

polymer communications

An application of temperature modulated differential scanning calorimetry to the exothermic process of poly(ethylene terephthalate) crystallization

Akihiko Toda*, Chiyoko Tomita and Masamichi Hikosaka

Faculty of Integrated Arts and Sciences, Hiroshima University, 1-7-1 Kagamiyama, Higashi-Hiroshima 739, Japan

and Yasuo Saruyama

Faculty of Textile Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan
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We have examined the applicability of a new analysing method of temperature modulated differential scanning calorimetry to the exothermic process of poly(ethylene terephthalate) crystallization. The method utilizes the change in the phase lag between modulation components of sample temperature and of heat flow, to introduce an apparent heat capacity of complex quantity. The phase lag showed a peak and a dip during the isothermal crystallization, above and below the temperature at which the growth rate of crystals becomes a maximum, respectively. The present method incorporates the change, and predicts negative and positive temperature dependence of crystal growth rate, for the peak and dip in the phase lag, respectively. The temperature dependence of crystal growth rate agreed well with the literature values obtained from the direct measurements of growth rate of spherulites by optical microscopy. © 1997 Elsevier Science Ltd.

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Introduction

In order to apply a new technique of temperature modulated differential scanning calorimetry (t.m.d.s.c.)^{1–3} to an exothermic or endothermic process, we have recently proposed an analysing method which utilizes the phase lag between modulation components of sample temperature and of heat flow^{4,5}. The method has been successfully applied to polyethylene crystallization, and has proved its usefulness especially in the independent determination of temperature dependence of crystal growth rate^{4,5}. In the present communication, the method is applied to the isothermal crystallization of poly(ethylene terephthalate) (PET) above and below the temperature, $T(G_{\max}) \sim 170^\circ\text{C}$, at which the maximum growth rate is attained⁶. It is a well known fact that the crystal growth rate, G , shows a reversal of the dependence on temperature, T , when crystallized above and below $T(G_{\max})$: $d(\ln G)/dT < 0$ and > 0 , respectively. Our analysing model suggests that this change brings the reversed change in the phase lag. In the following, we examine the behaviour and provide further evidence of the applicability of our analysing method to exothermic and endothermic processes.

The model

Our model^{4,5} assumes a linear response of the exothermic or endothermic heat flow, $F(t, T_s)$, against the modulation of sample temperature, T_s . Following the standard analysis of Wunderlich and coworkers^{7,8} under this assumption, we are able to introduce an apparent heat capacity of complex quantity, $\widetilde{\Delta C} e^{-i\alpha}$, expressed as

follows,

$$\widetilde{\Delta C} e^{-i\alpha} \equiv \Delta C + i \frac{1}{\omega} \left(\frac{\partial F}{\partial T} \right)_{t_0, \bar{T}_s} \quad (1)$$

where ω represents the angular frequency of modulation and $\Delta C \equiv C_s - C_r \cong mc_p$ represents the true heat capacity difference between the sample and reference heat capacities, C_s and C_r , which is approximately equal to the heat capacity of sample, mc_p , namely the specific heat of sample, c_p , multiplied by the sample weight, m . The absolute value, $\widetilde{\Delta C}$, of the apparent heat capacity can be determined by the standard method of t.m.d.s.c. and the phase α is defined as the change in the phase lag from its baseline during the exothermic and endothermic process.

In the expression of the apparent heat capacity, $\widetilde{\Delta C} e^{-i\alpha}$, of equation (1), both the true heat capacity, ΔC , and the temperature dependence of the exothermic or endothermic heat flow, $(\partial F/\partial T)$, are the frequency response functions against temperature modulation, and hence they are, in general, of complex quantities. For polymer crystallization⁵, however, we can reasonably neglect the imaginary parts of the frequency response functions of ΔC and $(\partial F/\partial T)$. In this case, the real part of the apparent heat capacity, $\widetilde{\Delta C} e^{-i\alpha}$, in equation (1), gives us the true heat capacity, ΔC , and the imaginary part determines the temperature dependence of the exothermic heat flow, $(\partial F/\partial T)$,

$$\Delta C = \widetilde{\Delta C} \cos \alpha \quad (2)$$

$$\left(\frac{\partial F}{\partial T} \right) = -\omega \widetilde{\Delta C} \sin \alpha \quad (3)$$

As a typical example of an exothermic process,

* To whom correspondence should be addressed

polymer crystallization has been examined in our previous papers^{4,5}. Polymer crystallization, in general, can be considered as the growth of spherulite or axialite formed by lamellar crystals. The exothermic heat flow can be expressed as the change in enthalpy per unit volume, Δh , multiplied by the total area of growth face, S_{total} , and the crystal growth rate, G .

$$F = \Delta h S_{\text{total}} G \quad (4)$$

For a small enough amplitude of temperature modulation, the response of the process under high supercooling can be considered as a periodic change in the crystal growth rate, G , while the total area of growth face, S_{total} , is irrelevant to the temperature modulation. Hence, the temperature dependence of the exothermic heat flow is determined by the dependence of crystal growth rate, G .

$$\left(\frac{\partial F}{\partial T}\right) = \Delta h S_{\text{total}} \frac{dG}{dT} \quad (5)$$

Then, the ratio of F and $(\partial F/\partial T)$ gives us the temperature dependence of $\log G$.

$$\begin{aligned} \frac{d(\ln G)}{dT} &= \frac{1}{F} \left(\frac{\partial F}{\partial T}\right) \\ &= \frac{-\omega \widetilde{\Delta C} \sin \alpha}{F} \end{aligned}$$

where the exothermic heat flow, F , can be experimentally obtained from the total heat flow of t.m.d.s.c., and $(\partial F/\partial T)$ is from the imaginary part of the apparent heat capacity (equation (3)). We have the great advantage that this method cancels out the total area of growth face, S_{total} , carrying the detailed information of the kinetics, and hence the method does not require any specific model of crystallization kinetics to determine the temperature dependence of crystal growth rate.

In the previous paper⁵, we have examined the frequency dependence of $\widetilde{\Delta C} e^{-i\omega t}$ for polyethylene crystallization from the melt and confirmed the dependence shown in equation (1) with ΔC and $(\partial F/\partial T)$ being real and constant. The values of $d(\ln G)/dT$ obtained by equation (6) agreed well with the results of direct measurements of crystal growth by microscopy. All those results supported the applicability of the analysing method.

Experimental

The DSC 2920 Module controlled with Thermal Analyst 2200 (TA Instruments) was used for all measurements. The raw data were transferred by a TA RMX Utility to calculate the phase lag from the raw data of modulated sample temperature and of modulated heat flow. The sample was an amorphous poly(ethylene terephthalate) film supplied by Toyobo. The sample weight was in the range of 8.5–13.8 mg. It was confirmed that there was no qualitative change by the sample weight in this range. Crystallization was quasi-isothermal, namely modulation was around a fixed temperature. When crystallized at 114–129°C below the temperature of $T(G_{\text{max}}) \sim 170^\circ\text{C}$ giving the maximum of growth rate, the sample temperature of amorphous PET film was raised from the room temperature. Above this temperature, the samples were crystallized at 210–224°C from the melt by lowering the temperature. The

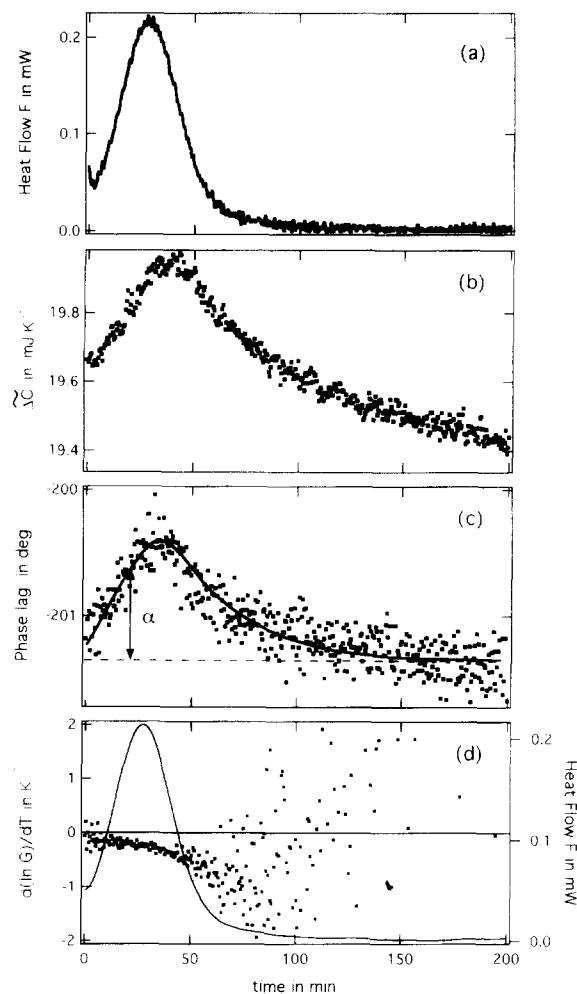


Figure 1 Time sequence of quasi-isothermal crystallization of PET from the melt at 222.0°C: (a) the exothermic heat flow F ; (b) ΔC ; (c) the phase lag between modulation components of sample temperature and of heat flow; (d) $d \ln G/dT$ determined by equation (6) and plotted along with F . The sample weight was 10.2 mg and the modulation period was 28 s. The definition of α is also shown in (c)

modulation period of 28 s was examined with the modulation amplitude of ± 0.2 K. The period of modulation is relatively short, to ensure that the kinetics do not change significantly during this time. The modulation amplitude was sufficiently small, as the following results show. There would be an optimal condition of period and amplitude, which needs to be considered for the refinement of the present method.

Results and discussion

Figures 1 and 2 show the typical results of t.m.d.s.c. (the total heat flow equivalent to the heat flow of conventional d.s.c., the magnitude of apparent heat capacity, and the change in the phase lag) and its analytical result (the temperature dependence of crystal growth rate determined by equation (6)) for the quasi-isothermal crystallization of PET above $T(G_{\text{max}})$ from the melt (Figure 1) and below $T(G_{\text{max}})$ from the glassy state (Figure 2). Following the crystallization, the rate of which shows a peak in the exothermic heat flow F (Figures 1a and 2a), we can confirm a peak and a negative peak (a dip) in the phase lag for the crystallization from the melt (Figure 1c) and from the glassy state (Figure 2c), respectively, though the magnitude of the peaks are quite small (~ 1) compared to the peak in polyethylene

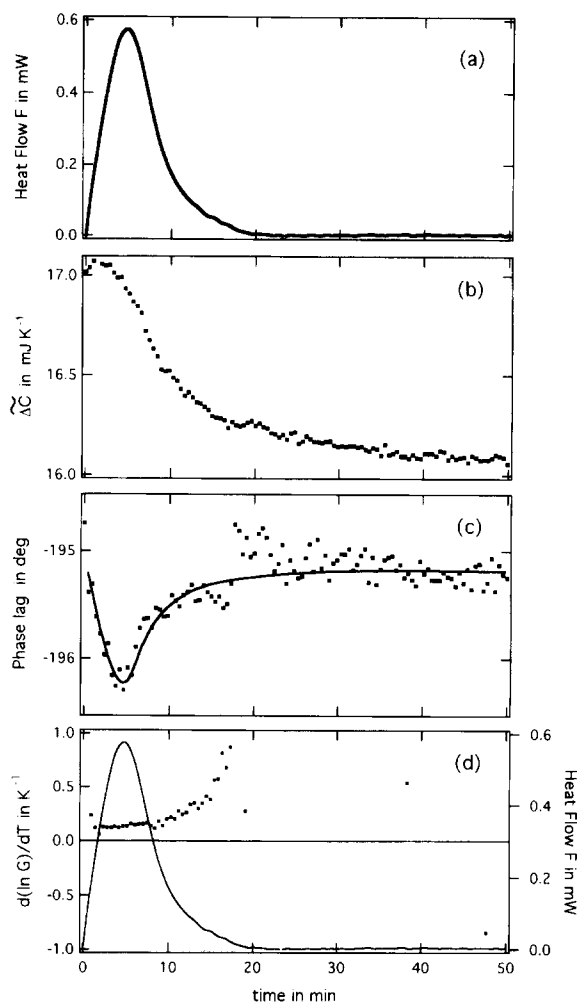


Figure 2 Time sequence of quasi-isothermal crystallization of PET from the glass at 118.0°C: (a) the exothermic heat flow F ; (b) $\Delta\bar{C}$; (c) the phase lag between modulation components of sample temperature and of heat flow; (d) $d(\ln G)/dT$ determined by equation (6) and plotted along with F . The sample weight was 10.2 mg and the modulation period was 28 s

crystallization ($>10^5$)^{4,5}. Equation (6) links the sign of the change in the phase lag to the sign of the temperature dependence of crystal growth rate $d(\ln G)/dT$. The positive peak in the phase lag (Figure 1c) indicates the negative dependence of crystal growth rate (Figure 1d) and vice versa (Figures 2c and 2d); it is the correct dependence of the crystal growth rate on temperature⁶.

The time sequence of $d(\ln G)/dT$ keeps a constant value in the early stage of growth, as in the case of polyethylene crystallization^{4,5}. We have examined the behaviour of $d(\ln G)/dT$ at several crystallization temperatures. If we plot the constant values of $d(\ln G)/dT$ against the crystallization temperatures, the plots are in good agreement with the literature values determined from the direct measurements of growth rate of spherulites by optical microscopy^{6,9,10}, as shown in Figure 3.

Concerning the heat capacity of the sample, since the change in the phase lag, α , is quite small ($\sim 1^\circ$), we can neglect the correction of equation (2) and the magnitude of the apparent heat capacity, $\Delta\bar{C}$, approximates to the true heat capacity, ΔC . When crystallized from the melt, the heat capacity showed a time sequence similar to that of polyethylene^{4,5}; the increase in $\Delta\bar{C}$, up to a maximum followed by a gradual decrease (Figure 1b). On

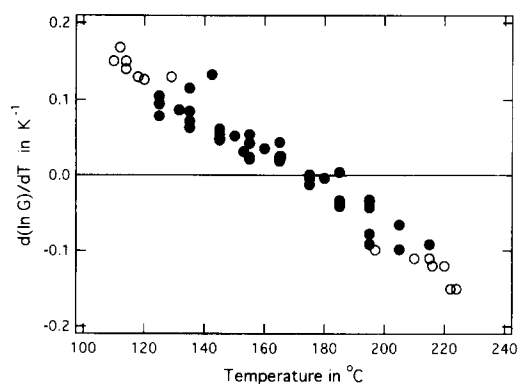


Figure 3 Plots of the temperature dependence $d(\ln G)/dT$. The t.m.d.s.c. results (O) were determined by equation (6). The data (●) are the results of direct measurements by microscopy^{6,9,10}

the other hand, crystallization from the glassy state showed a monotonous decrease with the progress of crystallization (Figure 2b). The heat capacity of the sample will be determined by the specific heat of crystals, c_s , and of the melt, c_l , and by the degree of crystallinity, $x(t)$,

$$\Delta C \cong m[c_s x(t) + c_l(1 - x(t))] \quad (7)$$

Under ordinary conditions, we have the relation of $c_s < c_l$ and hence the monotonous decrease in the heat capacity is expected, following the progress of crystallization. Therefore the increase in heat capacity in the early stage of crystallization near the melting point suggests a disordered structure of crystals, having excess degrees of mobility accompanying, e.g., thickening of lamellar crystals near the melting point.

Conclusion

We have examined the exothermic process of PET crystallization by t.m.d.s.c. The analysing method presented here has been successfully applied to the process. The following have been confirmed for PET crystallization.

1. The temperature dependence of crystal growth rate can be evaluated by the present method from the t.m.d.s.c. data of the total heat flow, the magnitude of apparent heat capacity and the change in the phase lag without any detailed assumption on the crystallization kinetics. We have confirmed the reversal of the temperature dependence, when crystallized above and below the temperature $T(G_{\max})$ at which the growth rate maximum is attained. The resultant temperature dependence agreed well with those of direct measurements by optical microscopy.
2. The apparent heat capacity determined by the standard method of t.m.d.s.c. approximates to the true heat capacity during crystallization, because the change in the phase lag was small enough during the crystallization of PET. The heat capacity showed an upward change in the early stage of crystallization above $T(G_{\max})$ and a monotonous decrease below $T(G_{\max})$. The upward change should be ascribed to the excess degree of mobility expected in the crystals near the melting point.

The application of the present method to the melting of PET crystals is now in progress. The result seems quite different from those of crystallization process presented here; the change in the phase lag becomes quite large

(>several tens of degrees) and the imaginary parts of the frequency response functions cannot be neglected anymore, as in the case of the melting of polyethylene crystals¹¹.

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