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Steady-state process and time-dependent effects in non-isothermal crystallization of poly(vinylidene fluoride)

Paweł Sajkiewicz[1]

Polish Academy of Sciences, Institute of Fundamental Technological Research, 21 Świętokrzyska St., 00-049 Warszawa, Poland

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Abstract

Non-isothermal crystallization of poly(vinylidene fluoride) during cooling at various rates was investigated by differential scanning calorimetry (d.s.c.). The data were analysed with the new model of non-isothermal crystallization developed by Ziabicki. The application of this model to experimental data allows separate determination of the rate of steady-state crystallization and the effect of time-dependent mechanisms. It was shown that the measured crystallization rate is higher than the rate of the steady-state process. It is probable that the accelerating factor is the athermal mechanism predicted by Ziabicki's model. The analysis presented of non-isothermal crystallization data gives the possibility of determining the steady-state crystallization rates over the whole temperature range of the crystallization process. The previous method of determination of crystallization rate from isothermal measurements applied to polymers with high crystallization rate, like poly(vinylidene fluoride) or polyethylene, can provide data only for a narrow temperature range lying at the end of the upper branch of the crystallization curve. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Early models of the kinetics of non-isothermal crystallization [1–4] considered variation of the crystallization rate, K, with time only as a result of the variation of external conditions (temperature, pressure, etc.). The crystallization rate was assumed to follow instantaneously varying external conditions.

The new model of non-isothermal crystallization developed recently by Ziabicki [5,6] assumes the direct dependence of crystallization rate K on time as a result of two additional time-dependent effects. First, relaxation effects cause some lag of variation of crystallization behind the changes of external conditions, giving rise to retardation of crystallization. This effect modifies that part of crystallization which is controlled by thermal nucleation. The second, athermal effect, is proportional to the rate of change of external conditions. If the rate of change of external conditions is relatively high in comparison with the relaxation time, the new criterion of a stable nucleus is applied to the old structure transferred from previous conditions. In this way part of the sub-critical nuclei can become stable under the new conditions.

The total crystallization rate, K, can be presented as the sum of thermal, K_{th}, and athermal, K_{ath}, crystallization rates [5,6]:

$$K(t) = K_{\mathrm{th}}(t) + K_{\mathrm{ath}}(t) = K_{\mathrm{th}}\left[1 + \dot{N}_{\mathrm{ath}}/\dot{N}_{\mathrm{th}}\right]^{1/m} = K_{\mathrm{th}}\left[1 - B_{\mathrm{ath}}\dot{T}\right]^{1/m} \tag{1}$$

where $\dot{N}_{\mathrm{th}}$ and $\dot{N}_{\mathrm{ath}}$ are thermal and athermal nucleation rate, respectively; m is the Avrami exponent; and B_{ath} is the athermal function.

It was shown [7] that in the case of constant cooling or heating rates, $\dot{T}$, thermal crystallization rates can be expanded in series to yield

$$K_{\mathrm{th}}[t, T(t)] = K_{\mathrm{st}}[T(t)]\left[1 + A_1\dot{T} + A_2\dot{T}^2 + A_3\dot{T}^3 + \dots\right] \tag{2}$$

with

$$A_1 = -\tau\left(\partial \ln K_{\mathrm{st}}/\partial T\right) \tag{2a}$$

$$A_2 = -\tau^2\left[\frac{1}{K_{\mathrm{st}}}\left(\partial^2 K_{\mathrm{st}}/\partial T^2\right) + \left(\partial \ln K_{\mathrm{st}}/\partial T\right)(\partial \ln \tau/\partial T)\right] \tag{2b}$$

$$A_3 = -\tau^3\left\{\frac{1}{K_{\mathrm{st}}}\left(\partial^3 K_{\mathrm{st}}/\partial T^3\right) + \frac{3}{K_{\mathrm{st}}}\left(\partial^2 K_{\mathrm{st}}/\partial T^2\right)(\partial \ln \tau/\partial T) + \left(\partial \ln K_{\mathrm{st}}/\partial T\right)\left[\left(\partial^2 \ln \tau/\partial T^2\right) + 2\left(\partial^2 \ln \tau/\partial T^2\right)\right]\right\} \tag{2c}$$

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[1] Tel.: + 48-22-8261281 ext. 148; fax: + 48-22-8269815.

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It is seen from Eq. (2) that the thermal crystallization rate K_{th} contains the steady-state crystallization rate, K_{st}, modified by the relaxation effect. The analysis of Eq. (2) shows that the relaxation effect can either increase or reduce the rate of non-isothermal crystallization depending on the actual temperature. In the case of cooling ($\dot{T} < 0$), the crystallization rate is reduced by the relaxation mechanism for temperatures above the temperature of the maximum steady-state crystallization rate ($\partial \ln K_{\mathrm{st}}/\partial T < 0$). If the temperature is lower than the temperature of the maximum steady-state crystallization rate ($\partial \ln K_{\mathrm{st}}/\partial T > 0$), the total crystallization rate during cooling should be increased by the relaxation mechanism over the rate of the steady-state process.

In the case of athermal correction, it can also be expanded in a series to yield [7]

$$\left[1 - B_{\mathrm{ath}}\dot{T}\right]^{1/m} = 1 + B_1\dot{T} + B_2\dot{T}^2 + B_3\dot{T}^3 + \ldots \tag{3}$$

with

$$B_1 = -B_{\mathrm{ath}}/m \tag{3a}$$

$$B_2 = (1-m)\cdot B_{\mathrm{ath}}^2/m^2 \tag{3b}$$

$$B_3 = (1-m)(1-2m)B_{\mathrm{ath}}^3/m^3 \tag{3c}$$

The athermal mechanism is expected to accelerate crystallization rate over the whole temperature range.

Substitution of both corrections for constant cooling rates (Eqs. (2) and (3)) into Eq. (1) yields an equation for crystallization rate in the form [7]

$$K[t, T(t)] = K_{\mathrm{st}}\left[1 + \left(A_1 + B_1\right)\dot{T} + \left(A_2 + B_2 + A_1B_1\right)\dot{T}^2 + \ldots\right] \tag{4}$$

Constant cooling or heating rate allows integration of the crystallization rate over temperature instead of time. The equation for the non-linear measure of crystallinity, P, used in Ziabicki's model [5,6]

$$P = [-\ln(1-x)]^{1/m} \tag{5}$$

where x is volume fraction of crystallinity and m is the Avrami exponent, assumes the following form

$$\begin{aligned} P(t) \rightarrow P[T(t)] &= \frac{1}{\dot{T}}\int_{T(0)}^{T(t)} K(T')\,\mathrm{d}T' \\ &= \frac{1}{\dot{T}}\int_{T(0)}^{T(t)} K_{\mathrm{st}}(T')\left\{1 + \left[A_1(T') + B_1(T')\right]\dot{T}\right. \\ &\quad \left. + \left[A_2(T') + B_2(T') + A_1(T')B_1(T')\right]\dot{T}^2\right\}\mathrm{d}T' \end{aligned} \tag{6}$$

Eq. (6) can be rearranged to the form (7), which is convenient for the analysis of experimental data

$$\begin{aligned} P[T(t)]\dot{T} &= \int_{T(0)}^{T(t)} K(T')\,\mathrm{d}T' = \int_{T(0)}^{T(t)} K_{\mathrm{st}}(T')\,\mathrm{d}T' \\ &\quad + \dot{T}\int_{T(0)}^{T(t)} \left[A_1(T') + B_1(T')\right]K_{\mathrm{st}}(T')\,\mathrm{d}T' + \ldots \end{aligned} \tag{7}$$

It is evident from Eq. (7) that the total crystallization rate is determined by the part related to the stationary process and the part containing non-stationary modifications.

In the present work our experimental results of non-isothermal crystallization during cooling were analysed with the new model of non-isothermal crystallization developed by Ziabicki. The purpose of this work is to determine the steady-state crystallization rate from non-isothermal measurements and to assess the significance of time-dependent effects during non-isothermal crystallization.

2. Experimental

2.1. Material

Poly(vinylidene fluoride) (PVDF), Kynar 880 N manufactured by Pennwalt, was investigated. According to our data, its weight-average molecular weight, M_{w}, is 400 000, the number-average molecular weight, M_{n}, is 149 000, and the content of head-to-head units is 5.2%.

2.2. Method

Non-isothermal crystallization during cooling with constant rates was investigated by differential scanning calorimetry (d.s.c.) (Perkin–Elmer DSC-7). The instrument was calibrated during heating of indium at a rate of 10°C min^{-1}. Samples were melted at 220°C for 10 min and then cooled at a constant rate to 0°C. Ten different cooling rates between 2 and 45°C min^{-1} were applied. A flow of nitrogen through the calorimeter cell was applied during the whole experiment. The weight of the samples was between 16 and 18 mg. The data were additionally corrected for the temperature lag between the sample and the furnace according to the method proposed by Janeschitz-Kriegl et al. [8,9]. The temperature of the furnace, $T_{\mathrm{f}}(t)$, was converted into internal temperature in the sample, $T(t)$, by using [9]

$$T(t) = T_{\mathrm{f}}(t) - \frac{\dot{T}}{\alpha} + \frac{\Phi(t)}{\gamma} \tag{8}$$

where $\dot{T}$ is the applied cooling rate ($=\dot{T}_{\mathrm{f}}$), γ is an effective heat transfer coefficient, Φ is the heating power, and α is given by

$$\alpha = \frac{\gamma}{m_{\mathrm{p}}c_{\mathrm{p}} + m_{\mathrm{s}}c_{\mathrm{s}}} \tag{9}$$

where m_{p} and m_{s} are the masses of the pan and of the sample, and c_{p} and c_{s} are the corresponding heat capacities.

Evaluation of experimental data is based on the comparison of crystallinities, P, found at the same final temperature, $T(t)$, at different but constant cooling rates, $\dot{T}$.

The non-linear measure of crystallinity P at the final temperature $T(t)$ was calculated with Eq. (5) and assuming

$m = 3$. The absolute values of crystallinity, x, necessary to calculate P were determined from d.s.c. thermograms using the equation

$$x = \frac{\int_{T(t)}^{T_\mathrm{m}} \left(\frac{\mathrm{d}Q/\mathrm{d}t}{\mathrm{d}T'/\mathrm{d}t} \right) \mathrm{d}T'}{m \Delta H_\mathrm{c}} \quad (10)$$

where $\mathrm{d}Q/\mathrm{d}t$ is the rate of evolution of crystallization heat which, after dividing by cooling rate, $\mathrm{d}T'/\mathrm{d}t$, is integrated in the temperature range above $T(t)$; m is the sample mass; and ΔH_c is the enthalpy difference per unit mass between amorphous and completely crystalline polymer, assumed to be 104.5 J g^{-1} [10].

According to Ziabicki's model, the experimental analysis of non-isothermal crystallization during cooling from a melt is based on a plot of $P \cdot \dot{T}$ versus $\dot{T}$ determined for various final temperatures, $T(t)$. In the case of cooling from the melt, the starting temperature, $T(0)$, is higher than the upper crystallization temperature, $T(t)$, at time t, and Eq. (7) is written in the form [7]:

$$P[T(t)]\dot{T} = -\int_{T(t)}^{T(0)} K(T')\,\mathrm{d}T' = -\int_{T(t)}^{T(0)} K_\mathrm{st}(T')\,\mathrm{d}T' - \dot{T} \int_{T(0)}^{T(t)} \left[A_1(T') + B_1(T')\right] K_\mathrm{st}(T')\,\mathrm{d}T' + \ldots \quad (11)$$

We analysed the plot of $-P \cdot \dot{T}$ against $-\dot{T}$. The intercept

$$\lim_{\dot{T} \to 0} \left(-\dot{T} \cdot P \right) = \int_{T(t)}^{T(0)} K_\mathrm{st}(T')\,\mathrm{d}T' \quad (12)$$

yields the integral of the steady-state crystallization rate taken from a given temperature $T(t)$ to the upper limit of crystallization $T(0)$. Differentiation of the intercept with respect to the end temperature allows determination of the steady-state crystallization rate, $K_\mathrm{st}(T)$

$$K_\mathrm{st}(T) = -\frac{\mathrm{d}}{\mathrm{d}T} \lim_{\dot{T} \to 0} \left(-\dot{T} \cdot P \right) \quad (13)$$

The initial slope

$$\lim_{\dot{T} \to 0} \mathrm{d}\left(-\dot{T} \cdot P\right)/\mathrm{d}\left(-\dot{T}\right) = -\int_{T(t)}^{T(0)} \left[A_1(T') + B_1(T')\right] K_\mathrm{st}(T')\,\mathrm{d}T' \quad (14)$$

is controlled by the sum of relaxation and athermal effects. The sum of $A_1(T) + B_1(T)$ is determined by differentiation of the initial slope and division by the previously determined steady-state crystallization rate [7]

$$A_1(T) + B_1(T) = \frac{\frac{\mathrm{d}}{\mathrm{d}T} \lim_{\dot{T} \to 0} \mathrm{d}\left(-\dot{T} \cdot P\right)/\mathrm{d}\left(-\dot{T}\right)}{K_\mathrm{st}(T)} \quad (15)$$

3. Results

Fig. 1 shows typical d.s.c. thermograms obtained at various cooling rates. The analysed exothermic peak of crystallization occurs in the temperature range between 147°C and 80°C. Below 70°C an additional small exothermic peak is registered. This low-temperature peak was observed previously during cooling and heating of PVDF [11,12]. The mechanism of this additional transition is not yet well understood. It was analysed as an endothermic phenomenon, a c_p jump, or both. Our analysis will be applied only to main crystallization occurring at higher temperatures.

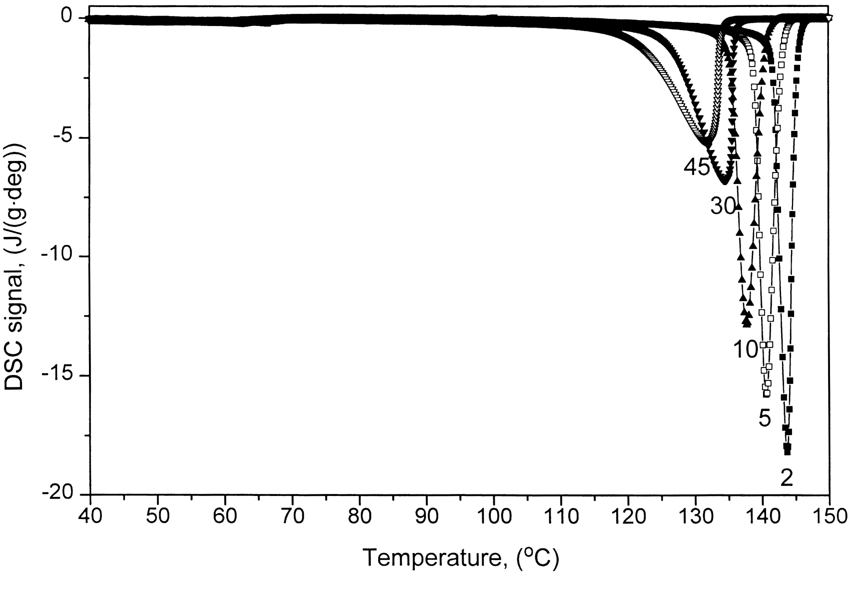

Fig. 1. D.s.c. thermograms for various cooling rates. Cooling rates indicated are in °C min^{-1}.

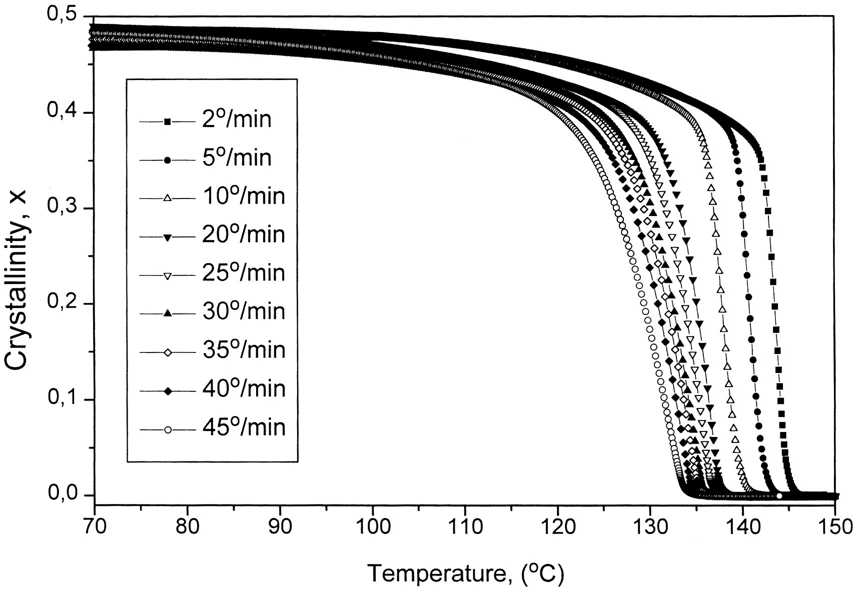

Fig. 2. Crystallinity x from d.s.c. thermograms versus temperature during cooling with various rates.

Fig. 2 illustrates an increase of crystallinity x during cooling at various rates. It is seen that crystallization starts earlier the lower cooling rate. The final crystallinity is very weakly affected by cooling rate.

Fig. 3 shows the dependences of the product $-P\cdot\dot{T}$ on $-\dot{T}$ determined for various final temperatures, $T(t)$. It is seen that the initial slope is always positive. For low final temperatures there is linear relationship between the product $-P\cdot\dot{T}$ and $-\dot{T}$ over the whole range of cooling rates investigated. For higher final temperatures the dependence of $-P\cdot\dot{T}$ on $-\dot{T}$ is non-linear with negative curvature.

Figs 4 and 5 show the intercept and the initial slope of the plot of $-P\cdot\dot{T}$ versus $-\dot{T}$ as a function of final temperature. Considering the non-linearity of the plot of $-P\cdot\dot{T}$ versus $-\dot{T}$ evident in Fig. 3, the intercept and the initial slope were determined by extrapolation from the data in the range of cooling rates between 2 and 15°C min^{-1} by using a third-order polynomial. Before extrapolation, the plot of $-P\cdot\dot{T}$ versus $-\dot{T}$ was numerically interpolated. It is seen in Fig. 4 that the intercept decreases with increasing temperature. Differentiation of the intercept with respect to temperature according to Eq. (13) yields the steady-state crystallization rate, K_{st} (Fig. 6).

Fig. 7 shows the temperature dependence of the sum of relaxation and athermal effects, determined from Eq. (15) by differentiation of the initial slope and division by the steady-state crystallization rate. It is seen that the sum of relaxation and athermal effects is negative for the whole

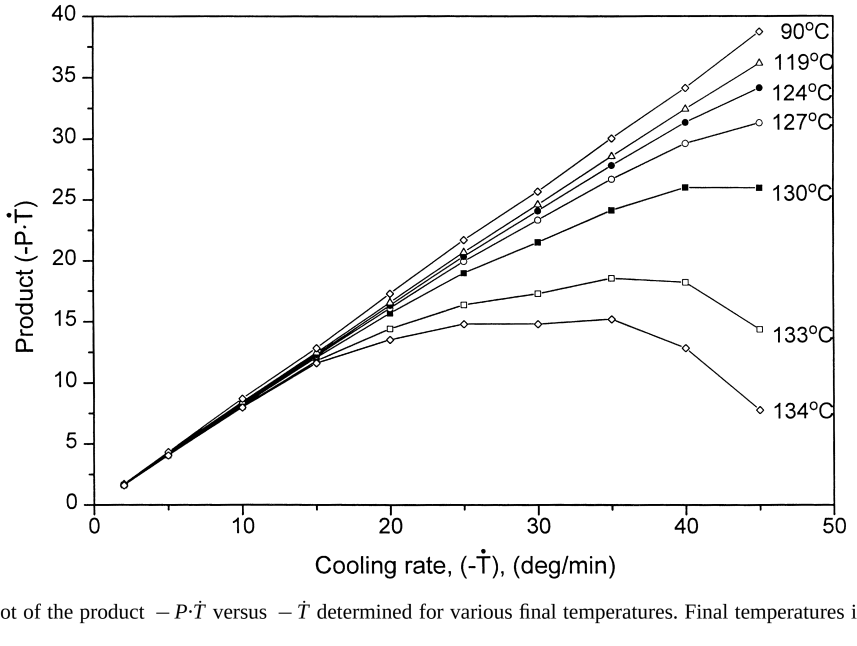

Fig. 3. Plot of the product $-P\cdot\dot{T}$ versus $-\dot{T}$ determined for various final temperatures. Final temperatures indicated.

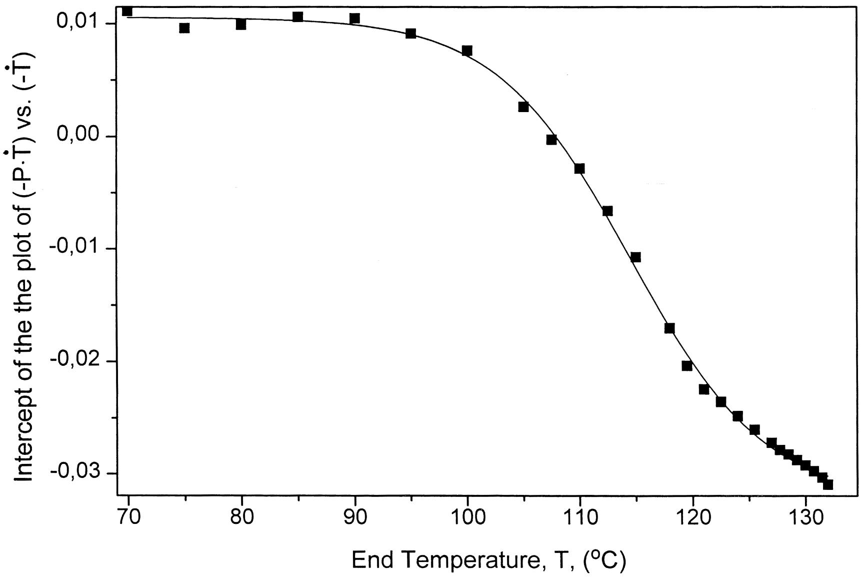

Fig. 4. The intercepts of the plot of the product $-P{\cdot}\dot{T}$ versus $-\dot{T}$ determined for various final temperatures.

process of crystallization. According to Eq. (4), a negative value of the sum $A_1 + B_1$ during cooling ($\dot{T} < 0$) indicates that crystallization rate is increased by time-dependent effects over the steady-state rate.

From the fact that crystallization rate is increased by time-dependent effects, it is expected that crystallization rate measured at a particular cooling rate (total effect) should be higher that the pure steady-state rate. Fig. 8 shows the crystallization rate determined for various cooling rates as a function of temperature. Crystallization rate, K, at particular cooling rate, $\dot{T}$, was determined from experimental data using the equation

$$K(T,\dot{T}) = -\frac{\mathrm{d}(-\dot{T}{\cdot}P)}{\mathrm{d}T} \tag{16}$$

It is seen in Fig. 8 that crystallization rate measured at a particular non-zero cooling rate is higher than the steady-state value and increases with cooling rate. Moreover, it is seen that the acceleration of crystallization due to application of a non-zero cooling rate increases with temperature. The increase of crystallization rate caused by application of non-zero cooling rate is so strong that, at a cooling rate of 5°C min^{-1}, the measured crystallization rate, K, increases continuously with temperature without any local maximum coming from the steady-state crystallization curve.

4. Discussion

According to Ziabicki's model, non-isothermal

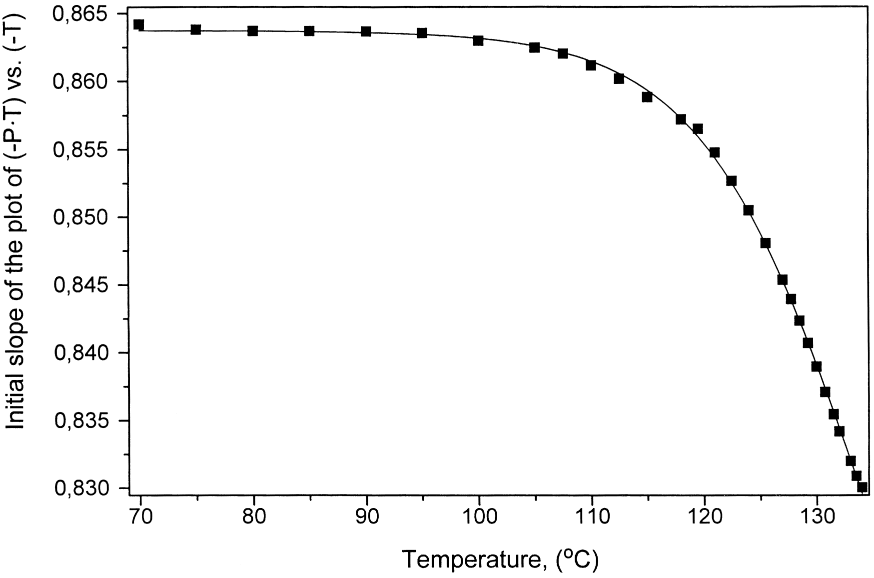

Fig. 5. Initial slopes of the plot of the product $-P{\cdot}\dot{T}$ versus $-\dot{T}$ determined for various final temperatures.

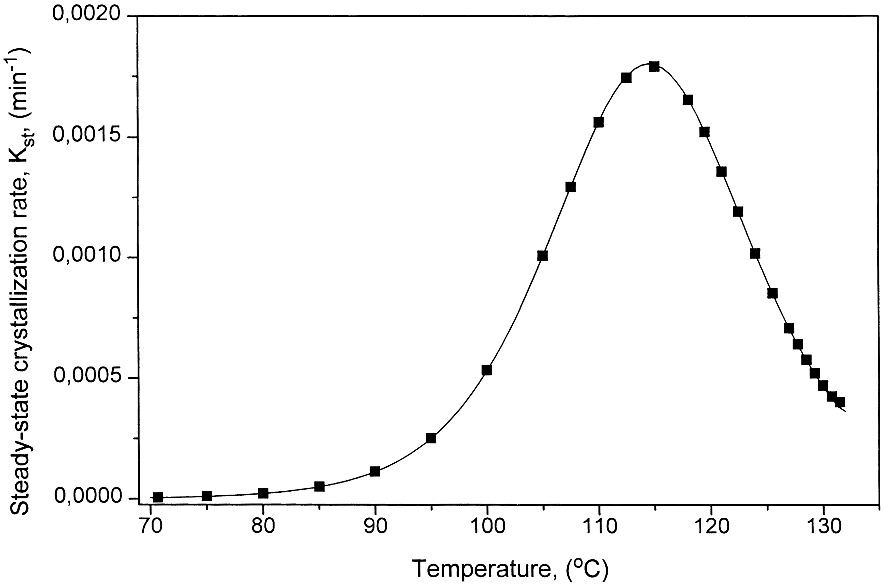

Fig. 6. Steady-state crystallization rate versus temperature.

crystallization can be described as a process composed of steady-state crystallization and a part which is time-dependent. Ziabicki predicts that two time-dependent mechanisms, relaxational and athermal, affect crystallization rate.

Application of this model to experimental data of non-isothermal crystallization allows determination of the steady-state crystallization rate and the sum of both time-dependent effects separately. Steady-state crystallization rate is determined from the intercept, and the sum of time-dependent effects from the initial slope of the plot of the product $P \cdot \dot{T}$ versus $\dot{T}$, where the P is a non-linear measure of crystallinity and $\dot{T}$ is the rate of temperature change, determined experimentally for various final temperatures. Our results show that the applied procedure provides the rate of steady-state crystallization over the wide temperature range of the crystallization process. It should be noted that the available kinetic results from isothermal crystallization of polymers with relatively high crystallization rate like polyethylene, polypropylene or PVDF, provide data only for a very narrow temperature range lying at the end of the upper branch of the crystallization curve. Therefore, in the case of fast crystallizing polymers, it is impossible to compare in a reliable way the steady-state crystallization rate determined from a non-isothermal process with the rate of isothermal crystallization. For PVDF with relatively high molecular weight, such as Kynar 880 N investigated here, it is very difficult to perform isothermal crystallization

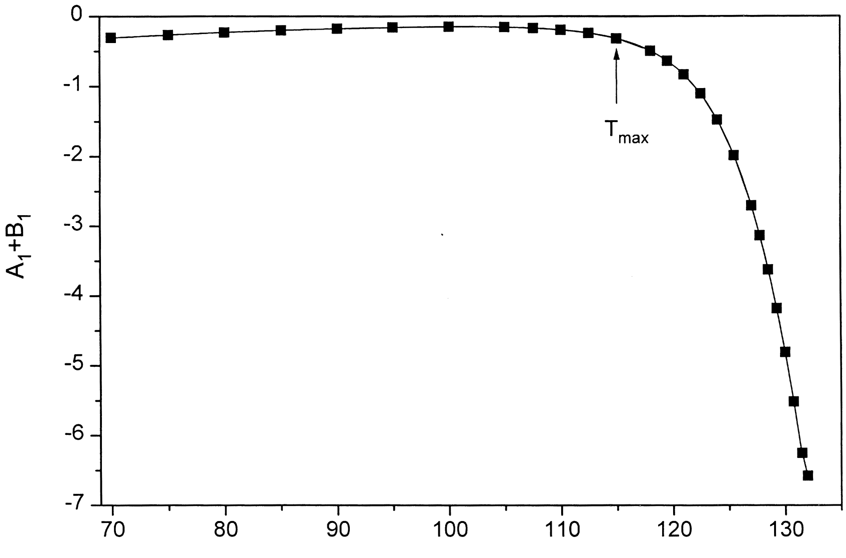

Fig. 7. The sum of relaxation and athermal effects as a function of temperature.

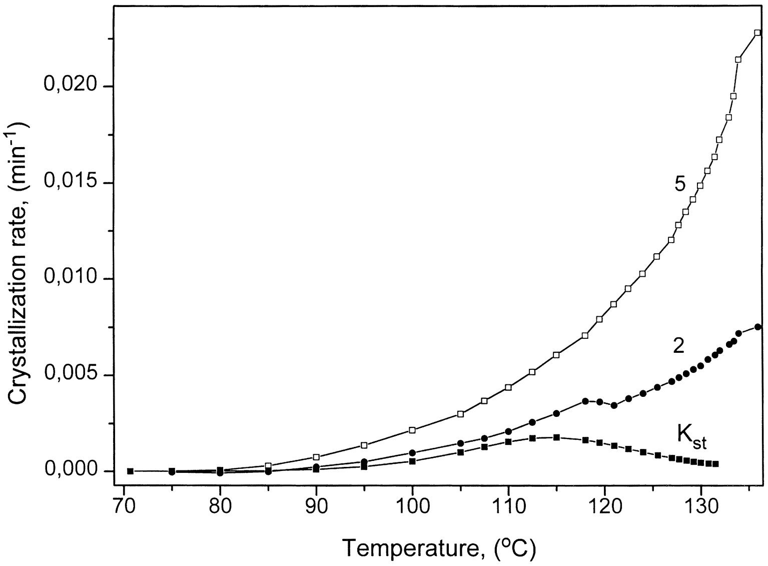

Fig. 8. Crystallization rates measured experimentally for various cooling rates as a function of temperature. Steady-state crystallization rate from Fig. 6 is presented.

below 150°C without earlier crystallization during cooling. Fig. 9 shows a comparison of the rate of the steady-state process determined by us from non-isothermal experiments with the rate measured during isothermal crystallization by Mancarella and Martuscelli [13]. According to [14], the molecular weight, M_w, of PVDF Kynar 301 crystallized isothermally by Mancarella and Martuscelli [13] is 39 000, being much lower than that of polymer used in our experiments. According to [15], crystallization of PVDF becomes slower with decreasing molecular weight, enabling therefore the extension of isothermal measurements towards lower temperatures. It is seen in Fig. 9 that the crystallization rate measured from isothermal experiments in [13] is similar to the rate of the steady-state process only for temperatures above 140°C. Below 140°C, crystallization rates obtained from isothermal measurements are much higher than the rates of the steady-state process determined from our procedure. Considering the effect of molecular weight on the crystallization rate of PVDF [15], it is expected that the difference between the rate measured isothermally and that of the steady-state process determined from non-isothermal experiments would be even higher. Moreover, it should be mentioned that high cooling rates are commonly applied for reaching the isothermal stage; in the case of PVDF investigated by Mancarella and Martuscelli [13], a cooling rate of 320°C min^{-1} was applied. It can not be

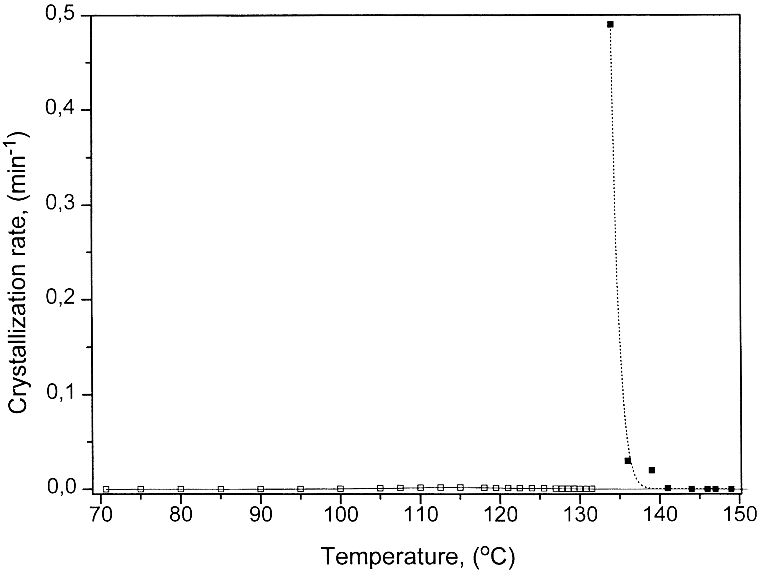

Fig. 9. Crystallization rate of PVDF measured during the isothermal process [13] (■) and the rate of the steady-state process determined from non-isothermal experiments (□).

excluded that the isothermal crystallization is indeed not a stationary process due to the high cooling rate applied before the isothermal stage.

We found relatively good agreement between the temperature of the maximum rate of steady-state crystallization of the PVDF investigated and the value predicted by Okui [16] on the basis of the empirical relationship between the maximum rate of crystallization and equilibrium melting temperature. Putting $T_m^\circ = 481.3$ K as the equilibrium melting temperature of α phase with 0% content of head-to-head defects [17], and the temperature of the maximum rate of steady-state crystallization determined by us as $T_{max} = 388.2$ K, we get the ratio of $T_{max}/T_m^\circ = 0.806$, which lies in the range between 0.76 and 0.89 observed by Okui [16] for several polymers.

Our experimental data indicate that the rate of non-isothermal crystallization of poly(vinylidene fluoride) is strongly affected by time-dependent effects. Ziabicki [5,6] predicts two time-dependent effects which could either accelerate or decelerate non-isothermal crystallization over the rate of the steady-state process. In the first mechanism, a relaxation effect causes a lag of crystallization behind the changes of external conditions. The second effect has athermal nature and causes the acceleration of non-isothermal crystallization during cooling due to a decrease of the size of critical nuclei in the system with relatively invariant distribution of nucleus size. This effect is proportional to the rate of change of external conditions. We found that the sum ($A_1 + B_1$) of both time-dependent mechanisms is negative over the whole range of crystallization temperatures. It is seen from Eq. (4) that a negative value of the sum $A_1 + B_1$ in the case of cooling ($\dot{T} < 0$) indicates that crystallization rate is increased by time-dependent effects over the steady-state rate ($K > K_{st}$). This fact is supported by direct comparison of the steady-state crystallization rate and the total rate measured experimentally at a particular cooling rate.

The rate of crystallization measured experimentally by d.s.c. at various cooling rates is much higher than the rate of the steady-state process. The importance of both factors, relaxation and athermal, for acceleration of crystallization rate can be discussed with reference to Eqs. (2) and (3). The analysis of Eqs. (2) and (3) indicates that for temperatures lying below the temperature of the maximum rate of the steady-state process ($\partial \ln K_{st}/\partial T > 0$), the crystallization rate during cooling ($\dot{T} < 0$) can be increased by both time-dependent effects, relaxation and athermal. When the temperature of the polymer during cooling is above the temperature of the maximum rate of the steady-state process ($\partial \ln K_{st}/\partial T < 0$, $\dot{T} < 0$), the athermal mechanism solely is responsible for acceleration of the crystallization process over the rate of the steady-state process. As is seen from Eq. (2), in the temperature range above the temperature of the maximum rate of crystallization, the relaxation mechanism during cooling causes a decrease of the crystallization rate below the rate of the steady-state process. From the above it can be concluded that the acceleration of crystallization (negative sign of the sum of relaxation and athermal effects) found by us above the temperature of the maximum rate of the steady-state process indicates the domination of athermal effects over the relaxation mechanism. Our results show that the acceleration of crystallization by the athermal factor is stronger the higher the cooling rate and temperature. This observation corresponds with theoretical predictions of Ziabicki's model [5–7].

However, at the end of the analysis of time-dependent effects, we should like to comment that in the light of the theoretical model it is slightly surprising that the athermal effect is so strong at the cooling rates investigated (below 45°C min^{-1}). According to the theory, the athermal effects should be visible at much higher rates than applied in our experiments. Therefore is not excluded that some other mechanisms, which are not predicted by Ziabicki's model, are also involved in the observed acceleration of the non-isothermal crystallization.

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