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A modeling of the irreversible melting kinetics of polymer crystals responding to temperature modulation with retardation of melting rate coefficient

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Abstract

An extension of the modeling proposed previously has been examined for the irreversible melting kinetics of polymer crystals on heating with response to temperature modulation. The previous modeling has been successful in the explanation of the frequency dependence of the apparent heat capacity obtained with temperature modulated DSC in the melting region of poly(ethylene terephthalate), polyethylene and poly(caprolactam). In the present work this modeling was extended to explain an unusual behavior reported by Schawe et al. for poly(ϵ-caprolactone) and syndiotactic polypropylene, in which the latent heat gave a substractive effect to the real part of the apparent heat capacity. A retardation of the melting rate coefficient in response to temperature change has been considered. The retardation implies an activation process in the melting kinetics of polymer crystals. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

We have proposed a phenomenological modeling of the melting kinetics of polymer crystallites on linear heating [1–3]. From the analysis of the kinetic response to a periodic modulation in temperature, we obtained the frequency-dependent apparent heat capacity roughly approximated by Debye's type, as shown in Fig. 1a and the following equation:

$$\widetilde{\Delta C}e^{-i\alpha} = C_s + f(\omega) \qquad (1)$$

$$f(\omega) \equiv f'(\omega) - if''(\omega) \cong \frac{-F_{\text{melt}}\beta^{-1}}{1 + i\omega\tau_c(\beta)} \qquad (2)$$

where F_{melt} represents the endothermic heat flow of melting, ω is the angular frequency of modulation and τ_c represents the mean time of melting of each crystallite and depends on the underlying linear heating rate, β. We have shown that the expression well explains the frequency and heating rate dependences of the apparent heat capacity obtained by temperature-modulated DSC (TMDSC) in the melting region of polymer crystals, such as poly(ethylene terephthalate) [1], polyethylene [2] and poly(caprolactam) [4]; typical experimental results are shown in Fig. 1b by open symbols.

On the other hand, Schawe et al. reported unusual frequency dependence in the melting region of poly(ϵ-caprolactone) [5] and syndiotactic polypropylene [6,7], as shown in Fig. 1a; we have recently reconfirmed similar frequency dependence in isotactic polypropylene as shown in Fig. 1b by filled symbols [8]. In these results, the melting response appears as a *subtractive* effect in the real part of the apparent heat capacity.

The conventional DSC exhibits an endothermic peak of melting on heating. This means that the latent heat gives an *additive* effect to the apparent heat capacity determined by TMDSC because of the following reason. When the melting occurs instantaneously compared to the time period of modulation, the endothermic heat flow appears only on the occasion of temperature change, and hence the response of melting is indistinguishable from the response due to true heat capacity which is also in proportion to the temperature change. In such limiting case [9], the response must have an additive contribution to the real part of heat capacity, as shown in Fig. 1a for $\omega\tau_c \to 0$. Therefore, the subtractive effect in the real part observed by Schawe et al. and us

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must turn over to the additive contribution for lower frequency. We expect a reasonable continuation to the expression of Eq. (2) with an additional effect in the melting kinetics discussed below.

In our previous modeling, we have assumed that the melting of a crystallite needs a finite time but the rate of melting responds to temperature change without delay. If the melting rate follows temperature change with delay, the retardation time, τ_r, must be in the contribution of kinetic response, which will be approximated as

$$f_{\tau_r}(\omega) \cong \frac{1}{1 + i\omega\tau_r} f(\omega) \tag{3}$$

With the additional frequency dispersion, we expect the subtractive nature in the real part for higher frequency as shown in Fig. 1c.

In the present paper, we extend the previous modeling to incorporate the retardation of melting rate coefficient in response to temperature change. The modeling provides a comprehensive explanation for the melting response, which can be roughly approximated by Eq. (3).

2. Brief review of the modeling of melting kinetics with response to temperature modulation [1–3]

In order to model the response in heat flow of the melting process of polymer crystals, we suppose that the aggregate of crystallites have a broad distribution of melting temperatures. The decrease in the crystallinity of each fraction, $\phi(t, T_m)$, is assumed to be described by a melting rate coefficient, R, as

$$\frac{d\phi(t, T_m)}{dt} = -R\phi(t, T_m) \tag{4}$$

Here, the melting rate coefficient is assumed to be a function of superheating, $\Delta T \equiv T_s - T_m$. The change in the crystallinity of the fraction for superheating only ($dT_s/dt > 0$) is then given as

$$\phi(\Delta t > 0) = \phi_0(T_m) \exp\left[-\int_0^{\Delta t} R(\Delta T(\Delta t'))\, dt' \right] \tag{5}$$

where $\Delta t \equiv t - t_0$ with $T_s = T_m$ at $t = t_0$ and $\phi_0(T_m)$ represents the distribution function of melting points. The endothermic heat flow of melting, $F_{melt}(t)$, is then expressed as

$$F_{melt}(t) = \Delta H \frac{d}{dt} \int_0^{\infty} \phi(t, T_m)\, dT_m \tag{6}$$

with the enthalpy change, ΔH, of the system.

In our previous treatment, we assumed that R follows the change in sample temperature without delay. Then, for a small sinusoidal modulation in temperature with underlying linear heating, $T_s = \beta t + \tilde{T}_s\, e^{i\omega t}$, the melting rate coefficient and the crystallinity of the fraction in Eqs. (5) and (6) can be expanded in terms of the modulation. Therefore, we can in principle calculate the response to temperature modulation.

In order to obtain the analytical expression for the steady response of melting kinetics, we suppose a uniform distribution of the initial fractions, $\phi_0(T_m) = \phi_0$. The steady response of heat flow to the sinusoidal modulation in temperature is then represented by Fourier series expressed as

$$F_{melt}(t) = \bar{F}_{melt} + F'_T(\omega)\tilde{T}_s\, e^{i\omega t} + \cdots \tag{7}$$

$$\bar{F}_{melt} = -\beta \Delta H \phi_0 \tag{8}$$

$$F'_T(\omega)\tilde{T}_s = \beta\phi_0 \int_{-\infty}^{\infty} e^{-i\omega t} F_{melt}(t)\, dt \tag{9}$$

The modulation component of total heat flow is the sum of contribution of heat capacity and of heat flow of melting represented as

$$-C_s \frac{d}{dt}\tilde{T}_s\, e^{i\omega t} + F'_T \tilde{T}_s\, e^{i\omega t} = -\left(C_s + \frac{i}{\omega} F'_T \right) \frac{d}{dt} \tilde{T}_s\, e^{i\omega t}$$

and hence, when arranged as a heat capacity, the kinetic contribution to the apparent heat capacity in Eq. (1), is expressed as

$$\begin{aligned} f(\omega) &= \frac{i}{\omega} F'_T(\omega) \\ &= -\bar{F}_{melt} \int_0^{\infty} e^{-i\omega x}\, e^{-\int_0^x R(\beta y)\, dy}\, dx \int_0^x e^{i\omega y} R'(\beta y)\, dy \end{aligned} \tag{10}$$

where $R' \equiv dR/d(\Delta T)$.

As a typical example, when the melting rate coefficient is linearly dependent on superheating, i.e. $R = a\Delta T$, the calculated result becomes as follows:

$$f(\omega) = \frac{-\bar{F}_{melt}/\beta}{\omega\tau_c} \left\{ e^{-(\omega\tau_c)^2} \int_0^{\omega\tau_c} e^{x^2}\, dx - i\frac{\sqrt{\pi}}{2}\left(1 - e^{-(\omega\tau_c)^2}\right) \right\} \tag{11}$$

$$\tau_c = \left(\frac{1}{2a\beta} \right)^{1/2} \tag{12}$$

The frequency dependence is roughly approximated by Debye's type, as shown in Fig. 3.

3. Modeling with retardation in the melting rate coefficient

In the present treatment, we assume that R follows the change in sample temperature with a delay characterized by a retardation time, τ_r, as shown in Fig. 2. The behavior can be expressed as

$$\Delta R = \left[1 - \exp\left(-\frac{t}{\tau_r} \right) \right] \Delta R_0 \tag{13}$$

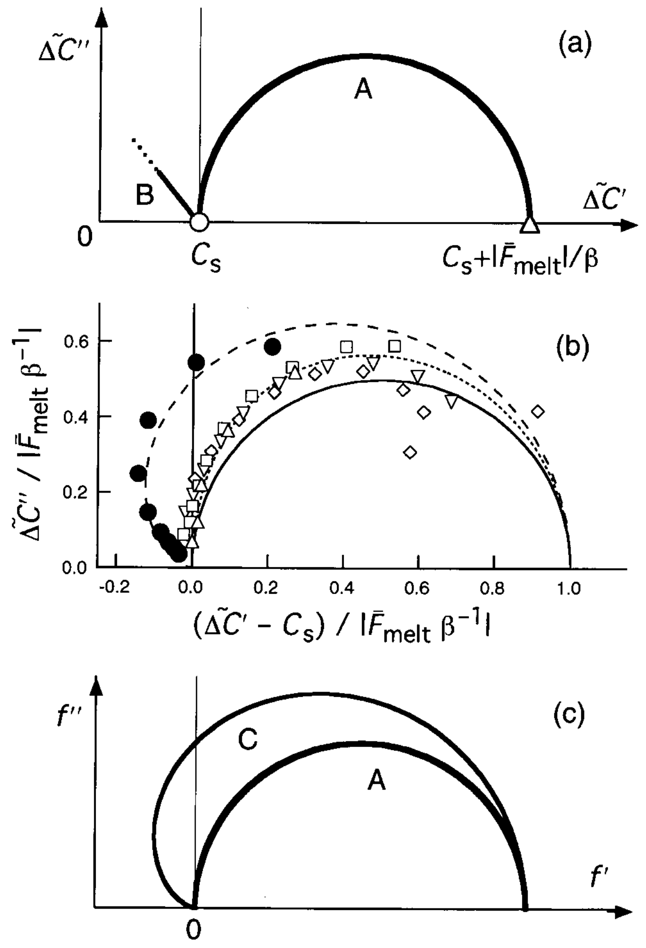

Fig. 1. Cole–Cole plot of the apparent heat capacity obtained in the melting region of polymer crystals with different modulation frequency; schematic plot in (a) and (c) and experimental results of polyethylene [2] (open symbols obtained with different heating rates) and isotactic polypropyrene [8] (filled symbols) in (b). Curve A represents the frequency response function of Debye type, which roughly approximates the experimental results of poly(ethylene terephthalate) [1], polyethylene [2] and poly(caprolactam) [4]. Curve B represents the results of poly(ε-caprolactone) [5], syndiotactic polypropylene [6,7] reported by Schawe et al. The symbols, ○ and △ in (a), represent the asymptotic values for $\omega\tau_c \to \infty$ and $\omega\tau_c \to 0$, respectively. The dotted and solid lines in (b) represent the analytic solutions for the melting rate linearly and exponentially depending on superheating, respectively. The broken line in (b) and curve C in (c) represent f_{τ_r} of Eq. (3) with f of Eq. (2).

with the melting rate coefficient for $t = \infty$ being $R_0(\Delta T)$. The consequent melting rate coefficient is then expressed as

$$R(t) = \int_{t_0}^{t} \left[1 - \exp\left(-\frac{t-s}{\tau_r}\right)\right] \frac{dR_0}{d(\Delta T)} \frac{d(\Delta T)}{ds}\, ds \tag{14}$$

The coefficient is rearranged in terms of Δt as

$$R(\Delta t) = R_0(\Delta T(\Delta t)) - \int_0^{\Delta t} e^{(s-\Delta t)/\tau_r} R_0' \frac{d(\Delta T)}{ds}\, ds \tag{15}$$

The corresponding contribution in heat capacity, $f_{\tau_r}(\omega)$, is

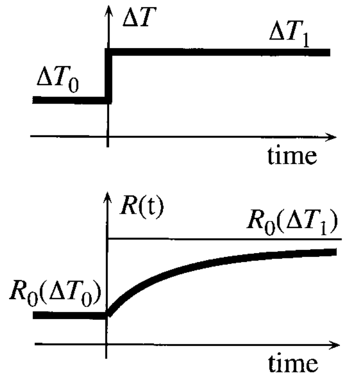

Fig. 2. Schematic representation of the retardation behavior of melting rate coefficient responding to temperature change.

calculated as

$$f_{\tau_r}(\omega) = -\bar{F}_{melt} \int_0^{\infty} e^{-i\omega x}\, e^{-\int_0^x R_3(\beta y)\, dy}\, dx \int_0^x R_4(\beta y)\, dy \tag{16}$$

$$R_3(\beta y) = \frac{1}{\tau_r} \int_0^y e^{s-y/\tau_r} R_0(\beta s)\, ds \tag{17}$$

$$R_4(\beta y) = \frac{1}{\tau_r} \int_0^y e^{(s-y/\tau_r)+i\omega s} R_0'(\beta s)\, ds \tag{18}$$

Fig. 3 shows the results of numerical calculation for the linear dependence on superheating of the melting rate coefficient. The mean time, τ_c, has been fixed at 100 s and the retardation times, τ_r, of 0.1, 10 and 100 s were examined. It is seen that the deviation of f_{τ_r} from f becomes larger with longer τ_r, and the expected change in the real part can be confirmed. Fig. 3 also shows that the formula of Eq. (3) is a good approximation for shorter τ_r.

For different dependences on superheating of the melting rate of coefficient, such as constant melting rate coefficient, $R = a$, and exponential dependence, $R = a(e^{c\Delta T} - 1)$, the influence of the retardation was similar to the case of $R = a\Delta T$.

4. Discussion

We have modeled the melting kinetics of polymer crystals on linear heating with additional periodic modulation in temperature. With the incorporation of the retardation of melting rate coefficient, we have obtained the kinetic contribution having a subtractive effect to the true heat capacity determined by TMDSC. The behavior will correspond to the experimental results reported by Schawe et al. [5–7] and reconfirmed by us [8]. The kinetic contribution for lower frequency turns over to the additive effect, which in turn corresponds to our experimental results explained by our previous modeling without retardation [1,2,4]. Therefore, the present modeling explains the whole spectrum of the dispersion of the apparent heat capacity in the melting region of polymer crystals.

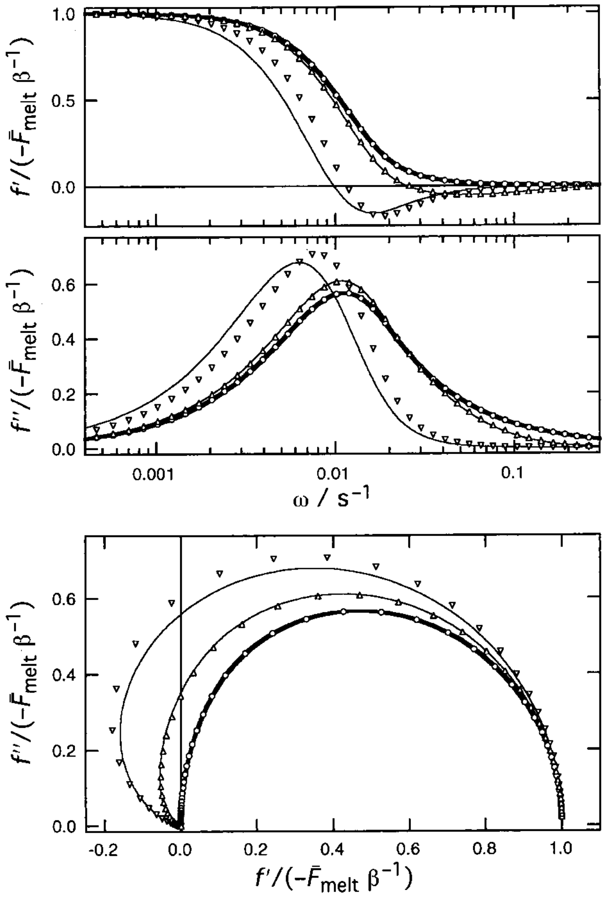

Fig. 3. Numerical calculation of the kinetic contribution in the apparent heat capacity for the linear dependence on superheating of melting rate coefficient. The symbols, ○, △ and ▽, represent the results of $\tau_r = 0.1$, 10 and 100 s, respectively. The thick line represents Eq. (11) and the thin lines are of Eq. (3) with respective τ_r. The mean time τ_c is fixed at 100 s.

The retardation of melting rate coefficient indicates that the temperature dependent melting kinetics needs a reconstruction of crystal–melt interface. Experimentally [1,2,4], it has been confirmed that the power, x, of heating rate dependence of the mean time of melting in $\tau_c \propto \beta^{-x}$ is larger than 0.5. The power is related to the superheating dependence of the melting rate coefficient [3] by the formula of $R \propto \Delta T^{x/(1-x)}$, and hence the power x larger than 0.5 indicates the superheating dependence stronger than linear dependence. Those results strongly indicate an activation process required for the melting of polymer crystals. The process may be controlled by a nucleation, the possibility of which has not been considered seriously in the melting process; a nonlinear melting rate has been reported only for a few polymers under restricted conditions [10,11]. The present explanation therefore has a great importance in the understanding of the melting kinetics of polymer crystals.

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