# Crystallization kinetics of poly(vinylidene fluoride)

**Carlo Mancarella and Ezio Martuscelli**
*Laboratorio di Ricerche su Tecnologia dei Polimeri e Reologia del CNR, Via Toiano 2, Arco Felice (Napoli), Italy*

*(Received 13 June 1977; revised 21 July 1977)*

Specimens of poly(vinylidene fluoride) were crystallized isothermally at a series of temperatures in the vicinity of the melting point. The α-form was the only crystalline polymorph present in the crystallized samples. Crystallization rates have been measured by differential scanning calorimetry. The results were analysed in terms of the Avrami equation. The rates of crystallization depend upon the undercooling and the data agree with a process of growth of spherulites controlled by a secondary surface coherent nucleation mechanism. The equilibrium melting temperature, the Avrami exponent, the free energy of formation of a nucleus of critical dimensions and the surfaces free energy of the lamellar crystallites were determined.

## INTRODUCTION

Poly(vinylidene fluoride) ($PVF_2$) is a polymeric material with very interesting scientific and technological properties. The polymer is characterized by piezoelectric and pyroelectric effects, non-linear optical susceptibility and an unusually high dielectric constant[1].

Further $PVF_2$ is known to exist in at least two crystallographic forms designated form I or β, form II or α[2]. In addition to these phases, several investigators have suggested the existence of a third polymorph of $PVF_2$[3]. Form II is obtained by crystallization of $PVF_2$ from the melt either isothermally or at slow cooling. An orthorhombic unit cell, having axes $a = 9.66$ Å; $b = 4.96$ Å; $c$ (chain axis) $= 4.64$ Å has been assigned to phase II.

The unit cell contains two polymer chains and four monomer units with a density of 1.90 g/cm$^3$. The chain backbone assumes in the crystal a $2_1$ helix conformation with a $tg_+tg_-$ rotation angles sequence[1]. In the present work the kinetics of the isothermal crystallization, from the melt, and the melting behaviour of the α-form of $PVF_2$ is studied by calorimetric techniques. It seemed interesting, both from fundamental and technological points of view, to determine for this polymer quantities such as half-times of crystallization, Avrami exponents and kinetic rate constants in the vicinity of the melting point. We are also concerned to derive the values of the energy of formation of a nucleus of critical dimensions and of the surface free energy of lamellar crystallites of $PVF_2$ in form II.

## EXPERIMENTAL

### *Materials*

The sample of $PVF_2$ chosen for the present study was provided by the Pennwalt Corp. under the trade name Kynar Resin Grade 301. The sample was completely characterized by Welch[4]. The amount of head-to-head structure was stated to be approximately 5.7%.

### *Apparatus*

All the measurements were carried out using a Perkin–Elmer DSC-2 differential scanning calorimeter operating under $N_2$ atmosphere. The temperature scale was calibrated against the melting temperatures of benzoic acid, In and Sn for an individual heating rate. For the determination of the apparent enthalpy of fusion In was used as standard material.

### *Isothermal crystallization*

The sample of $PVF_2$ was first melted at 157°C and afterwards heated for 15 min to a temperature 20°C above its melting temperature in order to destroy any traces of crystallinity. Subsequently the sample was cooled rapidly using a scan rate of 320°C/min to the predetermined crystallization temperature (133°, 136°, 139°, 141°, 144°, 146°, 147°, 149°C) and the exothermic crystallization curve was recorded.

The weight fraction $X_t$ of material that can crystallize at time $t$ was calculated from the equation[5]:

$$X_t = \int_0^t \left(\frac{dH}{dt}\right) dt \bigg/ \int_0^\infty \left(\frac{dH}{dt}\right) dt$$

zero time of crystallization was taken as the time when the central light came on, indicating thermal equilibrium.

Furthermore the melting curves of the crystals formed in the isothermal crystallization were recorded in order to correlate the fusion temperature $T_m$ with the crystallization temperature $T_c$. The maximum of d.s.c. endotherm of fusion was assumed as the $T_m$ of the polymer sample. A heating rate of 20°C/min was used throughout the experiments.

## RESULTS AND DISCUSSION

The half-time $t_{1/2}$ of conversion of α-form of $PVF_2$ at various crystallization temperatures $T_c$ was determined from the crys-

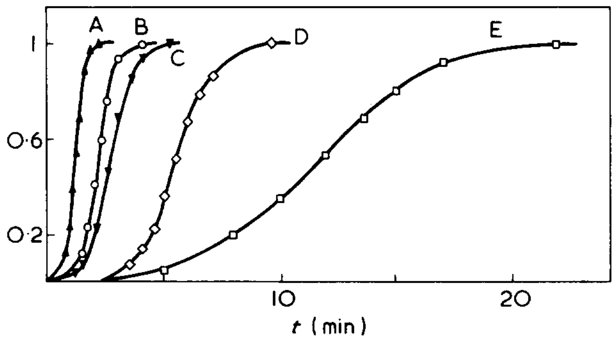

*Figure 1* Crystallization isotherms of PVF$_2$ in form II for different crystallization temperatures: A, $T_c$ = 407K; B, $T_c$ = 409K; C, $T_c$ = 412K; D, $T_c$ = 414K; E, $T_c$ = 417K

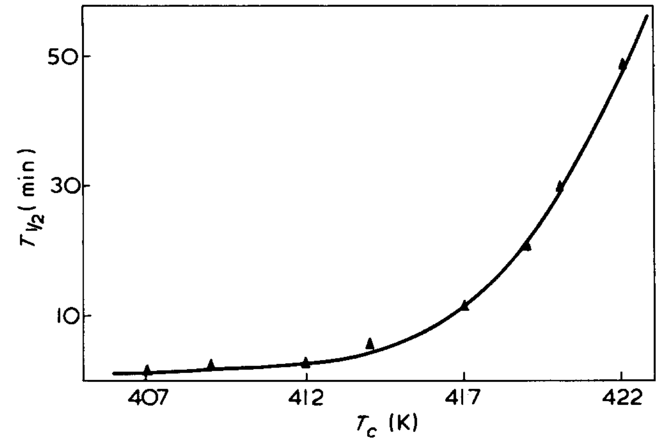

*Figure 2* Variation of $t_{1/2}$ with the crystallization temperature

tallization isotherms. Examples of such curves are reported in *Figure 1*. The dependence of $t_{1/2}$ upon the crystallization temperature is shown in *Figure 2*. As observed in all polymeric materials $t_{1/2}$ increases with $T_c$ for low undercoolings.

The kinetics of isothermal crystallization of PVF$_2$ has been quantitatively analysed by means of the Avrami equation[6]:

$$\log[-\log(1-X_t)] = n\log\frac{t}{2.3} + \log\frac{Z}{2.3} \qquad (1)$$

where $X_t$ is the weight fraction of crystallized material at time $t$, $n$ is the Avrami exponent and $Z$ the kinetic rate constant.

Avrami plots of PVF$_2$ are reported in *Figure 3*. Straight lines are obtained for all the $T_c$ examined. From the slopes of these straight lines $n$ was estimated.

The kinetic rate constant $Z$ was calculated by using the relation:

$$Z = \frac{\ln 2}{t_{1/2}^{n}} \qquad (2)$$

The values of $n$ and $Z$ for each $T_c$ are reported in *Table 1* together with the values of $t_{1/2}$. In the calculation of $Z$ we used for all $T_c$ an average value of 3.94 for $n$.

In the case of spherulitic growth with chain-folded lamellae where a coherent two-dimensional surface secondary nucleation process controls the radial growth of spherulites then the overall rate constant $Z$ may be expressed, according to the kinetic theory[7], by the following equation:

$$\frac{1}{3}\log Z = A_0 - \frac{\Delta F^*}{2.3kT_c} - \frac{\Delta\Phi^*}{2.3kT_c} \qquad (3)$$

In our analysis we assumed $A_0$ as constant, which means that the spherulite nucleus density is independent of time, melting temperature and crystallization temperature[8].

In equation (3), $\Delta F^*$ is the activation energy for the transport process across the liquid–crystal interface, and $k$ is the Boltzman constant. $\Delta\Phi^*$ is the free energy of formation of a nucleus of critical dimensions.

$\Delta\Phi^*$ is given by[7]:

$$\Delta\Phi^* = \frac{4b_0\sigma\sigma_e T_m^0}{\Delta H_F \Delta T} \qquad (4)$$

where $\sigma$ and $\sigma_e$ are the surface free energies per unit area parallel and perpendicular, respectively, to the molecular chain direction, $b_0$ is the distance between adjacent fold planes, $\Delta H_F$ is the enthalpy of fusion, $T_m^0$ is the equilibrium melting temperature and $\Delta T = T_m^0 - T_c$ is the undercooling. The combination of equations (3) and (4) leads to the equation:

$$\frac{1}{3}\log Z = A_0 - \frac{\Delta F^*}{2.3kT_c} - \frac{4b_0\sigma\sigma_e T_m^0}{2.3k\Delta H_F T_c \Delta T} \qquad (5)$$

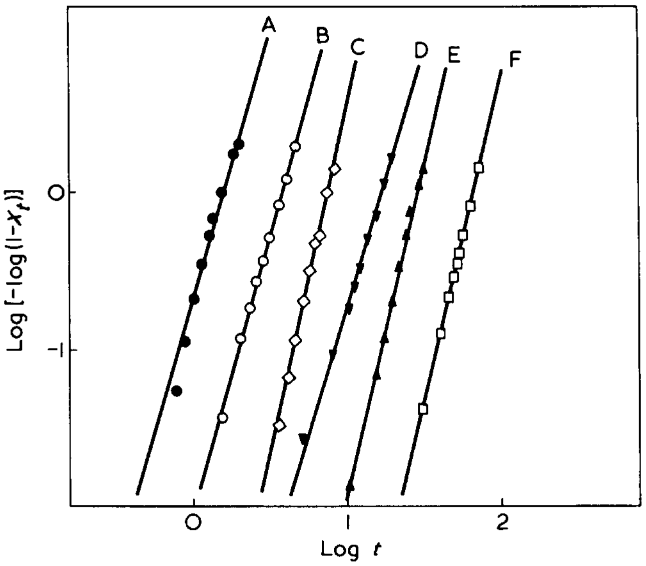

*Figure 3* Avrami plots for α-form of PVF$_2$ at various crystallization temperatures: A, $T_c$ = 407K; B, $T_c$ = 412K; C, $T_c$ = 414K; D, $T_c$ = 417K; E, $T_c$ = 419K; F, $T_c$ = 422K

*Table 1* Avrami exponent $n$, kinetic rate constant $Z$ and the half-time of conversion $t_{1/2}$ at various crystallization temperatures $T_c$

| $T_c$ (K) | $n$ | $Z$ (min$^{-3.94}$) | $t_{1/2}$ (min) |
|---|---|---|---|
| 407 | 3.82 | 0.49 | 1.09 |
| 409 | 4.62 | 0.03 | 2.15 |
| 412 | 3.62 | 0.02 | 2.60 |
| 414 | 4.60 | 87 X 10$^{-5}$ | 5.45 |
| 417 | 3.30 | 44 X 10$^{-6}$ | 11.60 |
| 419 | 4.35 | 46 X 10$^{-7}$ | 20.60 |
| 420 | 2.99 | 10 X 10$^{-7}$ | 30.00 |
| 422 | 4.23 | 15 X 10$^{-8}$ | 49.00 |

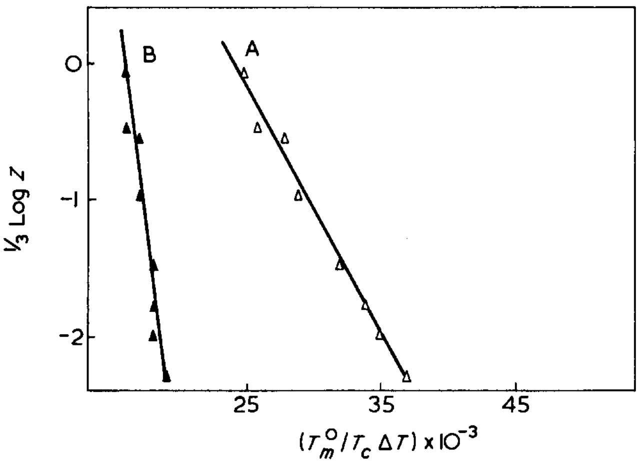

*Figure 4* Plot of 1/3 log $Z$ against $T_m^0/T_c\Delta T$: A, $T_m^0$ = 451K; B, $T_m^0$ = 483K

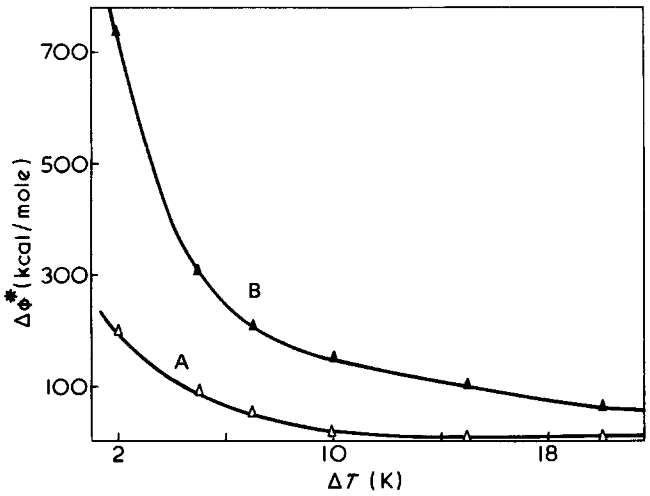

*Figure 5* Variation of $\Delta\Phi^*$ with the undercooling $\Delta T$: A, $T_m^0$ = 451K; B, $T_m^0$ = 483K

In the case of specimens of PVF$_2$ in form II the equilibrium melting point $T_m^0$ was derived by Nakagawa and Ishida[9] from the linear relation of the melting point and the annealing temperature. They found that in the case of their specimens when the annealing temperature is above 160°C, partial melting occurs and the melting point increases linearly with annealing temperature. By applying to their data the well-known equation[7]:

$$T_m = T_m^0\,\frac{\gamma-1}{\gamma} + \frac{T_a}{\gamma} \tag{6}$$

a value of 210°C for $T_m^0$ was obtained.

In a recent paper Welch and Miller[10] found a value of 178°C for the $T_m^0$ of the α-polymorph of PVF$_2$ that is far below that found by Nakagawa and Ishida[9].

As *Figure 4* shows a linear trend is observed in the plots of 1/3 log $Z$ against $T_m^0/T_c\Delta T$. Curves A and B of *Figure 4* refer to values of $T_m^0$ of 178° and of 210°C, respectively.

According to equation (5) this result indicates that, at least in the vicinity of the melting point and for the values of undercooling used, the transport term $\Delta F^*/kT_c$ may be considered as constant. From the slopes of the straight lines of *Figure 4* the quantity $4b_0\sigma\sigma_e/2.3k\Delta H_F$ is estimated to be 190 and 702K for equilibrium melting temperatures of 178° and 210°C, respectively.

By using equation (4) the free energy of formation of a nucleus of critical dimensions $\Delta\Phi^*$ may be calculated.

The dependence of $\Delta\Phi^*$ upon the undercooling is shown in *Figure 5* for $T_m^0$ = 178°C curve A and for $T_m^0$ = 210°C curve B.

According to the crystallographic data on the form II of PVF$_2$ of Lando, Olf and Peterlin[2] the most probable fold planes are the (200). Then the distance of two adjacent fold planes $b_0$ is estimated to be 4.83 Å. The enthalpy of fusion of the form α of PVF$_2$ was evaluated by Nakagawa and Ishida[9] from melting point depression data. They found for $\Delta H_F$ a value of $2.01\times10^9$ erg/cm$^3$. The quantity $\sigma\sigma_e$ may be calculated by substituting in the quantity $4b_0\sigma\sigma_e/2.3k\Delta H_F$ the known values of $b_0$ and $\Delta H_F$; $\sigma\sigma_e$ turns out to be equal to 627.4 and 2319.4 erg$^2$/cm$^4$ for values of the slopes of the straight lines of *Figure 4* of 190 and 702K, respectively.

From the well-known relation[7]:

$$\sigma = \alpha\Delta H_F b_0 \tag{7}$$

where α is equal to 0.1 for all polymers, the surface free energy parallel to the chain direction σ is estimated to be 9.7 erg/cm$^2$. From this, the surface free energy of folding $\sigma_e$, may be evaluated. We found for $\sigma_e$ values of 65 and 239 erg/cm$^2$ from $\sigma\sigma_e$, equal to 627.4 and 2319.4 erg$^2$/cm$^4$, respectively.

Nakagawa and Ishida[9] found for $\sigma_e$ a value of 5.1 kcal/mol of lamellar sequences (about 349 erg/cm$^2$) from the plot of the melting point *versus* reciprocal lamellar thickness obtained by electron microscopy. Values of $\sigma_e$ of 349 and 239 erg/cm$^2$ seem to us rather large when compared with the values of $\sigma_e$ reported in literature for other linear polymers[5,7-8,11].

This could be an indication that Nakagawa and Ishida used an overestimated value for $T_m^0$. Further the high value found by them for $\sigma_e$ is probably to be related also to the intrinsic difficulty in estimating by electron microscopy the true value of the lamellar thickness of crystallites.

## REFERENCES

1 Bergman, J. G., McFee, J. H. and Crane, G. R. *Appl. Phys. Lett.* 1971, **18**, 203; Murayama, N. *J. Polym. Sci. (Polym. Phys. Edn)* 1975, **13**, 929
2 Gallperin, Ye. L., Strogolin, Yu, V. and Mlenik, M. P. *Vysokomol. Soedin* 1965, **7**, 933; Hasegawa, R., Takahashi, Y., Chatani, Y. and Tadokoro, H. *Polym. J.* 1972, **3**, 600; Lando, J. B., Olf, H. G. and Peterlin, A. *J. Polym. Sci. (A-1)* 1966, **4**, 941
3 Zerbi, G. and Cortili, G. *Chem. Commun.* 1965, **13**, 295; Doll W. W. and Lando, J. B. *J. Macromol. Sci. (B)* 1968, **2**, 219
4 Welch, G. J. *Polymer* 1974, **15**, 429
5 Maglio, G., Martuscelli, E., Palumbo, R. and Soldata, I. *Polymer* 1976, **17**, 185
6 Sharples, A. 'Introduction to Polymer Crystallization', Arnold, London, 1966
7 Hoffman, J. D. *SPE Trans.* 1964, **4**, 315; Hoffman, J. D. and Weeks, J. *J. Chem. Phys.* 1962, **37**, 1723
8 Godowsky, Yu. K. and Slonimisky, G. L. *J. Polym. Sci. (Polym. Phys. Edn)* 1974, **12**, 1053
9 Nakagawa, H. and Ishida, Y. *J. Polym. Sci. (Polym. Phys. Edn)* 1973, **11**, 2153
10 Welch, G. J. and Miller, R. L. *J. Polym. Sci. (Polym. Phys. Edn)* 1976, **14**, 1683
11 Martuscelli, E. and Pracella, M. *Polymer* 1974, **15**, 306