

polymer communications

A new method of analysing transformation kinetics with temperature modulated differential scanning calorimetry: application to polymer crystal growth

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A new method is presented to analyse endothermic or exothermic process with temperature modulated differential scanning calorimetry, utilizing the shift in phase lag between sample temperature and heat flow. It has been shown that the temperature coefficient of transformation rate, e.g. of crystal growth, is obtainable by the analysis. The method is applied to polymer crystallization and the validity has been examined with the experimental results of polyethylene crystallization. Copyright © 1996 Elsevier Science Ltd.

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Introduction

Temperature modulated differential scanning calorimetry (t.m.d.s.c.) is a new technique applying sinusoidal temperature modulation to a conventional d.s.c. run and analysing the response in heat flow^{1–3}. This technique has been well established in heat capacity determination without exothermic or endothermic process^{4,5}. Concerning a process such as first order phase transition, it has been reported that the melting of polymer crystals, for example, produces peaks not only in the total heat flow but also in the heat capacity and in the phase lag between the oscillation components of sample temperature and of heat flow^{2,3,6}. The physical meaning of those peaks has not been clarified. Further investigation has been required on the interpretation of the response during exothermic and endothermic processes. This communication is a brief report of quantitative analysis of the kinetics during exothermic or endothermic process, utilizing the shift in phase lag. In the following, we firstly introduce a model and a method to analyse the kinetics. The method is then applied to polymer crystallization.

Model

In this and subsequent sections, we introduce several assumptions and out-line the method to analyse the kinetics; the justification of those assumptions and the details of the model will be given in a forthcoming paper. Firstly, concerning the absorbed or released heat by the sample per unit time, F , during the process of first order phase transition or chemical reaction, we assume that $F(t, T)$ can be regarded as a function of only temperature T during the period of oscillation; namely $F(t, T) \approx F(T)$. This assumption means that the degree of transformation remains almost unchanged during the period. It is further assumed that the expansion of first order approximates to the

formula of $F(T)$ for a small temperature modulation; namely, $F(\bar{T} + \tilde{T}e^{i\omega t}) \approx F(\bar{T}) + F'(\bar{T}) \cdot \tilde{T}e^{i\omega t}$, where \bar{T} and \tilde{T} represent the mean temperature and the oscillation amplitude, respectively, ω the frequency of oscillation and $F'(T) \equiv dF(T)/dT$.

In a conventional d.s.c. of heat flux type, heat flow is proportional to the temperature difference $\Delta T = T_s - T_r$ between sample and reference temperatures. Under the approximations made above, we analysed the fundamental equation of this type of d.s.c.⁴,

$$C_r \cdot \frac{d(\Delta T)}{dt} + \Delta C \cdot \frac{dT_s}{dt} = -K \cdot \Delta T + F(T_s) \quad (1)$$

with the modulations of $T_s = \bar{T}_s(t) + \tilde{T}_s e^{i(\omega t + \epsilon)}$ and $\Delta T = \Delta \bar{T}(t) + \Delta \tilde{T} e^{i(\omega t + \delta)}$, where $\Delta C \equiv C_s - C_r$ represents the difference between sample and reference heat capacities, C_s and C_r and K the Newton's law constant.

Standard analysis of the equation gives the following conclusions. Firstly, due to the temperature dependence of exothermic or endothermic process, the phase lag $\epsilon - \delta$ undergoes a shift α expressed as

$$\alpha \equiv (\epsilon - \delta) - (\epsilon - \delta)_0 \quad (2)$$

$$\tan \alpha = -\frac{F'(\bar{T}_s)}{\omega \Delta C} \quad (3)$$

where $(\epsilon - \delta)_0$ represents the baseline of the phase lag. Secondly, following the shift in phase lag, the apparent heat capacity ΔC_{app} obtained by the usual method of t.m.d.s.c. becomes larger than the actual ΔC by the factor of $1/|\cos \alpha|$,

$$\Delta C_{app} = \frac{\Delta C}{|\cos \alpha|} \quad (4)$$

Therefore, we can expect a peak in the profile of apparent heat capacity ΔC_{app} as well as in that of total heat flow, if the phase lag α exhibits a peak in the course of exothermic or endothermic process.

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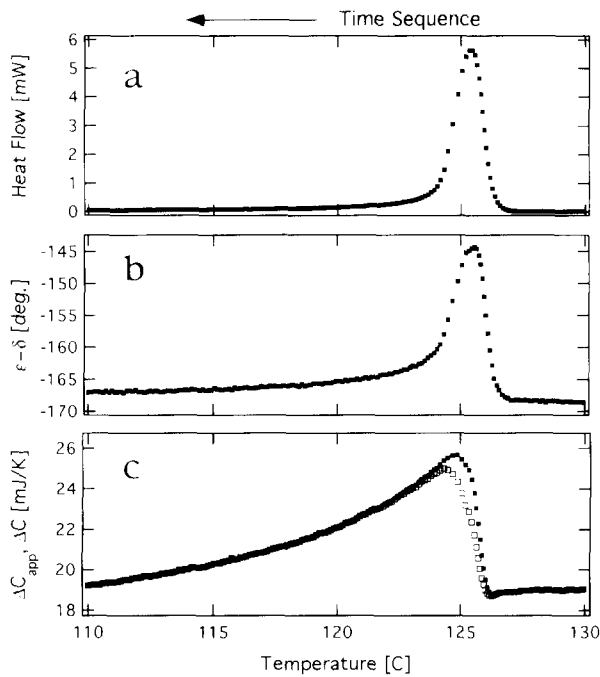


Figure 1 T.m.d.s.c. results of polyethylene crystallization: (a) total heat flow, (b) phase lag $\epsilon - \delta$ and (c) apparent heat capacity ΔC_{app} (■) and the corrected ΔC (□) calculated from equation (4). Cooling run at a rate of 1 C min^{-1}

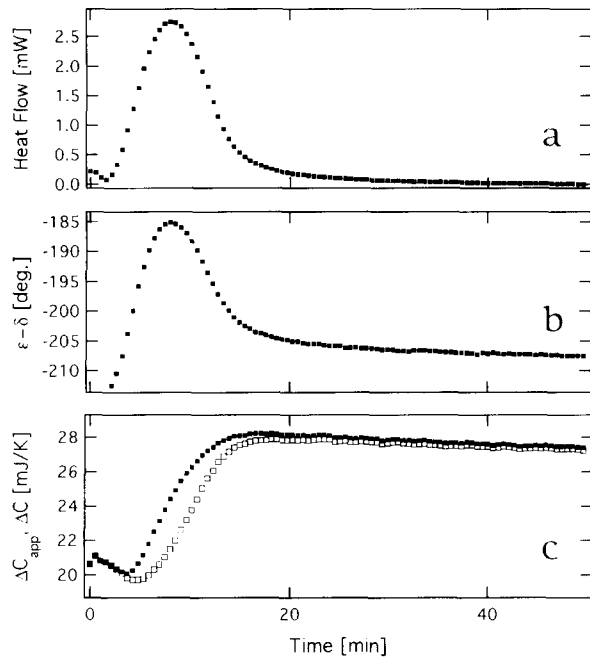


Figure 2 T.m.d.s.c. results of polyethylene crystallization: (a) total heat flow, (b) phase lag $\epsilon - \delta$ and (c) apparent heat capacity ΔC_{app} (■) and the corrected ΔC (□) calculated from equation (4). Isothermal crystallization at 126.5 C

From the expression of $\tan \alpha$ in equation (3), we can determine F' experimentally. F represents the absorbed or released heat by the sample per unit time and F' is the temperature coefficient. We define the total transformation rate of the sample volume (or mass) as R and the enthalpy difference between the initial and final stage per unit volume (or mass) as Δh . Accordingly, F and F' are expressed as, $F = -\Delta h \cdot R$ and $F' = -\Delta h \cdot dR/dT$. Therefore, the ratio of the two

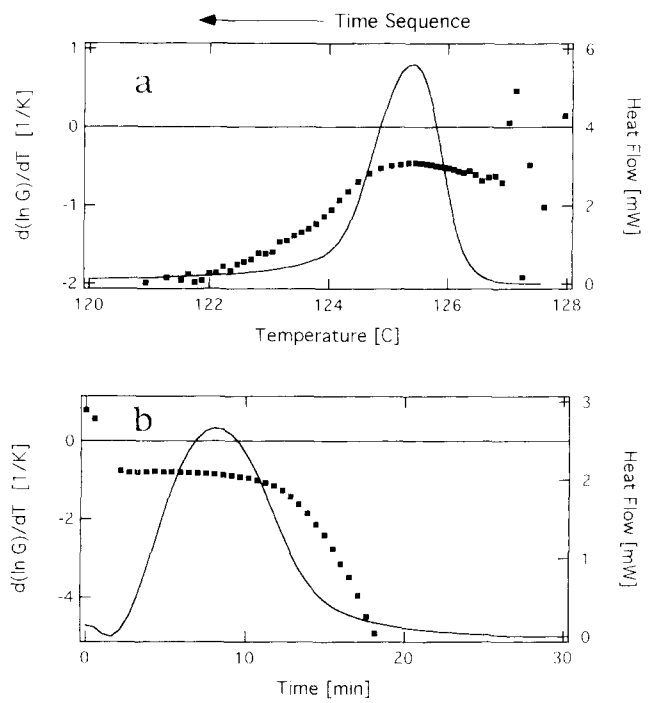


Figure 3 Temperature or time sequence of $d \ln G / dT$ determined by equation (6) from the experimental data of (a) the cooling run shown in Figure 1 and (b) the isothermal crystallization in Figure 2. The curve of total heat flow (---) is also shown

values, $F'/F = 1/R \cdot dR/dT$, gives us the dependence of $\ln R$ on temperature, as follows

$$\frac{d \ln R}{dT} = \frac{F'}{F} = -\frac{\omega \Delta C \tan \alpha}{|F(T_s)|} \quad (5)$$

Polymer crystallization

The total transformation rate R can be expressed by the crystal growth rate G multiplied by the total area of growth face S as $R = G \cdot S$. The temperature coefficient of R is given by $dR/dT = S \cdot dG/dT$. Therefore the ratio of R and dR/dT gives $1/R \cdot dR/dT = 1/G \cdot dG/dT$, without knowledge of the total area of growth face S . Consequently, we are able to obtain the experimental dependence of growth rate on temperature by the t.m.d.s.c. run, as follows

$$\frac{d \ln G}{dT} = \frac{F'}{F} \quad (6)$$

where F' is evaluated from equation (3). The exotherm F is given by the total heat flow in the mode of isothermal crystallization. In the case of cooling with a constant rate, we can assume that the deviation of the total heat flow from its baseline represents the exotherm at that point of time because the crystallization of polymers is a slow process occurring at a temperature well below the equilibrium melting point.

Experimental results and discussion

In this communication, we present a brief report on the experimental data of polyethylene crystallization; we will report the details in the forthcoming paper. The d.s.c. 2920 Module controlled with Thermal Analyst 2200 (TA Instruments) was used for all measurements and the raw data were transferred by a TA RMX Utility.

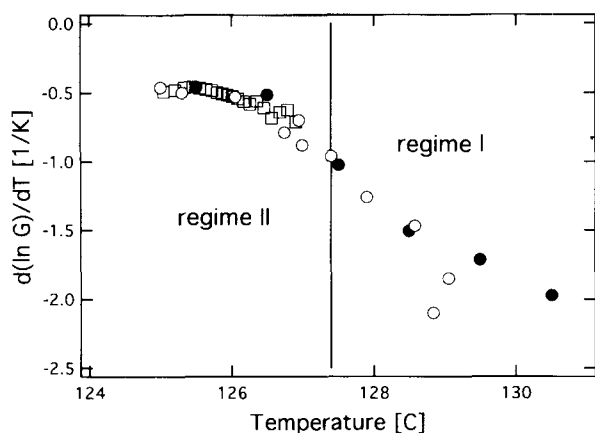


Figure 4 Temperature dependence of $d\ln G/dT$ determined by equation (6) from the experimental data during the steady growth: the sequence in the cooling run shown in Figure 3 (□) and the mean values during isothermal crystallization at each temperature (○). The results of direct measurements of growth rate⁹ are also plotted (●)

The phase lag $\epsilon - \delta$ was determined from the raw data of modulated sample temperature and of modulated heat flow. The sample was a fractionated polyethylene (NIST SRM1483) of 7–10 mg in weight: $M_w = 3.21 \times 10^4$ and $M_w/M_n = 1.11$. The mode of d.s.c. run was either cooling with a constant rate or under an isothermal condition. The modulation period was 24 or 32 s and the amplitude was $\pm 0.2^\circ\text{C}$.

Figures 1 and 2 show the results of a cooling run at a rate of 1°C min^{-1} and of an isothermal run, respectively; the data points are plotted at every period of modulation. It is clearly seen that the exothermic peak in the total heat flow due to crystallization is followed by a peak in the phase lag $\epsilon - \delta$. Figures 1c and 2c show the apparent heat capacity ΔC_{app} and the heat capacity ΔC after the correction of equation (4). The increase in ΔC after the correction is still appreciable; the detailed discussion of the profile will be the subject of the forthcoming paper.

Utilizing equation (6), $d\ln G/dT$ was calculated from the data shown in Figures 1 and 2 and plotted against temperature or time in Figure 3. It is seen that $d\ln G/dT$ becomes level in the vicinity of the peaks of total heat flow, namely during the steady growth of crystals. The absolute values of the temperature coefficient $d\ln G/dT$ shows a sharp rise out of the range in the later stage of

the time sequences. Such a change in the temperature dependence of growth rate is supposed to be due to molecular weight fractionation.

We are concerned with the temperature coefficient during the steady growth of crystals. All results of the temperature coefficient during the steady growth are plotted in Figure 4 along with the values obtained from the optical measurements of the linear growth rate of spherulites or axialites⁹. The agreement between those results is satisfactory and supports the present method. We are able to confirm a drastic change in the temperature coefficient in the course of the regime I–II transition of polyethylene crystallization^{7–11}.

In conclusion, for the determination of temperature dependence of crystal growth rate of polymers, the present method will compare with the direct measurements with optical microscopy. It should be stressed that the method does not require the detailed information on the growth kinetics or the geometry of growth domains. The present method also has great possibilities in the application to other transformation processes such as melting of polymer crystals and chemical reactions.

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References

- Gill, P. S., Sauerbrunn, S. R. and Reading, M. *J. Therm. Analysis* 1993, **40**, 931
- Reading, M., Elliott, D. and Hill, V. L. *J. Therm. Analysis* 1993, **40**, 949
- Reading, M., Luget, A. and Wilson, R. *Thermochim. Acta* 1994, **238**, 295
- Wunderlich, B., Jin, Y. and Boller, A. *Thermochim. Acta* 1994, **238**, 277
- Boller, A., Jin, Y. and Wunderlich, B. *J. Therm. Analysis* 1994, **42**, 307
- Nishikawa, M. and Saruyama, Y. *Thermochim. Acta* 1995, **267**, 75
- Hoffman, J. D., Frolen, L. J., Ross, G. S. and Lauritzen, J. I., Jr. *J. Res. Natl Bur. Stand.* 1975, **79A**, 671
- Labaij, J. J. PhD Thesis, Faculty of Science, University of Strasbourg, 1978
- Toda, A. *Colloid Polym. Sci.* 1992, **270**, 667
- Toda, A. and Keller, A. *Colloid. Polym. Sci.* 1993, **271**, 328
- Toda, A. *Faraday Discuss. Chem. Soc.* 1993, **95**, 129