

PERIODICALLY MODULATED DRIVING FORCE APPLIED WITH TMDSC TO THE CRYSTALLIZATION AND MELTING KINETICS OF ICE CRYSTALS CONFINED IN A POROUS SILICA GEL

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Abstract

The application of a periodically modulated driving force has been examined in the melting and crystallization kinetics of ice crystals confined in a porous media. The kinetic response of transformation gives the real and imaginary parts of the ‘apparent’ heat capacity obtained with a temperature modulated differential scanning calorimetry (TMDSC). Based on a modelling of the kinetics, the detailed examination of the frequency dispersion and its dependence on underlying heating/cooling rate enables us to evaluate the transformation rate and the dependence of the rate coefficient on the driving force, i.e. the degree of supercooling or superheating. The experimental results indicate that the transformation processes are limited by heat diffusion from the growth interface of each crystallite to surroundings.

Keywords: crystallization, ice, melting, silica gel, TMDSC

Introduction

We have recently proposed an analytical method of periodically modulated driving force which has been applied to the crystallization [1], melting [2], chemical reaction [3], and solid state transformation kinetics [4] in polymeric systems. With the method, we apply a periodic modulation to the driving force, e.g. the degree of supercooling or superheating, ΔT , and examine the response of transition kinetics. When examined with a temperature modulated differential scanning calorimetry (TMDSC) [5], the kinetic response appears in the ‘apparent’ heat capacity $\Delta C e^{-i\omega t}$, determined from the modulation components of temperature, T_s , and of heat flow, \dot{Q} , as follows,

$$T_s = \beta t + \operatorname{Re}[\tilde{T}_s e^{i(\omega t + \epsilon)}] \quad (1)$$

$$\dot{Q} = \bar{Q} + \operatorname{Re}[\tilde{Q} e^{i(\omega t + \delta)}] \quad (2)$$

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$$\bar{Q}e^{i(\omega t+\delta)} = -\tilde{\Delta}C_e^{\pm i\alpha} \frac{d}{dt} \tilde{T}_s e^{i(\omega t+\epsilon)} \quad (3)$$

By examining the apparent heat capacity in a frequency range of modulation, we obtain a kinetic response spectrum of transformation, which should be distinguished from the dynamic heat capacity in a relaxation process and needs to be explained by the kinetic modelling of transformations.

The most crucial argument on the applicability of temperature modulation to phase transition is concerned with the condition of steady state of response, which will be a prerequisite for the examination of the response to a periodic modulation. For the collection of crystallites having a broad distribution of transition points, such as the case of the melting region of polymer crystals, if we apply a linear heating passing through the transition region, a quasi-steady response of the kinetics as a total sum of individual transitions will be attained. Then, we can apply a periodic modulation in addition to the linear heating and the (quasi-)steady response of the kinetics is expected.

When the time interval required for the completion of individual transition in each crystallite is comparable with the modulation period, the apparent heat capacity exhibits frequency dispersion, from which the mean time of transition, τ , can be evaluated. Faster underlying rate, β , means faster increase in ΔT , and hence τ is a function of β . The examination of the dependence on underlying rate, β , of frequency dispersion reveals ΔT dependence of transition rate.

For the melting region of polymer crystals [2], the frequency dispersion of apparent heat capacity could be approximated by a frequency response function of Debye's type with the characteristic time, τ , dependent on underlying heating rate, as follows,

$$\tilde{\Delta}C_e^{-i\alpha} \cong C_s + \frac{\left| \frac{\bar{F}}{\beta} \right|}{1+i\omega\tau(\beta)} \quad (4)$$

where C_s represents the true heat capacity and \bar{F} is the underlying heat flow of transformation. The dependence of τ on β could be represented as,

$$\tau \propto \beta^{-x} \quad (5)$$

with x in the range of 0.7–0.85 depending on polymers. The characteristic time, τ , has the physical meaning of the mean time required for the completion of melting of each crystallite. The power x is determined by ΔT dependence of a melting rate coefficient, R , expressed as,

$$R \propto \Delta T^y \quad (6)$$

$$x = \frac{y}{y+1} \quad (7)$$

Therefore, the values of x for the melting of polymer crystallites mean a non-linear dependence of the melting rate on ΔT , i.e. $\nu=2-5.7$, which is an indication of an activation process such as nucleation for melting.

In this paper, we examine the kinetic response spectrum in the melting and crystallization of ice crystallites confined in a porous silica gel. Because of the effect of surface tension, the transition regions go down by about 10 K from the transition temperature of bulk crystals. As is clearly seen in Fig. 1 (thick lines), the transitions have broad peaks which correspond to the distribution of pore size [6, 7]. The broad distribution of transition points is suitable to attain a quasi-steady state, as described above.

Experimental

The DSC 2920 Module controlled with Thermal Analyst 2200 (TA Instruments) was used for all measurements. This module is a differential scanning calorimeter of heat flux type with the capability of temperature modulation by changing the furnace temperature [5]. Helium gas with a flow rate of 40 mL min⁻¹ was purged through the cell. The DSC runs consisted of initial cooling to -40°C to form ice and then cyclic heating and cooling between -32 and -2°C with different modulation periods and underlying heating/cooling rates for a single sample. The rate was in the range of 0.2–3.2 K min⁻¹. The modulation period of 10–100 s was examined with the modulation amplitude satisfying a heating/cooling only condition of $dT_s/dt > 0$ or < 0 ($\tilde{T}_s < |\beta|/\omega$). With this condition, if the sample temperature once becomes higher than the transition temperature of a crystallite on heating, temperature will never go down below the transition point. Therefore, this condition guarantees the one-way transformation of each constituent, and hence the interpretation is straightforward.

TMDSC is a new technique of calorimetry and there has been no standard method of heat capacity (magnitude and phase angle) correction during those processes having a large kinetic response. The calibration is required to remove the effect of the time constant of instrument [8]. It has been argued that the calibration constant is also dependent on the heat capacity of the sample itself [9]. We have done the correction based on Hatta's model without reference pan [9] by examining the heat capacity of aluminum thin sheets with several different number of sheets; the details are in [10]. It should be noted that the correction is crucial for the present case because the characteristic time, τ , is in the same order as the time constant of instrument (~1 – several seconds). The sample mass of 3 and 8 mg corresponding to the thickness of 40 and 110 μm has been examined and we confirmed that the effect of different sample mass (and thickness) was negligible in this range.

The characteristics of the porous silica gel (Wakogel C-200, Wako Pure Chemical Industries) are as follows: particle size of 75–150 μm and mean pore radius of 7.0 nm. Silica gel was saturated with distilled and deionized water (Wako) and was sealed with a tiny amount of water in a sample pan, which ensures good thermal conductivity and the broad transitions in pores.

Results and discussion

Figure 1 shows the raw data and the corrected apparent heat capacity converted to heat flow, namely ‘reversing’ heat flow, $-\beta C_0$ in (a) and $-\beta \Delta C$ in (b). In the transition regions, the ‘reversing’ heat flow shows a strong dependence on the applied modulation frequency. For lower frequencies, the peak approaches the underlying heat flow. The asymptotic behavior is the direct proof of the kinetics which follows the modulation without delay. The approach is more advanced in the melting peak and indicates that the melting process is faster than crystallization. For highest frequencies, the peak height gradually decreases since the kinetics becomes less sensitive to the modulation compared to the contribution from true heat capacity. In the regions outside the transitions, the frequency dependence is due to the time constant of instrument.

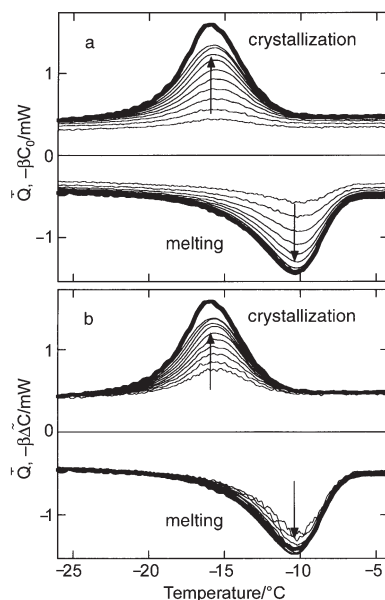


Fig. 1 Plot of the underlying heat flow, \bar{Q} , (thick line) and the ‘reversing’ heat flow of $-\beta C_0$, (thin lines in (a)) converted from the raw data of the apparent heat capacity, $C_0 \equiv \bar{Q}/(\omega T_s)$, and the corrected apparent heat capacity, ΔC , (thin lines in (b)) at the underlying heating/cooling rate of 0.8 K min^{-1} for the modulation periods of 10, 13, 17, 22, 28, 36, 47, 60, 78 and 100 s. The arrows indicate the direction of longer modulation period

The frequency dependence of the corrected apparent heat capacity at the peak temperatures of melting and crystallization is shown in Figs 2 and 3, respectively. A dispersion is clearly seen in the dependence of the real and imaginary parts. The apparent heat capacity for different heating/cooling rate shifts along the x-axis in a consistent manner indicating the dependence on underlying heating/cooling rate of the characteristic time. The apparent heat capacity in Figs 2 and 3 has been fitted to

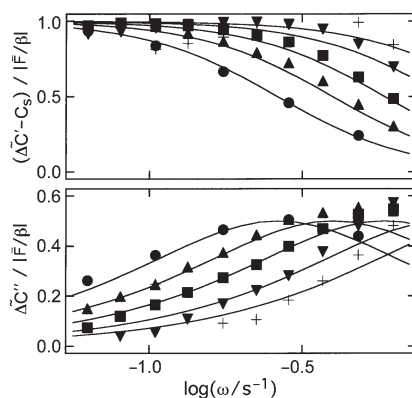


Fig. 2 Frequency dependence of the real and imaginary parts of the apparent heat capacity taken at the peak temperature of melting, -10.0°C , for different underlying heating rates. The symbols represent the following rates: \bullet -0.2 ; \blacktriangle -0.4 ; \blacksquare -0.8 ; \blacktriangledown -0.6 and $+$ -3.2 K min^{-1} . The heat capacity was normalized by the underlying endothermic heat flow, $|F/\beta|$ and the contribution of the heat capacity, C_s , which was obtained by a quasi-isothermal run has been subtracted in the real part. The solid lines represent the fitting by the frequency response function of Debye's type, assuming the expression of Eq. (4). The errors of 10% are estimated from 10% errors in the measurements of C_0 and phase angle

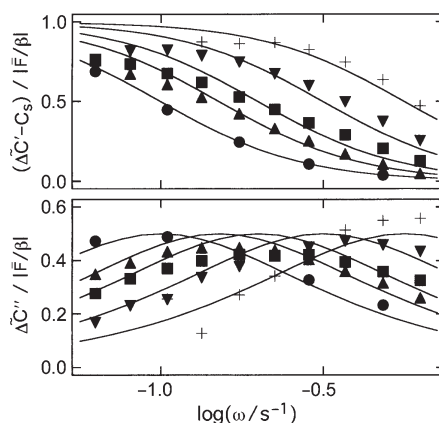


Fig. 3 Frequency dependence taken at the peak temperature of crystallization, -16.0°C , for different cooling rates. The meanings of the symbols and lines are the same as in Fig. 2

Eq. (4) and the characteristic time, τ , has been determined as a fitting parameter. The heating/cooling rate dependence of τ is shown in the logarithmic plot of Fig. 4. It is seen that the characteristic time for the melting is actually shorter than that of crystallization; if the frequency dependence in Figs 2 and 3 is solely due to the instrumental effect, we will not see the difference. The experimental results prove the capability of this method in differentiating the transformation kinetics. It is noted that the corre-

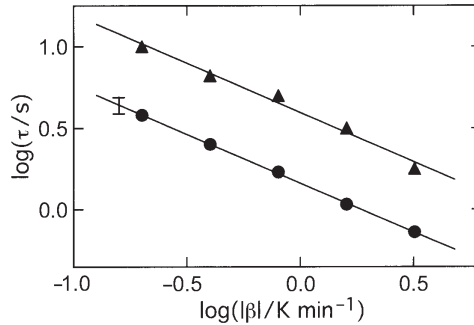


Fig. 4 Logarithmic plots of the characteristic time, τ , chosen for the fitting in Figs 2 and 3 vs. underlying heating/cooling rate, $|\beta|$. The symbols represent the values for the \bullet – melting and \blacktriangle – crystallization. The slope of the straight lines is -0.6 . The error bar represents the maximum error of 10% for the determination of τ

sponding $\Delta T = |\beta| \tau$ is quite small in both transitions: 0.013–0.039 and 0.033–0.095 K for the melting and crystallization, respectively.

The exponent, x , of the melting and crystallization of ice crystals is close to -0.5 , and hence the coefficient of transformation rate will be nearly proportional to ΔT . It means that the transformations do not require an activated process such as nucleation and seems to be unusual for crystallization. However, since the coexistence of ice crystals surrounding silica gels is essential for the broad peaks of crystallization, the crystallization in pores proceeds from the ice crystals acting as seeds.

The linear dependence of transformation rate on ΔT indicates the growth limited by surface kinetics on an atomically rough interface or by heat diffusion from the interface of each crystallite in pores to surroundings. In the case of surface kinetics, the growth rate is represented as [11],

$$V_{\text{kin}} = \beta^T \Delta T = a \left(\frac{a}{\lambda_0} \right)^2 \text{vexp} \left[-\frac{E}{kT} \right] \frac{\Delta S}{kT} \exp \left[-\frac{\Delta S}{k} \right] \Delta T \quad (8)$$

where β^T is the kinetic coefficient determined by the size of growth unit, a , the surface density of kinks, $(a/\lambda_0)^2$, mobility factor, $\text{vexp}[-E/kT]$, and activation factor, $\Delta S/kT \exp[-\Delta S/k]$, with the entropy change, ΔS , on transition for the growth unit. On the other hand, the steady growth limited by thermal diffusion for a spherical growth domain of radius R (or a one-dimensional growth in a pore of length R) is represented as [11],

$$V_{\text{dif}} = \frac{\kappa}{\rho \Delta H} \frac{\Delta T}{R} \quad (9)$$

where κ is thermal conductivity, ρ density, and ΔH heat of fusion per unit mass.

For the transformation of ice crystals, the kinetic coefficient is evaluated to be $\beta^T \sim 21 \text{ cm s}^{-1} \text{ K}^{-1}$ with $a=0.32 \text{ nm}$, $(a/\lambda_0)^2=0.1$, $\text{vexp}[-E/kT]=10^{13} \text{ s}^{-1}$, and $\Delta S/k=2.9$. For the obtained characteristic time of melting, $\tau=1.5 \text{ s}$, with $\beta=1 \text{ K min}^{-1}$, the velocity, V_{kin} , predicts the growth of $\beta^T \beta \tau^2/2 \sim 3.9 \text{ mm}$. The estimated length will be too large for the transformation in a pore, because the particle size of silica gel is only 75–150 μm and the pore radius determining the transition temperature will not be uniform in a single channel. In other words, if we assume the one-dimensional heat diffusion from the interface with thermal conductivity of ice, ca $2.2 \text{ W m}^{-1} \text{ K}^{-1}$, Eqs (8) and (9) predict that the length of the channel, R , for the process to be limited by interfacial kinetics must be smaller than 32 nm, which will be too small as the length of a single domain. Therefore, it is most probable that the growth is limited by heat diffusion from the interface of each growth domain to surroundings.

The characteristic time for the growth limited by heat diffusion is in proportion to $(\rho \Delta H_f / \kappa \beta)^{1/2}$. The thermal conductivity of water at 0°C is about $0.6 \text{ W m}^{-1} \text{ K}^{-1}$, and that of silica and silica gel is 1.4 and $0.3 \text{ W m}^{-1} \text{ K}^{-1}$, respectively; hence, the conductivity of ice ($\sim 2.2 \text{ W m}^{-1} \text{ K}^{-1}$) is the highest. If it is the growth of a spherical domain in a mother media, the growth is limited by the heat diffusion out of the interface in the mother media, and hence the factor of about 2 for $\tau_{\text{cryst.}}/\tau_{\text{melting}}$ in Fig. 4 can be explained by the difference in thermal conductivity of ice and water. However, the transformation occurs in a pore, and hence the heat diffusion in both sides of the interface will be effective. Therefore, it is unlikely to expect the difference in τ by the difference in the thermal conductivity.

As mentioned above, the bulk ice crystals surrounding silica gels act as the seed for the crystallization in the pores, and hence the crystallization must be always inward growth from the surface of silica gels. On the other hand, melting can start without nucleation in the pores, and creates two interfaces on both sides. Therefore, even in the case that the rate coefficients for crystallization and melting are the same, the time required for the completion of melting of each crystal domain can be half of the time for crystallization. This explanation satisfactorily applies to the experimental results in Fig. 4 indicating the growth most probably limited by heat diffusion for both of crystallization and melting with only difference in the ratio, $\tau_{\text{cryst.}}/\tau_{\text{melting}}$, of factor 2.

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