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Temperature modulated d.s.c. study of poly(ethylene terephthalate) crystallization:
2. Applicability to non-isothermal process

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The non-isothermal crystallization of poly(ethylene terephthalate) has been examined by temperature modulated differential scanning calorimetry (TMd.s.c.). A new analytical model of TMd.s.c. has been applied to the process, taking account of the response of exothermic heat flow to temperature modulation in an apparent heat capacity of complex quantity. By examining the frequency dependence of the apparent heat capacity, the applicability has been successfully examined for the non-isothermal process. The method is capable of determining the temperature dependence of crystal growth rate from TMd.s.c. data analysis. The results agree well with the dependence determined from literature values of spherulite growth rate measured by optical microscopy. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Temperature modulated differential scanning calorimetry (TMd.s.c.) is a new technique in which a sinusoidal temperature modulation is applied to analyze the response in heat flow[1–3]. We have recently proposed a new analytical model of TMd.s.c. applicable to the polymer crystallization process[4–6]. The response of crystallization to temperature modulation has been taken into account in order to explain the change in an apparent heat capacity of a complex quantity, $\Delta\tilde{C}\,e^{-i\alpha}$

$$\Delta\tilde{C}\,e^{-i\alpha} = \Delta\tilde{C}'(\omega) - i\Delta\tilde{C}''(\omega) \tag{1}$$

The absolute value of $\Delta\tilde{C}$ represents the magnitude of the apparent heat capacity, and the phase α is defined by the change in the phase lag, $(\epsilon - \delta)$, from its baseline, $(\epsilon - \delta)_0$, during the exothermic process. Here ϵ and δ represent the phases of the modulation components of the sample temperature ($T_s = \bar{T}_s + \tilde{T}_s\,e^{i(\omega t+\epsilon)}$) and heat flow ($Q = \bar{Q} + \tilde{Q}\,e^{i(\omega t+\delta)}$), respectively. Our new method analyzes the change in the imaginary part of the apparent heat capacity during crystallization. The method has been successfully applied to the quasi-isothermal ($\bar{T}_s$ constant) crystallization of polyethylene and has proved its usefulness especially in the determination of the temperature dependence of the crystal growth rate[4,5]. In the first part of this series[6], we have further confirmed the applicability to the quasi-isothermal crystallization of poly(ethylene terephthalate) (PET). In the case of PET crystallization[6], the imaginary part changes its sign, which is related to the temperature dependence of the growth rate as will be shown here. In the present paper, we discuss the applicability to the non-isothermal ($\bar{T}_s = T_0 + bt$) crystallization of PET under heating and cooling runs. We first introduce our model briefly, and then discuss the non-isothermal crystallization of PET.

MODEL[5]

For the irreversible transformation of exo- or endothermic processes, we have proposed that the heat flow will be given as

$$\tilde{Q}\,e^{i(\omega t+\delta)} = -mc_p(\omega)\,\frac{d}{dt}\tilde{T}_s\,e^{i(\omega t+\epsilon)} + F_T'(\omega)\tilde{T}_s\,e^{i(\omega t+\epsilon)} \tag{2}$$

where mc_p is the true heat capacity of the sample, namely the specific heat of the sample, c_p, multiplied by the sample weight, m. In the second term, F_T' represents the coefficient of linear response of the exo- or endothermic heat flow to the sinusoidal modulation of T_s, while the true heat capacity is the coefficient of (dT_s/dt) in the heat flow expression. The expansion of the exo- or endothermic heat flow about the sample temperature implicitly assumes that the process is irreversible, *e.g.* irreversible crystallization under supercooling conditions. Since the apparent heat capacity was defined as

$$\tilde{Q}\,e^{i(\omega t+\delta)} = -\Delta\tilde{C}\,e^{-i\alpha}\,\frac{d}{dt}\tilde{T}_s\,e^{i(\omega t+\epsilon)} \tag{3}$$

the following equation was obtained

$$\Delta\tilde{C}\,e^{-i\alpha} = mc_p(\omega) + i\frac{1}{\omega}F_T'(\omega) \tag{4}$$

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Because of the orthogonal relationship between the modulation components of ($\mathrm{d}T_s/\mathrm{d}t$) and T_s, $F_T{}'$ is multiplied by (i)/(ω). With the expression of the apparent heat capacity given by equation (4), the next step is to derive the term $F_T{}'$ from a proper physical model of the transformations.

Polymer crystallization, in general, is a process of nucleation and growth of spherulites formed by lamellar crystals. The development with time of the crystallinity can be described by the Avrami equation, although the analysis under non-isothermal condition will be highly complicated. Instead of taking this approach, we analyze the transformation rate, R, which can be expressed by the crystal growth rate, G, multiplied by the total area of the growth face, S_{total}, as $R = GS_{\mathrm{total}}$. The total transformation rate, R, and the difference in enthalpy per unit volume, $\Delta h(>0)$, gives us an expression for the exothermic heat flow, F

$$F = \Delta h\, R = \Delta h\, S_{\mathrm{total}} G \tag{5}$$

In most cases, polymer crystallization requires high supercooling (above about 10°C). Therefore, for a small temperature modulation (around ± 0.2°C), we will be able to treat the response as a periodic change in the growth rate, $G(T_s)$, expressed as

$$G(T_s) = G(\bar{T}_s) + \frac{\mathrm{d}G(\bar{T}_s)}{\mathrm{d}T}\,\tilde{T}_s\, e^{i(\omega t+\epsilon)} \tag{6}$$

On the other hand, the total area of the growth face, S_{total}, is supposed to be almost irrelevant for the temperature modulation if the amplitude is small and the supercooling is high enough. The coefficient of the linear response of the exothermic heat flow to sinusoidal modulation of the sample temperature, $F_T{}'$, is then represented by the underlying exothermic heat flow, $\bar{F}(T_s)$, which carries information about the time-dependent kinetics of the transformation, and by the temperature dependence of the crystal growth rate, (d)/(dT) ln G, which characterizes the transformation, as follows

$$\bar{F}(t) = \Delta h\, S_{\mathrm{total}}(t) G(\bar{T}_s) \tag{7}$$

$$F_T{}'(t) = \Delta h\, S_{\mathrm{total}}(t)\,\frac{\mathrm{d}}{\mathrm{d}T} G(\bar{T}_s) = \bar{F}(\bar{T}_s)\,\frac{\mathrm{d}}{\mathrm{d}T}\ln G(\bar{T}_s) \tag{8}$$

The apparent heat capacity of equation (4) is therefore given as

$$\Delta\tilde{C}\, e^{-i\alpha} = mc_{\mathrm{p}} + i\frac{1}{\omega}\bar{F}(\bar{T}_s)\,\frac{\mathrm{d}}{\mathrm{d}T}\ln G(\bar{T}_s) \tag{9}$$

It is noted that crystallization is a time-dependent process exhibiting complicated non-linear behaviour. As shown in equation (8), the coefficient, $F_T{}'$, is dependent on the underlying exothermic heat flow, $\bar{F}(\bar{T}_s)$, which is a function of the degree of conversion and behaves non-linearly. Even though the whole process demonstrates complicated non-linearity, we are still able to apply this technique for slow transitions which do not undergo a substantial change in $F_T{}'(t)$ (and hence in $\bar{F}(\bar{T}_s)$) during the period of modulation. Under the specified conditions, we are able to observe time-dependent behaviour of $F_T{}'(t)$ by this technique.

Experimentally, we have examined the crystallization process of polyethylene under quasi-isothermal conditions[5], and have determined the frequency dependence of the apparent heat capacity at a certain stage of crystallization. The dependence can be expressed as

$$\Delta\tilde{C}\, e^{-i\alpha} = A + i\frac{B}{\omega} \tag{10}$$

where A and B are constants; namely, the terms mc_{p} and $F_T{}'$ in equation (4) can be taken to be real quantities. The physical significance of the imaginary part, (i)/(ω)$F_T{}'$, has been recognized by our model, for the first time.

If $F_T{}'$ in the imaginary part is given by equation (8), we are able to determine a very important parameter for the crystallization process, namely the temperature dependence of the crystal growth rate, (d)/(dT) ln G, by taking the ratio between the imaginary part and the underlying exothermic heat flow, $\bar{F}$

$$\frac{\mathrm{d}}{\mathrm{d}T}\ln G(\bar{T}_s) = -\frac{\omega\Delta\tilde{C}''}{\bar{F}} \tag{11}$$

The applicability of equation (11) has been successfully examined in the case of the quasi-isothermal crystallization of polyethylene and PET[4–6].

The present paper describes the crystallization of PET observed using TMd.s.c. under non-isothermal conditions. First, we examined the frequency dependence of the apparent heat capacity during PET crystallization by heating runs from the glass (cold crystallization) and cooling runs from the melt. Subsequently, we also examined the applicability of equation (11) by evaluating (d)/(dT) ln $G(\bar{T}_s)$ from the TMd.s.c. data, then to be compared with the available data for the temperature dependence of the spherulite growth rate.

EXPERIMENTAL

A DSC 2920 module controlled by a Thermal Analyst 2200 (TA Instruments) was used for all measurements. The raw data were transferred by a TA RMX Utility in order to calculate the phase lag from the raw modulated sample temperature and modulated heat flow data. The sample was an amorphous poly(ethylene terephthalate) film supplied by TOYOBO Co., Ltd. The sample weight was in the range 2–14 mg. It was confirmed that there was no qualitative change in the sample weight in this range. Non-isothermal crystallization was examined during heating runs from the glass (cold crystallization) and cooling runs from the melt at 290°C. The cooling and heating rates were in the range 0.5–3.0 K min^{-1}. The modulation period of 24–52 s was examined with the modulation amplitude fixed at ± 0.2 K.

We have examined the frequency dependence of the calibration constant on the true heat capacity[5], and a correction was made for the magnitude of the apparent heat capacity in the present analysis. We did not subtract the contribution of the true heat capacity (the so-called 'reversing' component) from the total heat flow in order to evaluate the exothermic heat flow, because the correction was not significant for the crystallization. The data points in all the figures are plotted at intervals of the modulation period.

RESULTS AND DISCUSSION

Frequency dependence of the apparent heat capacity

Figures 1 and 2 show the frequency dependence during crystallization under heating and cooling runs at rates of 1.0 K min^{-1} and 2.0 K min^{-1}, respectively. From the change in the exothermic heat flow in *Figure 1a* and *Figure 2a*, we can confirm that the crystallization processes are not affected by a change of modulation period. *Figure 1b* and *Figure 1c*, and *Figure 2b* and *Figure 2c* show the real and imaginary parts of $\Delta\tilde{C}\, e^{-i\alpha}$. It is clearly seen that the ω dependence of the imaginary parts is significant.

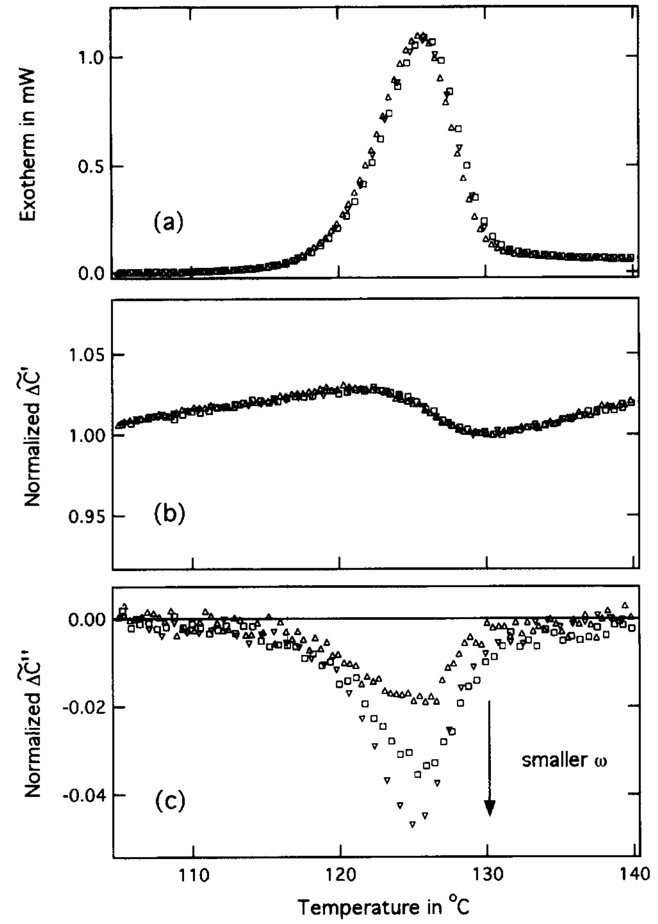

Figure 1 Frequency dependence of the TMd.s.c. of cold crystallization by heating runs of 14.24 mg of amorphous PET at a rate of 1.0 K min^{-1}: (a) exothermic heat flow; (b) the real part of the apparent heat capacity $\Delta\tilde{C}'$; and (c) the imaginary part of the apparent heat capacity $\Delta\tilde{C}''$. The magnitude of the apparent heat capacity was normalized by the magnitude at 130°C. The symbols represent the following modulation periods: (△) 24 s; (□) 36 s; and (▽) 52 s.

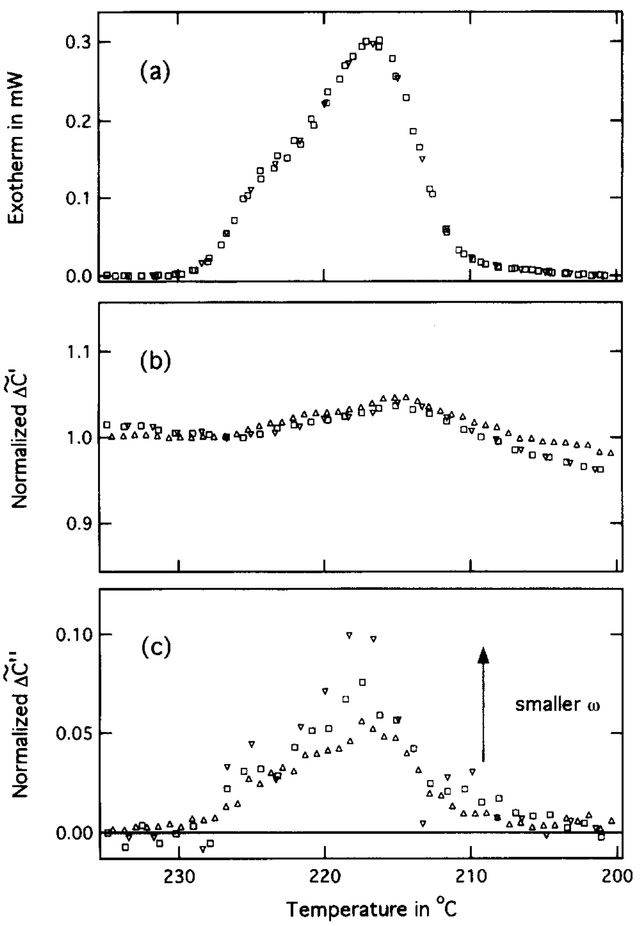

Figure 2 Frequency dependence of the TMd.s.c. of crystallization by cooling runs of 1.97 mg of amorphous PET at 2.0 K min^{-1}: (a) exothermic heat flow; (b) the real part of the apparent heat capacity $\Delta\tilde{C}'$; and (c) the imaginary part of the apparent heat capacity $\Delta\tilde{C}''$. The magnitude of the apparent heat capacity was normalized by the magnitude at 230°C. The symbols represent the following modulation periods: (△) 24 s; (□) 36 s; and (▽) 52 s.

In order to examine the frequency dependence of the apparent heat capacity, we plotted the real and imaginary parts at the peak temperature of the phase lag *versus* modulation period, which is proportional to $(1)/(\omega)$ (*Figure 3*). *Figure 3a* shows that the real part stays almost constant, while the imaginary part in *Figure 3b* is proportional to $(1)/(\omega)$. Such behaviour can also be seen in the Cole–Cole plot of the real and imaginary parts in *Figure 4*. Therefore, we confirm the frequency dependence of equation (10) for the non-isothermal crystallization of PET with modulation periods of 24–52 s. It is noted that, for the slower cooling rates in *Figure 3b*, the small deviation from the linear fit will be due to a small change in the baseline of the phase lag, $(\epsilon - \delta)_0$, which has already been recognized in polyethylene crystallization[5]. The slope of the $(1)/(\omega)$ dependence in *Figure 3b* is determined by $\bar{F}(t)$ and $(\mathrm{d})/(\mathrm{d}T) \ln G(\bar{T})$, as shown in equation (9), and is therefore dependent on the cooling and heating rates because of the change in the peak height of $\bar{F}(t)$, which becomes larger for higher heating and cooling rates.

Temperature dependence of crystal growth rate

Since we have confirmed the expected frequency dependence of the apparent heat capacity, we are able to apply equation (11) to determine the temperature dependence of the crystal growth rate. The time (temperature) sequences of $(\mathrm{d}(\ln G)/\mathrm{d}T)$ are shown in *Figure 5a* and *Figure 5b* along with the exothermic heat flow. A gradual change can be seen in $(\mathrm{d}(\ln G)/\mathrm{d}T)$, which is, of course, temperature dependent. We have examined the behaviour for different cooling and heating rates. *Figure 6* shows plots of the values obtained at the peak temperatures of the total heat flow. In *Figure 6*, the results for the quasi-isothermal crystallization are also plotted with the literature values determined from direct measurements of the growth rate of spherulites carried out by optical microscopy[7–9]. All data points seem to be on a single line, and this fact guarantees the applicability of the analysis method.

For cold crystallization, it should be noted that the negative $\Delta\tilde{C}''$, and equivalently, a dip in the phase lag, has been reported before[10] and remains to be explained because the second law of thermodynamics requires a positive $\Delta\tilde{C}''$ of the true heat capacity in equilibrium. The negative $\Delta\tilde{C}''$ needs to be explained as a kinetic effect under non-equilibrium conditions such as crystallization. Actually, the present model suggests that the sign of $\Delta\tilde{C}''$ is determined by that of the temperature dependence of the crystal growth rate, as shown in equation (11). It is a well-known fact that the crystal growth rate, G, of polymers has a bell-shaped temperature dependence, and hence $\mathrm{d}(\ln G)/\mathrm{d}T$ is below zero when they are crystallized near the melting point, and

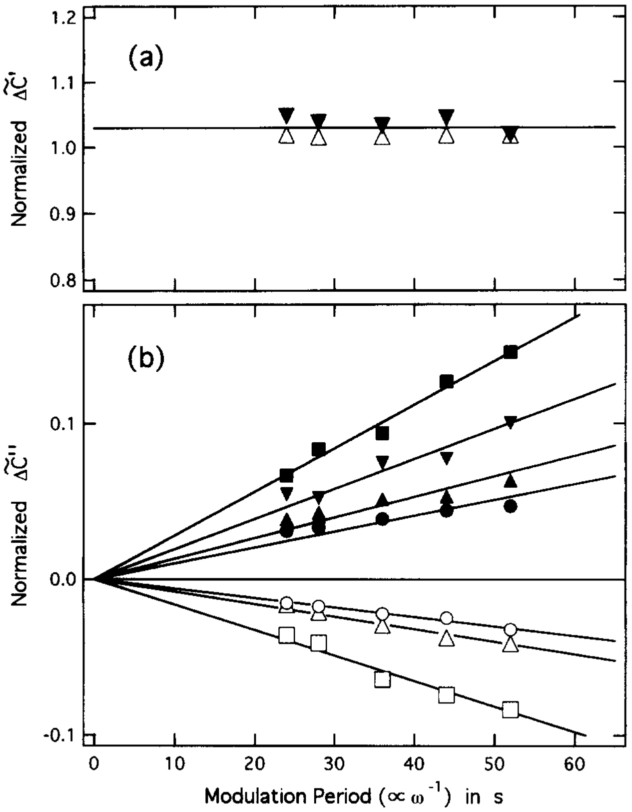

Figure 3 Plots of (a) the real and (b) the imaginary parts of the (normalized) apparent heat capacity during the crystallization of PET *versus* modulation period. The symbols represent the following rates (K min^{-1}): (◦) + 0.5; (△) + 1.0; (□), + 3.0; (•) − 0.5; (▲) − 1.0; (▼) −2.0; and (■) − 3.0. The data are taken at the peak temperatures of the phase lag, which were (°C) (▼) 119.6; (△) 125.5; (□) 134.5; (•) 226.3; (▲) 221.6; (▼) 216.8; and (■) 213.5 . The heating and cooling runs are for 14.24 mg and 1.97 mg of PET, respectively.

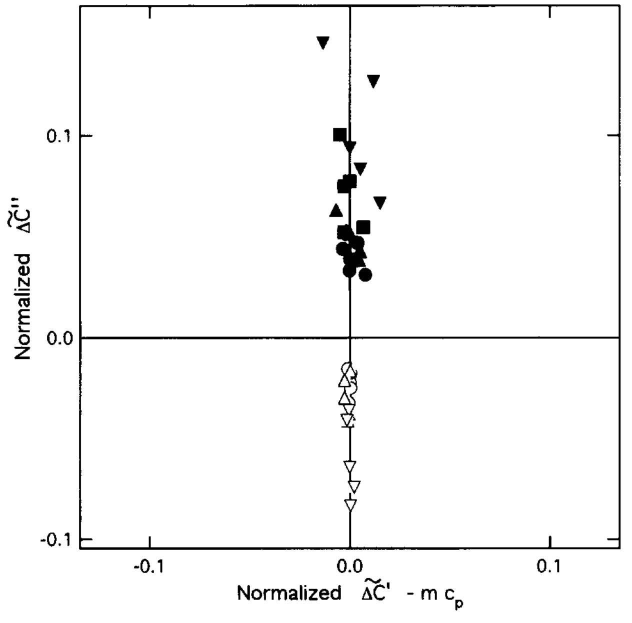

Figure 4 Cole–Cole plot of the data shown in *Figure 3*. The real part was sifted to cancel out the change in the true heat capacity due to the shift of the peak temperatures for different heating and cooling rates.

above zero when crystallized near the glass transition temperature[7] (*Figure 6*). A negative $\tilde{\Delta C}''$ is the direct consequence of a positive temperature dependence of the growth rate for cold crystallization; by increasing the temperature during the cold crystallization, the crystal growth rate becomes faster and the exothermic heat flow increases, which is contrary to LeChatelier's principle expected near equilibrium.

Change in the real part of the apparent heat capacity

Since the change in the phase lag, α, is quite small during crystallization (less than a few degrees), the magnitude of the apparent heat capacity, $\Delta\tilde{C}$, approximates to the real part. For the cold crystallization by heating runs from the glass, the real part showed a monotonic decrease during crystallization (*Figure 1b*), which will be the expected change in the specific heat, c_p, in equation (9). On the other hand, when crystallized from the melt by cooling runs, the real part increased up to a maximum value, followed by a gradual decrease (*Figure 2b*). Such unusual behaviour has also been recognized in the quasi-isothermal crystallization of polyethylene[4,5] and PET[6]. We have postulated that the increase could be that of the specific heat, which may be due to disordered crystals having excess degrees of mobility accompanying such effects as the thickening of lamellar crystals near the melting point. On the other hand, Okazaki and Wunderlich[11] suggested another possibility: reversible melting and crystallization following the temperature modulation. Since the reversible process is not distinguishable from the contribution of the true heat capacity[12], we may not be able to draw a conclusion from the TMd.s.c. data alone. Here, it should be mentioned that, in the case of polyethylene crystallization, the change in the real part follows the change in crystallinity; these changes have the same Avrami constant[5]. Hence, even though the unusual behaviour may be due to reversible processes, the total rate of the processes must be proportional to the crystallinity. Such processes cannot occur at the growth face because the total surface area of the growth face, S_{total}, will be proportional to the surface area of the spherulites and hence does not follow the change in crystallinity, which should be proportional to the total volume of the spherulites. The total volume will be proportional to the total area of the fold surfaces if the lamellar thickness does not change, and hence we may be able to expect reversible surface melting and crystallization at the fold surfaces of lamellar crystals.

Non-linearity

So far, we have assumed a linear response of the exothermic heat flow to temperature modulation during crystallization. In order to justify this assumption, we need to examine the second harmonic of the response of the heat flow[12]. We have confirmed that the second harmonic is less than 1% of the linear response even at the peak temperature of the heat flow. Such a small non-linearity will guarantee the applicability of our treatment based on a linear response of the crystal growth rate.

CONCLUSIONS

We have examined the non-isothermal crystallization of PET during cooling runs from the melt and during heating runs from the glass. By examining the frequency dependence of the apparent heat capacity, it has been argued that our new analytical model is applicable not only to isothermal crystallization but also to non-isothermal processes. The model assumes the modulation of the crystal growth rate to be the response of the heat flow to temperature modulation, and the temperature dependence of the crystal growth rate is obtainable from the data analysis (equation (11)). The crystal growth rate determined

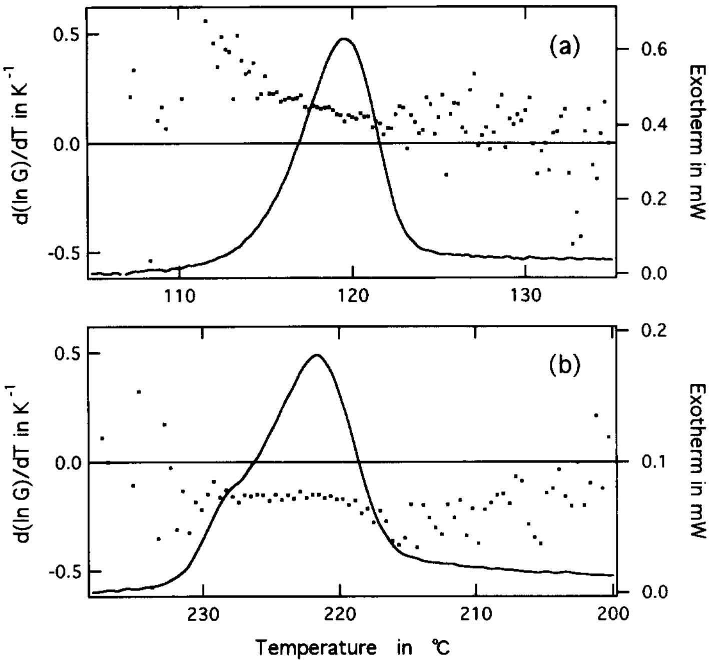

Figure 5 Plots of (d ln *G*/d*T*) determined by equation (11) for (a) heating and (b) cooling runs at 0.5 K min^{-1} and 1.0 K min^{-1}, respectively. The exothermic heat flow is also plotted. The heating and cooling runs are for 14.24 mg and 1.97 mg of PET, respectively. The modulation period was 28 s.

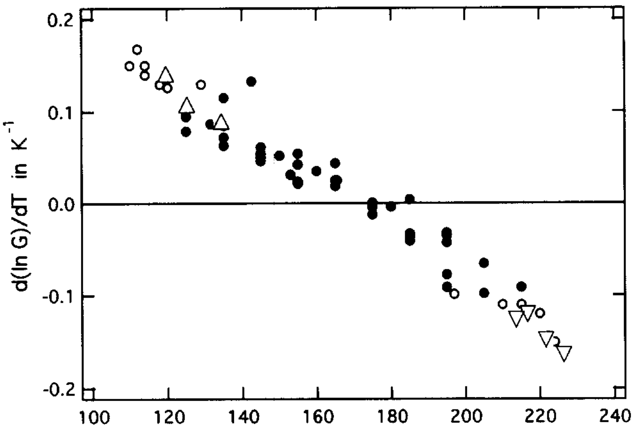

Figure 6 Plots of the temperature dependence of the crystal growth rate, (d ln *G*/d*T*). The non-isothermal TMd.s.c. results (△, ▽) and the quasi-isothermal TMd.s.c. results (○)[6] were determined using equation (11). The (●) data are the results of direct measurements by microscopy[7–9].

for non-isothermal and quasi-isothermal crystallization agreed well with the temperature dependence of the spherulite growth rate measured by optical microscopy. Concerning the change in the real part of the apparent heat capacity, TMd.s.c. may not be able to distinguish the change in the true specific heat from reversible melting and crystallization as the response to temperature modulation.

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