about the formation of long range ordering in further detail, we measured the cold-crystallization region by DSC–XRD. The values of ΔH_r of samples for this measurement were 0.0 and 5.8 J g^{-1}. Fig. 6 shows the results of simultaneous DSC–XRD measurement of annealed PET ($\Delta H_r = 5.8$ J g^{-1}) on heating at 2 K min^{-1}.

As shown in XRD three-dimensional profile in Fig. 6(B), a diffraction peak due to the long period appeared at around 122 °C and it is after the DSC exothermic peak appears. The q value of the diffraction peak is 0.49 nm^{-1} and the long period calculated from $2\pi/q$ is 12.8 nm for the annealed PET. It was observed that the diffraction peak for the quenched PET appeared at higher temperature. It reveals that the formation of long period ordering occurs earlier for the annealed PET than the quenched PET.

4. Conclusions

From the simultaneous DSC–FTIR and DSC–XRD observations of ordering process of PET, the nucleation and the conformational ordering were stimulated by structural relaxation of glassy state. The ordering of aromatic units was faster than that of ethylene units during the cold-crystallization. Further, the long range orderings such as ordering of position and orientation occurred earlier for the annealed PET than the quenched PET. For the quenched PET, the heat of cold-crystallization was mainly due to the conformational ordering. For the annealed PET the heat of cold-crystallization was due to the long range ordering addition with conformational ordering.

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