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A STUDY OF THE CRYSTALLIZATION KINETICS OF PVF_2 BY DSC AND DILATOMETRY

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ABSTRACT

Poly(vinylidene fluoride) was crystallized isothermally from the melt at several temperatures. Crystallization rates have been measured using dilatometry and differential scanning calorimetry. The results were analysed in terms of the Avrami equation. The different methods yielded similar values for the kinetic parameters. The surface free energy of the lamellar crystallites has been determined.

INTRODUCTION

Poly(vinylidene fluoride) PVF_2 has interesting scientific and technological properties. The polymer exhibits piezoelectric and pyroelectric effects, nonlinear optical susceptibility, and an unusually high dielectric constant. A number of studies relating to its structure and physical properties have been made. However, detailed studies on its isothermal crystallization kinetics are lacking. Such studies are important both from the fundamental and technological points of view. Only one [1] such study has been reported in the literature. The authors of this investigation employed the conventional calorimetric method using a DSC. As discussed in an earlier publication [2], the calorimetric method employed by Mancarella and Martuscelli [1] has only a limited applicability. Their results refer only to short half-crystallization times or a large degree of undercooling. Therefore, an extension of these measurements to longer half-crystallization times is in order. The present paper reports results on the crystallization kinetic parameters of PVF_2 as obtained from dilatometry and the two calorimetric methods: (a) the conventional method; and (b) the new method reported earlier [2].

The surface free energy of lamellar crystallites of PVF_2 in the α-form has also been determined.

EXPERIMENTAL

The PVF_2 sample used in the present study was obtained from Poly Science Inc., U.S.A. The number average molecular weight of the polymer used was 1.7×10^5. The sample granules had a melting point of 434 K. The amount of head-to-head structure was estimated to be about 6% [3].

The calorimetric measurements were performed using a Perkin-Elmer differential scanning calorimeter (model DSC-1B). The temperature scale of the instrument was calibrated against the melting temperature of indium.

The design of the dilatometer used in the present work is described elsewhere [3].

ISOTHERMAL CRYSTALLIZATION

The isothermal crystallization was carried out either in a dilatometer or in the sample can of the DSC. In both cases, the sample of PVF_2 was first melted and kept at a temperature of 460–470 K in order to destroy any traces of crystallinity. Subsequently, the sample was cooled rapidly to the predetermined crystallization temperature. In the dilatometric method, the height of the mercury meniscus was recorded as a function of time. In the conventional calorimetric method, one generally measures the rate of evolution of heat during crystallization. The exotherm is recorded as a function of time until it returns to the original baseline position. The area under this curve from the start of the crystallization up to a given time is a measure of the extent of crystallinity developed in the sample. Such exotherms were recorded for various crystallization temperatures. Details of the new calorimetric method employed are given elsewhere [2]. In this method, the isothermal crystallization was terminated at a predetermined time by cooling the sample rapidly. The cooling curve was recorded. The area under the crystallization peak was then determined. This area is proportional to the fraction of the sample which remained uncrystallized at the termination of crystallization. At each crystallization temperature this procedure was repeated for different crystallization times.

ANALYSIS OF THE CRYSTALLIZATION ISOTHERMS

The time dependence of crystallization can be represented by the Avrami equation [4]

$$1 - v_c = \exp(-Zt^n) \tag{1}$$

where v_c is the crystalline fraction at any time t, Z is the rate constant, and n is the Avrami exponent. To analyse any experimental data, it is convenient to express eqn. (1) in the form

$$1-\frac{X_t}{X_\infty}=\exp(-Zt^n) \tag{2}$$

where X_t and X_∞ are the weight fractions of the crystallized material at time t and at an infinitely long time, respectively. Equation (2) can further be written as

$$\log\left[-\ln\left(1-\frac{X_t}{X_\infty}\right)\right]=n\log t+\log Z \tag{3}$$

This equation is used to determine the Avrami exponent, n. The rate constant, Z, is then calculated from the half-crystallization time, $t_{1/2}$, using the relation

$$Z=\frac{0.693}{t_{1/2}^n} \tag{4}$$

In the dilatometric method eqn. (3) takes the form

$$\log\left[-\ln\left(\frac{h_t-h_\alpha}{h_0-h_\infty}\right)\right]=n\log t+\log Z \tag{5}$$

where h_0, h_t and h_∞ are the heights of the mercury column at times equal to zero, t and ∞, respectively.

In the conventional calorimetric method, as the DSC measures the rate of evolution of heat, $\mathrm{d}H/\mathrm{d}t$, during crystallization, it follows that

$$\frac{X_t}{X_\infty}=\frac{\int_0^t\left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t}{\int_0^\infty\left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t} \tag{6}$$

This equation, in conjunction with eqn. (3), can be used to analyse the data obtained.

In the calorimetric method suggested in ref. 2, eqn. (3) can be written as

$$\log\left[-\ln\left(\frac{A_t-A_\infty}{A_0-A_\infty}\right)\right]=n\log t+\log Z \tag{7}$$

where A_0, A_t and A_∞ are the areas under the crystallization peaks corresponding to crystallization times equal to zero, t and ∞, respectively.

The data obtained from the three methods have been analysed by making use of eqns. (3), (5), (6) and (7).

RESULTS AND DISCUSSION

The progress of crystallization in PVF_2 was followed by the three methods as mentioned earlier. The crystallization isotherms obtained by the dilato-

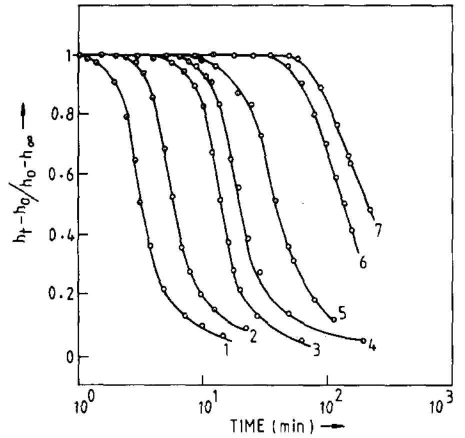

Fig. 1. Crystallization isotherms at different crystallization temperatures for PVF_2 as obtained from the dilatometric method: $T_c = 420(1)$, $422(2)$ $424(3)$, $426(4)$, $428.5(5)$, $430(6)$ and 431 K(7).

metric and the new calorimetric methods are shown in Figs. 1 and 2. The corresponding Avrami plots are shown in Figs. 3 and 4. The values of the kinetic parameters, n and $t_{1/2}$ obtained by the three methods are given in Table 1. The three sets of values agree well with each other. As observed for several other polymers, the Avrami exponent, n, for PVF_2 is also found to be independent of the crystallization temperature having an average value of 3.1. The dependence of $t_{1/2}$ upon the crystallization temperature is shown in Fig. 5. The agreement between the results obtained from the three different methods is evident from this figure. In the calculation of the rate constant, Z, from eqn. (4), the average value of the Avrami exponent, n, has been used. The values of Z for various crystallization temperatures as obtained from the three methods are also given in Table 1.

The results on the kinetic parameters obtained in the present investigation

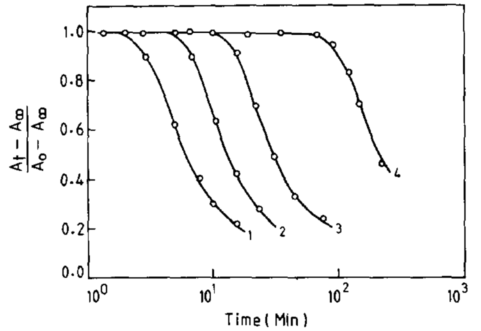

Fig. 2. Crystallization isotherms at different crystallization temperatures for PVF_2 as obtained from the calorimetric method based on the area under the crystallization peak: $T_c = 422(1)$, $424(2)$, $428(3)$ and 431 K(4).

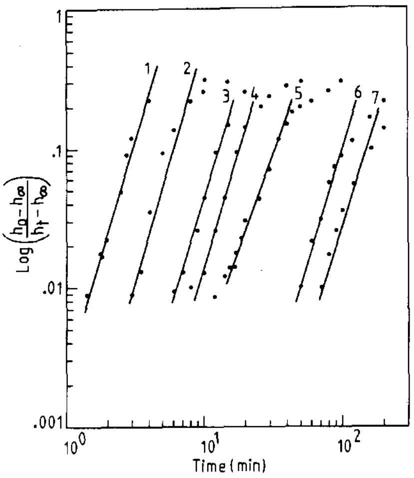

Fig. 3. Avrami plots at different crystallization temperatures as obtained from the data shown in Fig. 1. $T_c = 420(1), 422(2), 424(3), 426(4), 428.5(5), 430(6)$ and 431 K(7).

are in qualitative agreement with those reported by Manacarella and Martuscelli [1]. However, at any crystallization temperature the values of the kinetic parameters n and $t_{1/2}$ obtained in the present investigation are lower than those reported in ref. 1. This difference could possibly be due to differences in the characteristics of the two samples employed in these investigations.

According to the kinetic theory [5] for the case of spherulitic growth with chain folded lamellas where a coherent two-dimensional surface secondary nucleation process controls the radial growth of spherulites, the overall rate

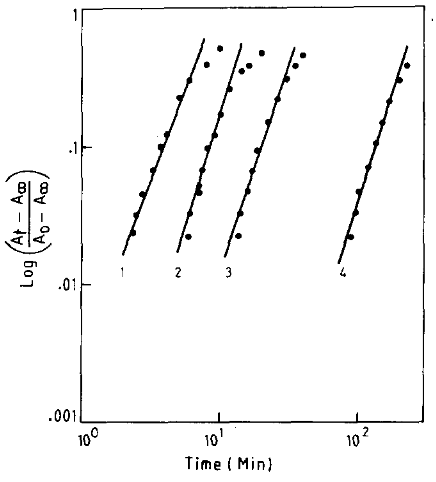

Fig. 4. Avrami plots at different crystallization temperatures as obtained from the data shown in Fig. 2. $T_c = 422(1), 424(2), 428(3)$ and 431 K(4).

TABLE 1

Values of the kinetic parameters n, Z and $t_{1/2}$ for PVF_2 obtained by three different methods

T_c (K)	n	Z ($\min^{-3.1}$)	$t_{1/2}$ (min)
(a) Dilatometric method			
420	3.3	1.88×10^{-2}	3.2
422	3.3	2.68×10^{-3}	6
424	3.2	1.94×10^{-4}	14
426	3.2	6.42×10^{-5}	20
428.5	2.9	8.78×10^{-6}	38
430	3.4	1.94×10^{-7}	130
431	3.4	$5.1\ \times10^{-8}$	200
(b) Calorimetric method (conventional)			
420	2.9	1.88×10^{-2}	3.2
424	2.9	3.12×10^{-4}	12
426	3.1	1.28×10^{-4}	16
428	2.9	1.83×10^{-5}	30
(c) Calorimetric methods (based on crystallization peak area)			
422	2.8	2.68×10^{-3}	6
424	3.2	1.57×10^{-4}	15
428	3.0	1.65×10^{-5}	31
431	3.0	$4.7\ \times10^{-8}$	205

constant, Z, may be expressed by the equation

$$\tfrac{1}{3}\log Z = A_0 - \frac{\Delta F^*}{2.3RT_c} - \frac{\Delta\phi^*}{2.3RT_c} \qquad (8)$$

where A_0 can be regarded as a constant provided the spherulite density is independent of time and melting and crystallization temperatures [6]. In this relation ΔF^* is the activation energy for the transport process across the liquid–crystal interface, $\Delta\phi^*$ is the free energy of formation of a nucleus, and

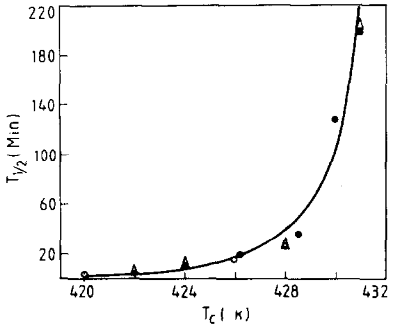

Fig. 5. Variation of $t_{1/2}$ with the crystallization temperature for PVF_2: (●) dilatometry; (○) conventional calorimetric method; (△) calorimetric method based on the area under the crystallization peak.

T_c is the crystallization temperature. $\Delta\phi^*$ is given by

$$\Delta\phi^* = \frac{4b_0\sigma\sigma_e T_m^0}{\Delta H_F \Delta T} \tag{9}$$

where σ and σ_e are the surface free energies per unit area parallel and perpendicular, respectively, to the molecular chain direction, b_0 is the distance between the adjacent fold planes, ΔH_F is the enthalpy of fusion, T_m^0 is the equilibrium melting temperature, and $\Delta T(= T_m^0 - T_c)$ is the undercooling. From eqns. (8) and (9) one gets the relation

$$\tfrac{1}{3}\log Z = A_0 - \frac{\Delta F^*}{2.3RT_c} - \frac{4b_0\sigma\sigma_e}{2.3k\Delta H_F}\,\frac{T_m^0}{T_c\Delta T} \tag{10}$$

In this equation, for the range of crystallization temperatures employed in the present investigation, the transport term $\Delta F^*/RT_c$ can be regarded as constant. Hence a plot of 1/3 log Z vs. $(T_m^0/T_c\Delta T)$ is expected to be a straight line having a slope equal to $(4b_0\sigma\sigma_e)/(2.3R\Delta H_F)$. Such a plot for the Z values corresponding to different crystallization temperatures as obtained in the present investigation is shown in Fig. 6. In drawing this plot at any crystallization temperature, an average of the Z values obtained from the three different methods has been used. The value of the equilibrium melting temperature, T_m^0, has been taken to be 451 K as obtained from a plot of T_m vs. T_c [3]. A similar value of T_m^0 was reported by Welch and Miller [7]. The slope of the straight line plot shown in Fig. 6 is found to be 111 K, using a value of 2.01×10^9 erg cm^{-3} for ΔH_F [7], the heat of fusion, and $b_0 = 4.83$ Å [8], we get a value of 367.6 erg^2 cm^{-4} for $\sigma\sigma_e$. The surface energy, σ, parallel to the chain direction is estimated to be 9.7 erg cm^{-2}. From these values for $\sigma\sigma_e$ and σ the surface energy of folding, σ_e, may be evaluated. The estimated value of σ_e from the present set of measurements is found to be 38 erg cm^{-2}.

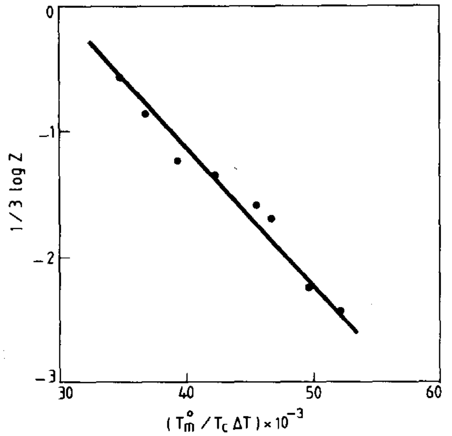

Fig. 6. A plot of 1/3 log Z vs. $T_m^0/T_c\Delta T$ for $T_m^0 = 451$ K.

This value compares well with the values of σ_e reported in the literature for other linear polymers [5,6,9,10]. However, the present value is lower than that found by Mancarella and Martuscelli [1]. This could be attributed to the higher crystallization temperatures employed in the present study. The surface energy, σ_e, is expected to decrease with increasing crystallization temperature owing to an increased chain mobility and fold-surface smoothing. Such an effect has been observed in a number of polymers [11].

As can be seen from the above discussion, the value of σ_e estimated from the crystallization kinetics strongly depends on the value of T_m^0 used. A small change in the value of T_m^0 can change the estimated value of σ_e considerably. The value of 451 K for T_m^0 seems to be more reasonable, since it has been obtained from two independent measurements. Although a higher value of 483 K for T_m^0 has also been reported in the literature [12].

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