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Periodically modulated driving force applied to polymer crystallization in a visco-elastic measurement with temperature modulation

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Abstract

The method of “periodically modulated driving force” has been applied to the kinetics of polymer crystallization examined by a dynamic visco-elastic measurement with temperature modulation. The dynamic elasticity obtained by the measurement shows a strong nonlinearity in its dependence on the degree of crystallinity, and hence the simple time derivative does not represent the rate of crystallization. With the application of periodic modulation in temperature and the examination of the response of crystallization kinetics appearing in the modulation in the elasticity, it has been shown that the temperature dependence of growth rate can be determined even with the nonlinear dependence of this quantity. The method is applied to the crystallization of polyethylene, poly(vinylidene fluoride) and isotactic polypropylene. The agreement with the results from the direct measurement of growth rate by optical microscopy is satisfactory.

Keywords: Temperature modulation; Crystallization; Polymer; Elastic modulus

1. Introduction

The visco-elastic properties of polymer materials are the function of crystallinity in the sample, and those quantities such as elastic modulus change in the course of crystallization from the viscous liquid to the elastic solid. It is well known that the elastic modulus undergoes a change of several orders of magnitude, clearly indicating a nonlinear dependence on the degree of crystallinity [1–3]. Therefore, the analysis of the kinetics with the obtained data has been a difficult problem.

In the present paper, we discuss the applicability of the method of “periodically modulated driving force”, in which supercooling is modulated in a periodic manner and the response of the kinetics is analyzed. With slow crystallization process which requires much longer time compared to the modulation period applicable with an instrument, we can attain a (quasi-)steady response of the kinetics and the Fourier analysis is applicable to the kinetics. The response of crystallization kinetics appears as the modulation of growth rate of crystals for the modulation in temperature small enough compared to the preset degree of supercooling, and hence the temperature dependence of growth rate determines the magnitude of response. Based on this position, we have reported the successful application with heat flow data obtained by a temperature modulated differential scanning calorimetry (TMDSC) [4–9]. The exothermic heat flow on crystallization is

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apparently in proportion to the rate of change in total crystallinity, and hence the analysis has been straightforward [10,11]. In the present paper, we examine the applicability to the physical quantity such as elastic modulus which shows strong nonlinearity in its dependence on the degree of crystallinity.

In the following, we firstly discuss the modeling of "periodically modulated driving force" when applied to a quantity showing nonlinear dependence on crystallinity. The method is applied to the dynamic visco-elastic measurement with periodic temperature modulation in the course of crystallization of polyethylene, poly(vinylidene fluoride) and isotactic polypropylene.

2. Modeling

In the modeling, we specify the application of this method to the crystallization of polymers. The method will be applicable to other kinetics if the conditions mentioned below are satisfied.

When a physical quantity, E, is a monotonous function of the degree of transformation, X, which is crystallinity in the case of crystallization, the time development of this quantity on transformation at a constant temperature, T, will be represented as

$$\left(\frac{\partial E}{\partial t}\right)_T = \left(\frac{\partial E}{\partial X}\right)_T \left(\frac{\partial X}{\partial t}\right)_T \tag{1}$$

Because of the nonlinear dependence of E on X, $(\partial E/\partial X)_T$ is not kept at a constant value, and hence the time derivative, $(\partial E/\partial t)_T$, is not in proportion to the rate of transformation, $(\partial X/\partial t)_T$.

If there is only a single process, the rate of transformation can be arranged as

$$\left(\frac{\partial X}{\partial t}\right)_T = R(T)Y(t) \tag{2}$$

with the term dependent on temperature, $R(T)$, and the term independent of temperature change, $Y(t)$. In the case of crystallization, $R(T)$ is determined by the growth rate depending on supercooling, $\Delta T \equiv T_\mathrm{m} - T_\mathrm{c}$, where T_m and T_c represent melting point and crystallization temperature, respectively, and $Y(t)$ represents the total sum of the area of growth face. For chemical reaction, $R(T)$ is determined by the activation energy and $Y(t)$ depends on the details of the reaction.

The total time derivative of $E(X)$ with temperature change will be represented as

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \left(\frac{\partial E}{\partial t}\right)_T + \left(\frac{\partial E}{\partial T}\right)_t \frac{\mathrm{d}T}{\mathrm{d}t} \tag{3}$$

where $(\partial E/\partial T)_t$ represents the temperature dependence of $E(X)$ at the fixed degree of transformation of $X(t)$.

A periodic modulation around a constant temperature, namely quasi-isothermal modulation in temperature, is expressed as

$$T = T_0 + \tilde{T} \sin(\omega t) \tag{4}$$

with the constant temperature, T_0, the amplitude of modulation, $\tilde{T}$, and the angular frequency, ω. For the periodic modulation in temperature, the modulation in the growth rate, $R(T)$, will have an expansion expressed as follows, if the amplitude of temperature is small enough compared with ΔT and the modulation period is short enough compared with the time interval required for the completion of transformation,

$$R(T) \simeq R(T_0) + \frac{\mathrm{d}R(T_0)}{\mathrm{d}T} \tilde{T} \sin(\omega t) \tag{5}$$

The total time derivative of $E(X)$ is then represented as follows from Eqs. (1)–(5)

$$\begin{aligned} \frac{\mathrm{d}E}{\mathrm{d}t} &\equiv \bar{\dot{E}} + \tilde{\dot{E}}\sin(\omega t + \delta) \\ &\simeq \left(\frac{\partial E}{\partial X}\right)_T Y(t) \left[R + \frac{\mathrm{d}R}{\mathrm{d}T}\tilde{T}\sin(\omega t)\right] \\ &\quad + \left(\frac{\partial E}{\partial T}\right)_t \omega\tilde{T}\cos(\omega t) \end{aligned} \tag{6}$$

where $\bar{\dot{E}}$ and $\tilde{\dot{E}}$ represent the steady response and the amplitude of periodic response of $\dot{E}$, respectively, and δ represents the phase lag between the modulation components of $\dot{E}$ and temperature. The periodic response of transformation kinetics, $(\partial E/\partial X)_T Y(t)(\mathrm{d}R/\mathrm{d}T)\tilde{T}\sin(\omega t)$, which is in phase with the modulation in temperature, $\tilde{T}\sin(\omega t)$, can be separated from the response of temperature dependence of $E(X)$, $(\partial E/\partial T)_t \omega\tilde{T}\cos(\omega t)$, which is out of phase. Therefore, the distinction between those components is straightforward by Fourier analysis. By taking the ratio between the modulation component in phase with temperature, $\tilde{\dot{E}}\cos(\delta)$, and the steady response of the kinetics, $\bar{\dot{E}}$, we are able to determine the temperature dependence of growth rate even though the response of $E(X)$ is nonlinear in terms of temperature, as follows,

$$\frac{\mathrm{d}}{\mathrm{d}T}\ln R = \frac{\tilde{\dot{E}}\cos(\delta)}{\bar{\dot{E}}} = \left[\left(\frac{\partial E}{\partial X}\right)_T Y(t)\frac{\mathrm{d}R}{\mathrm{d}T}\right]\left[\left(\frac{\partial E}{\partial X}\right)_T Y(t)R\right]^{-1} \quad (7)$$

3. Experimental

The dynamic elasticity measurement has been done with a rheometer of MR300 (Rheology Co. Ltd.) under the following conditions: parallel plate of diameter 1.8 cm, sample thickness of 500 μm, and a sinusoidal oscillation with amplitude of 0.2′, frequency of 1 Hz and sampling period of 12 s. In terms of the modulation in temperature, a saw-tooth pattern of modulation around a constant temperature with alternating linear heating and cooling has been applied by controlling the furnace temperature with the precision of 0.1 K. The temperature has been calibrated by the output of a thermocouple inserted in a sample. The temperature modulation (highest temperature − lowest temperature) was set to be 1.0 for polyethylene and 2.0 K for isotactic polypropylene and poly(vinylidene fluoride). The modulation period was 2 or 4 min.

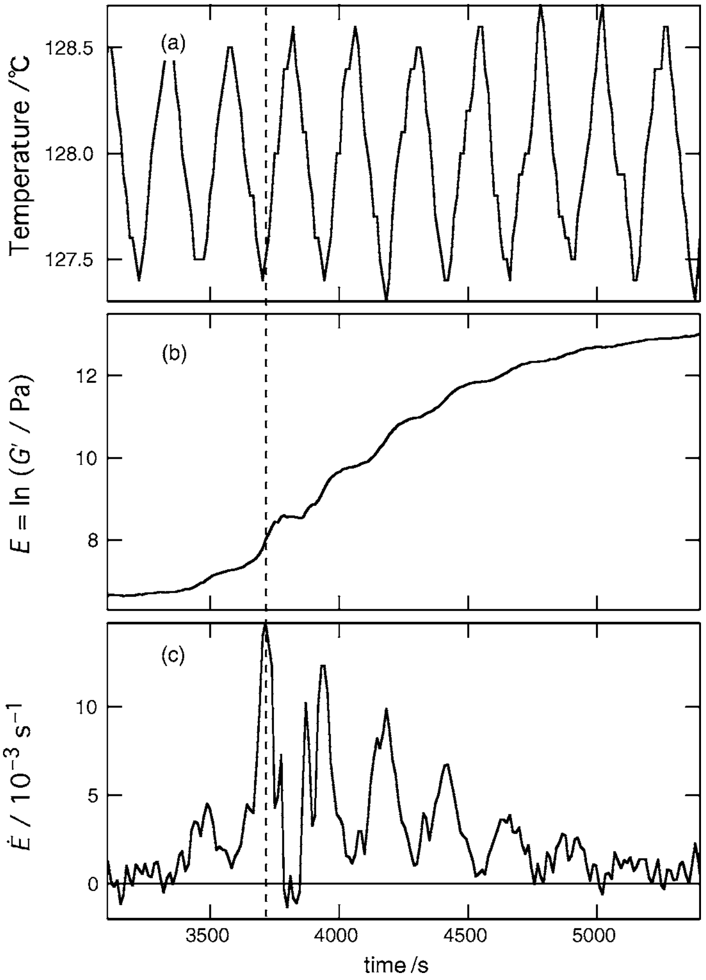

Fig. 1. (a) Applied temperature profile: periodic heating and cooling around a constant temperature, 128.0 ± 0.5 °C, with the period of 4 min. (b) Logarithmic plot of the change in elastic modulus on crystallization with the temperature modulation. (c) Time derivative of E shown in (b).

The samples were polyethylene PE, NIST SRM 1483 ($M_w = 32100$, $M_w/M_n = 1.11$), isotactic polypropylene (iPP, Scientific Polymer Products Inc.) and poly(vinylidene fluoride) (PVDF, Kureha Chemicals Inc., KF1000).

4. Results and discussion

For the saw-tooth modulation around constant temperature (Fig. 1a). Fig. 1b shows the response of dynamic elasticity in the course of crystallization of PE. The logarithm of the elasticity is taken as the quantity E (=ln G′) in the following discussion, but the choice is not essential and another choice of $E = G'$ has the same results. Fig. 1c shows the time derivative of E, which is analyzed by the above mentioned manner with Eqs. (6) and (7).

Fig. 2a shows the amplitude of the modulation component of $\dot{E}$ in Fig. 1c. In Fig. 2a, the change is compared with the change in $\bar{\dot{E}}$, which represents the steady response of $\dot{E}$ averaged over every period of

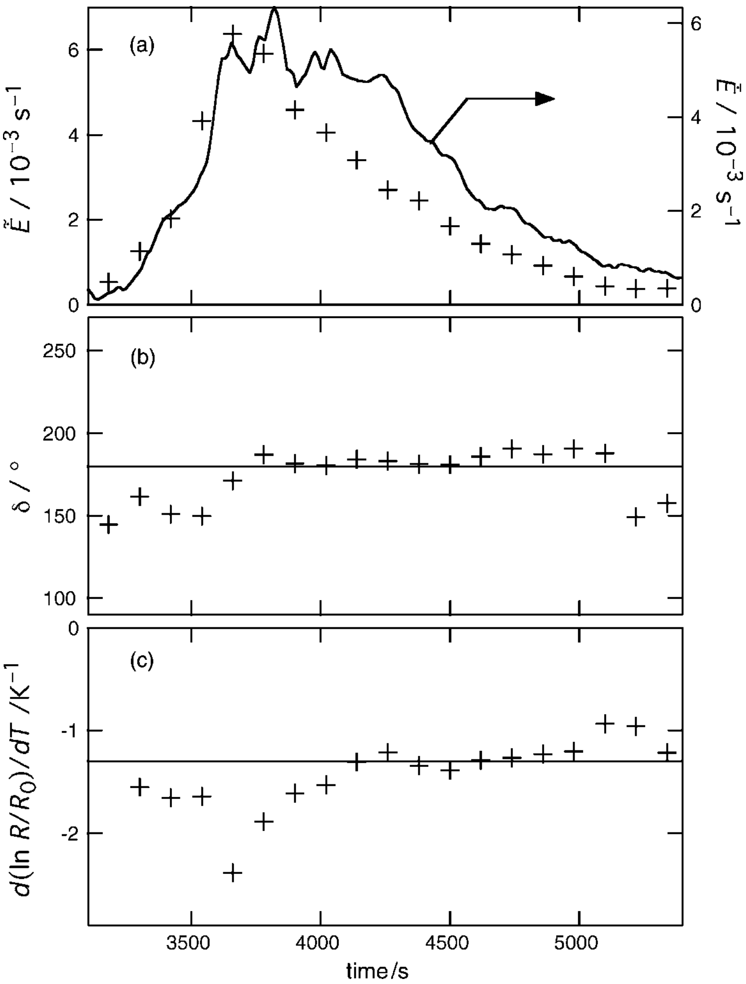

Fig. 2. (a) Amplitude of modulation component, $\tilde{\dot{E}}$, (+) of $\dot{E}$ shown in Fig. 1c, compared with $\bar{\dot{E}}$ (curved line) averaged over every period of modulation. (b) Phase lag, δ, (+) between the modulation components of $\dot{E}$ in Fig. 1c and temperature in Fig. 1a. The horizontal line represents 180°. (c) Temperature dependence of growth rate, $(\mathrm{d}(\ln(R/R_0))/\mathrm{d}T)$, (+) determined by the present method. The horizontal line represents literature value [11] determined from the plot of linear growth rate vs. crystallization temperature.

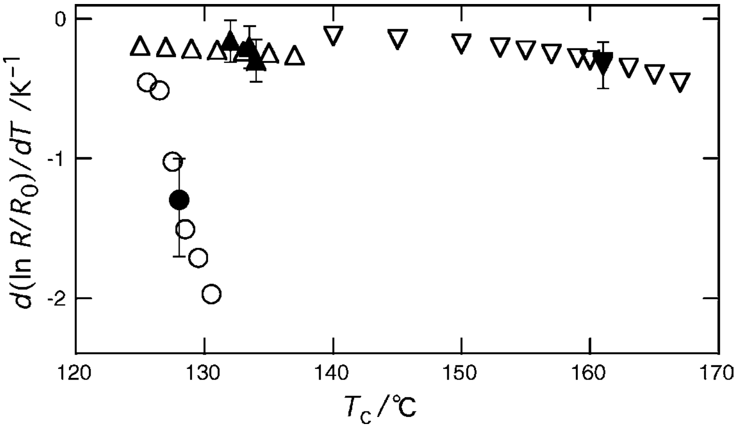

Fig. 3. Plots of the temperature dependence, $(d(\ln(R/R_0))/dT)$, against crystallization temperature, T_c: the present results (filled symbols) and the results of direct measurements by microscopy (open symbols) [11]. The symbols represent the results of PE (○, ●), iPP (△, ▲) and PVDF (▽, ▼). The error bars represent the scattering of the values in the main peak of $\dot{\tilde{E}}$ on the way of crystallization.

modulation. It is seen that the peak positions correspond to each other, and hence the ratio, namely $d(\ln R)/dT$ from Eq. (7), will be constant around the main peak. Fig. 2b shows the phase lag, δ, of modulation component in $\dot{E}$ from that of temperature. The phase lag is at about 180°, as is confirmed by the broken line in Fig. 1, and this relationship confirms that the response due to temperature dependence of E in Eq. (6), which is out of phase by 90°, is negligibly small compared with the response of crystallization kinetics which is in-phase, namely with $\delta = 0$ or 180°. Fig. 2c shows the results of temperature dependence of growth rate determined from the present method based on Eq. (7). The dependence keeps a constant value in the later stage of growth, where the crystallization is dominated by the growth of spherulites. The constant value is in good agreement with the result determined from the plot of linear growth rate versus crystallization temperature; the plot was obtained from a direct observation of growing spherulites by an optical microscopy [11].

Fig. 3 summarizes the results of crystallization of PE, iPP and PVDF, which clearly confirms the applicability of this method for those polymers. The rather large error bars are due to the scattering of the values in the course of crystallization around the crystallization peak. The scattering must be due to the long sampling interval (12 s) of the data and to the long period of modulation in temperature, which is limited by the experimental setup with the temperature control of the furnace and introduces the change in $\dot{\tilde{E}}$ even in a single period of modulation.

5. Conclusion

In the present paper, we have examined the application of the method of "periodically modulated driving force" to the kinetics of crystallization of polymers monitored by a dynamic visco-elastic measurement with temperature modulation. For the crystallization kinetics, the present method gives us a useful information about the temperature dependence of growth rate, from which we can determine a surface free energy for the nucleation process. The method is applicable even if the observed physical quantity exhibits strong nonlinearity in its dependence on the degree of transformation, as in the case of elastic modulus on crystallization. In principle, the modulation in driving force does not need to be temperature and can be pressure or applied electric field in other transitions. Further examination of the applicability will be required for those systems.

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