Crystallization kinetics of vinylidene chloride/vinyl chloride copolymers

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An understanding of the crystallization kinetics of a polymer melt is pertinent to the processing and properties of a polymer. In this study the crystallization kinetics and structure development of vinylidene chloride/vinyl chloride (VDC/VC) copolymers were studied using differential scanning calorimetry (d.s.c.) and hot stage/optical microscopy. The time and temperature dependence of the growth and nucleation rates were determined along with the crystal growth geometry. Using hot stage/optical microscopy, the growth rate was found to be linear and the maximum rate occurs around 373 K. Both d.s.c. and microscopy indicate that nucleation is via nuclei that survive the melt and nuclei that grow in as crystallization proceeds. The maximum nucleation rate occurs around 283 K and the time dependence due to supercooling was found to follow a first-order rate law. Thermal decomposition of the polymer was found to be an important aspect of the crystallization kinetics.

(Keywords: vinylidene chloride copolymers; crystallization kinetics; differential scanning calorimetry; nucleation; growth)

INTRODUCTION

An understanding of the crystallization behaviour of a semicrystalline polymer is important to the processing of the material and also to the final physical properties of the product. This behaviour is affected not only by the inherent physical properties of the polymer, such as chemical composition and molecular weight distribution, but also by the conditions of crystallization. The crystallization conditions can affect such properties as the size of the crystallites, the degree of crystallinity, and the molecular structure of the lamellar crystallites and the interfacial amorphous region. Thus, by controlling the crystallization conditions, the thermal and mechanical properties of the polymer can be varied.

Previous studies of the crystallization kinetics and morphology of vinylidene chloride/vinyl chloride (VDC/VC) copolymers focused on fibre spinning of the polymer[1,2]. Work by Okuda *et al.*[2] used a density gradient column and X-ray diffraction techniques to monitor the crystallization process. In this paper the crystallization kinetics and structure development of VDC/VC were studied using differential scanning calorimetry and hot stage/optical microscopy. The time and temperature dependence of the growth and nucleation rates were determined along with the crystal growth geometry.

EXPERIMENTAL

Materials

The following copolymers were used in these studies (wt% VDC/wt% VC): 85/15; 80/20; and 72/28. All the studies were performed on a 85/15 wt VDC/wt VC copolymer unless otherwise stated. The material properties of a 85/15 wt VDC/wt VC copolymer are given in *Table 1*. These copolymers are known to have compositional drift, thus the information given in *Table 1* should be considered only as general property values.

Table 1 85/15 wt VDC/wt VC copolymer material constants

Constant	Value
T_m (K)	471
T_g (K)	270
ΔH_f (kcal mol^{-1})	1.1
ρ (g/cm^3)	
amorphous	1.67
crystalline	1.80

Differential scanning calorimetry (d.s.c.)

All d.s.c. measurements were made with a DuPont 912 differential scanning calorimeter interfaced to a DuPont 9900 computer/thermal analyser. Resin samples of approximately 10 mg were weighed into aluminium pans. A two-step crystallization experiment was used to study nucleation. The general procedure is as follows:

1. Premelt sample at 468 K for 2 min in a small oven.
2. Quench in liquid nitrogen.
3. Place on d.s.c. cell at temperature T_1 for time t_1.
4. Quench in liquid nitrogen (d.s.c. equilibrated at T_2).
5. Place on d.s.c. cell at temperature T_2 until crystallization is complete.

The values of T_1 in this study were 273 K, 278 K, 283 K, 288 K and 293 K and those of t_1 were 3, 5, 9, 15 and

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25 min. The value of T_2 was 313 K for all crystallization experiments.

The crystallization kinetics were calculated by integrating partial areas under the exotherm as a function of time.

Optical microscopy

The growth rate was studied using hot stage/optical microscopy. A small amount of polymer (<10 mg) was placed on a glass microscope slide. A cover slip was put on the slide and the slide was placed for 4 min in a Mettler FP2 hot stage which had been equilibrated at 468 K. After the melting, the slide was transferred to a Mettler FP82 hot stage with a FP80 controller which had been equilibrated to the crystallization temperature.

The sample was observed using a Zeiss Universal microscope with a 40 × long working distance objective. The sample was illuminated with a xenon arc between a pair of crossed polarizers to permit observation of the development of the crystalline phase via birefringence. A video camera recorded the crystallization process. The time was recorded on the video tape using a time base input. The measurements of spherulite diameters were made on the video screen. With the exception of the measurements at 313 K and 413 K, where they were made on several spherulites from single samples, all linear growth rates were determined for at least two separate samples and at least six different spherulites.

RESULTS AND DISCUSSION

Growth geometry of crystals

In the past, the crystal growth geometry has not been clearly defined. D.s.c. and dilatometry studies rely on the interpretation of the Avrami equation for information on the geometry. *Figure 1a* shows the crystal structure resulting from crystallization on a microscope slide with a cover slip and *Figure 1b* a cross-section of the sample. Viewing from the two directions allows direct evaluation of the geometry in three dimensions. It is quite clear that the VDC/VC copolymer crystallizes in a spherical structure. Constricting the sample under a cover slip has caused two-dimensional growth for other polymers[3]. This complication is avoided in these polymers, most likely because of the small spherulite size. This same study was performed on a sample crystallized in the d.s.c. cell. The results were the same: the VDC/VC copolymer crystallizes as spheres in the d.s.c. cell.

Growth rate measurements

Measurements of spherulite growth were made at temperatures from 313 K to 413 K. No systematic deviations from a linear growth rate were found. *Figure 2* is a representative plot of spherulite radius as a function of time. Time zero on the time scale indicates the time at which the first measurement of the spherulite was made. Measurements made on spherulites that impinged indicated that growth rate was constant, at least through the start of impingement.

The effect of copolymer composition on the growth rate is given in *Table 2*. The higher VDC content copolymers have greater growth rates. This effect would be expected from the greater number of longer VDC sequences which would not be hindered by VC defect sites. However, the relationship between growth rate at constant temperature and copolymer composition is complicated by the different supercooling ($T_m - T$). The difference in supercooling arises from the decrease in T_m which is expected with the addition of VC. The melting temperature decreases by only 5 K as the copolymer composition changes from 88/12 to 70/30 wt VDC/wt VC[1]. Thus the effect of melting point difference (supercooling difference) is not likely to account for the over six times decrease observed in growth rate.

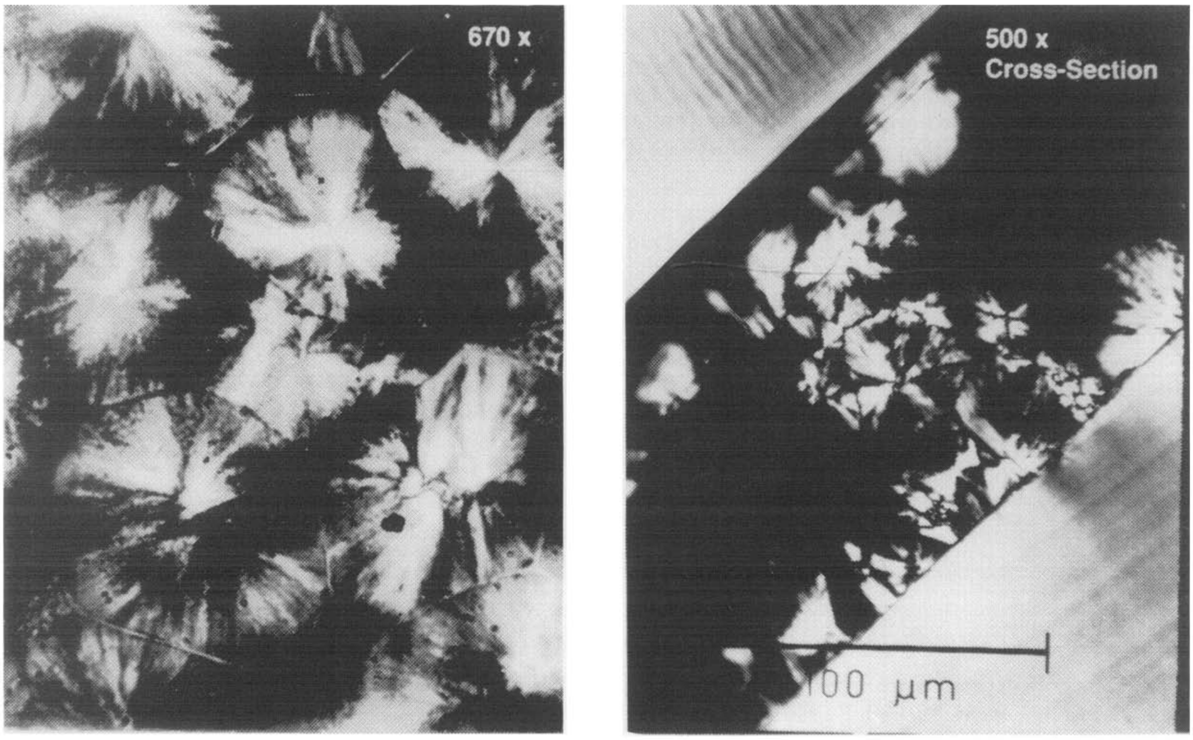


Figure 1 Photomicrographs of 85/15 wt VDC/wt VC copolymer crystallized at 413 K

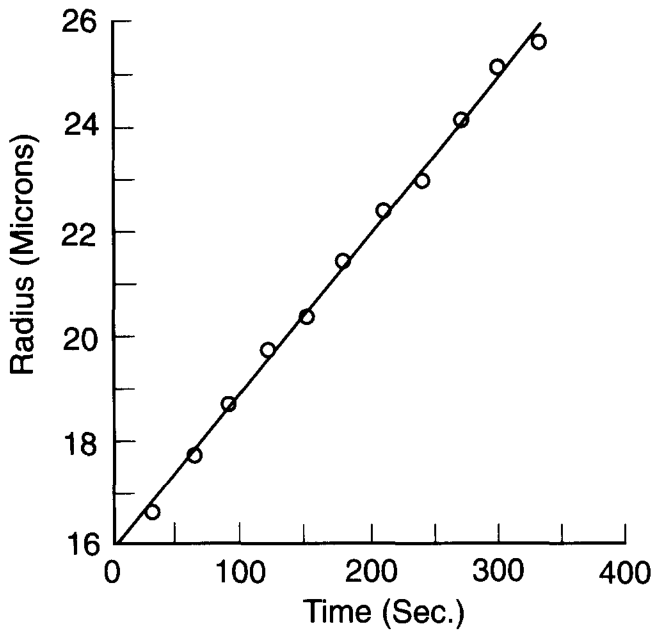


Figure 2 Increase in crystal radius with crystallization time for 85/15 wt VDC/wt VC copolymer crystallized at 403 K

Table 2 Effect of copolymer composition on linear growth rate (crystallized 353 K)

Copolymer composition (wt% VDC/wt% VC)	Growth rate (μm/min)
85/15	3.4
80/20	1.4
72/28	0.5

The effect of additional defect sites is also observed during degradation. *Table 3* shows the decrease in growth rate as a function of time at 468 K. VDC/VC copolymers are thermally unstable at melt temperatures[4]. The consequences of degradation include the formation of double bonds along the polymer backbone. These double bonds fulfil the same role as VC sequences in that they are defect sites and cause decreased growth rates.

Growth rate – temperature dependence

The following equation was fit to the growth rate data[5]:

$$G = G_0 \exp[-B/R(T-T_\infty)] \exp[-K_g T_m/T\Delta T] \quad (1)$$

where G is the growth rate, G_0 is a constant, T is the crystallization temperature, T_∞ is the temperature at which the viscosity reaches an infinite value and ΔT is the extent of supercooling from the equilibrium melt temperature T_m. The first exponential term is the activation energy for transport across the melt/solid interface and the second is the enthalpic driving force, assuming that the growth is controlled by a Gibbs-type nucleation and that the new crystallites are nucleated on the faces of existing ones. A number of linear polymers have values between 1.0–1.6 kcal mol^{-1} for B and approximately 30 K for the difference $T_g - T_\infty$[5]. The analysis of the data in this case was done by setting $T_g - T_\infty$ equal to 30 K and determining the constants G_0, B and K_g. The fit of equation (1) to the data is shown in *Figure 3* as the linear relationship $\ln G + B/R(T-T_\infty)$ *versus* $1/T\Delta T$. The data point corresponding to a crystallization temperature of 313 K does not lie on the same line as the rest of the data set. Although this may be a true phenomenon, it is also possible that it is a result of the difficulty of measuring the growth rate at this low temperature due to the rapid nucleation rate.

Nucleation rate measurements

Nucleation in VDC/VC copolymers is complicated due to the inevitable presence of crystallites remaining from the melt. Samples cannot be held at high temperatures for a sufficient time to ensure complete crystallite melting due to the thermal sensitivity of the polymer. If all nucleation occurred via intact nuclei from the melt or impurities (heterogeneous nucleation), then all spherulites would occur in the same location upon recrystallization. Also, heterogeneous nucleation results in all spherulites having the same diameter until the time of impingement because they would be growing at the same rate starting from the same time.

Evidence for heterogeneous nucleation was found using hot stage microscopy. A sample melted at 468 K for 3 min was crystallized at 403 K, and the positions of the spherulites were noted. It was then remelted at 468 K and cooled to 403 K. In some cases a distinct pattern of spherulites could be identified in both crystallizations,

Table 3 Effect of degradation on linear growth rate (crystallized 403 K)

Time at 468 K (min)	Growth rate (μm/min)
2	2.7
3	2.1
4	2.1
5	1.5

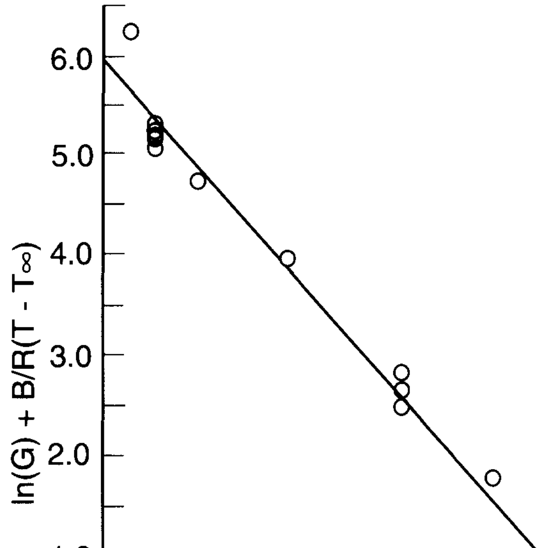
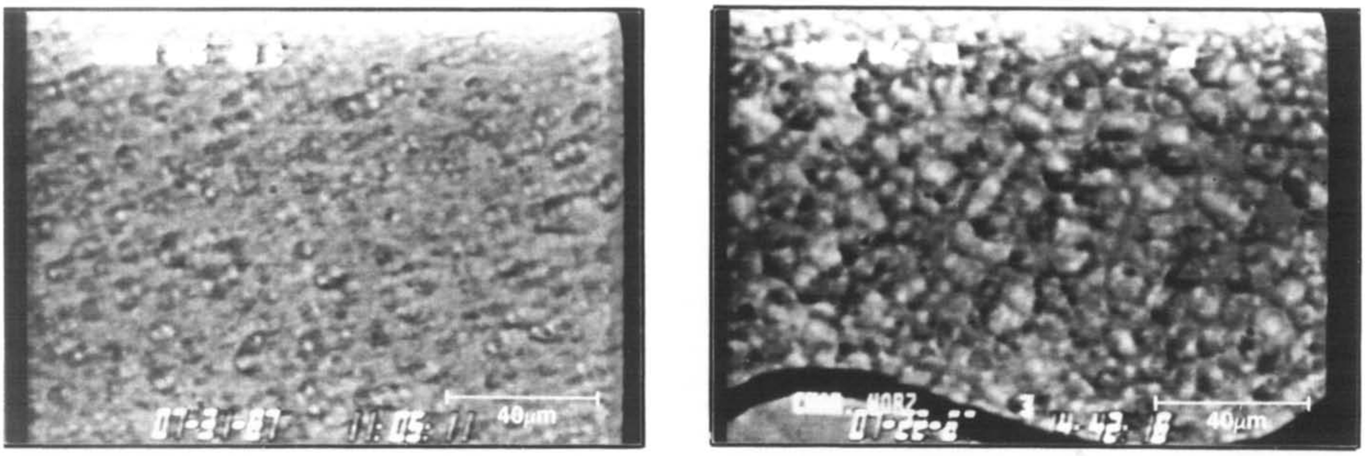
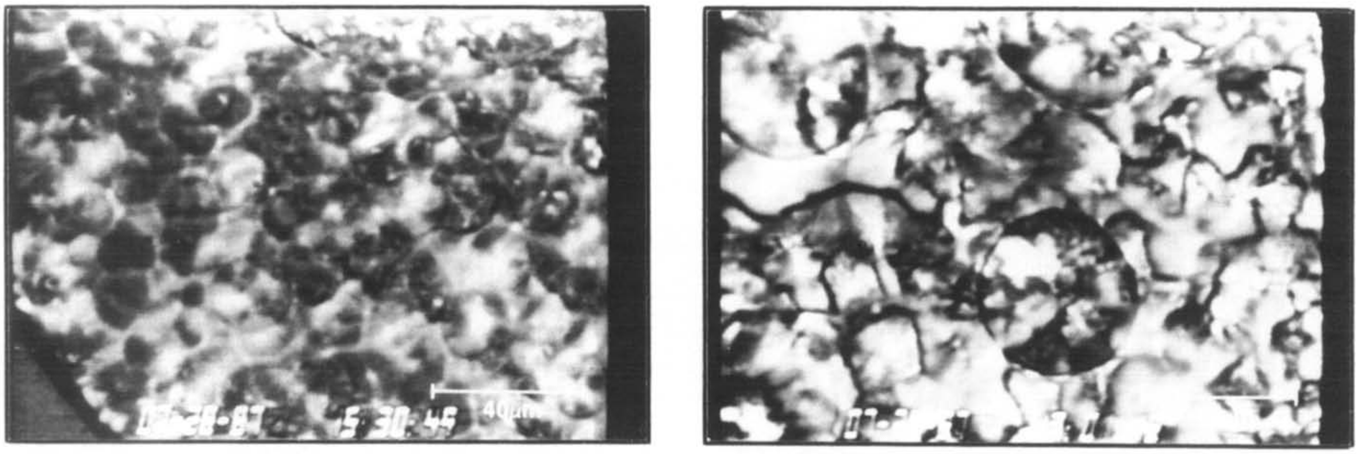


Figure 3 Plot of $\ln(G) + B/R(T-T_\infty)$ against $T_m/T(\Delta T)$ for 85/15 wt VDC/wt VC for the case $B = 1.69$ kcal mol^{-1}, $T_\infty = T_g$ - 30 K, $T_m = 471$ K, $K_g = 499$ K and G measured in μm/min



Temperature: 313K
Crystallization Time: 22 min.

Temperature: 353K
Crystallization Time: 100 sec.



Temperature: 373K
Crystallization Time: 130 sec.

Temperature: 403K
Crystallization Time: 11½ min.

Figure 4 Photomicrographs of 85/15 wt VDC/wt VC copolymer crystallized at different temperatures

indicating the presence of heterogeneous nuclei. As mentioned above, the thermal sensitivity of these copolymers prevents complete melting of primary nuclei, thus contributing to the number of heterogeneous nuclei. Close examination of the first and second crystallizations showed there were also spherulites which appeared at a later time, indicating the possibility of spontaneous nucleation or nuclei from another source than intact nuclei from the melt. Furthermore, there were some spherulites which did not reappear in the second melt and spherulites in the second crystallization at positions where there were none in the first crystallization.

Quantitative measurements of the number of spherulites in a given volume as a function of time could not be made using the optical microscope due to large variations in the nucleation density within a sample. However, the pattern of spherulites at each temperature clearly indicates the change in the relative rates of growth and nucleation with temperature. In *Figure 4*, photomicrographs of samples crystallized at temperatures from 313 K to 403 K are shown. It is clear from the number of spherulites and their average diameter that the nucleation density, which is proportional to the quotient of the nucleation rate to the growth rate, increases as the level of supercooling rises.

Further information on nucleation can be gained from two-step crystallization experiments performed on a d.s.c. In a two-step crystallization experiment the sample is held at a specified temperature between 273 K and 293 K where nucleation is rapid and growth, as shown by d.s.c., is negligible. The sample is then crystallized at 313 K. If growth does not occur at the lower temperature and nucleation does not take place at 313 K, then the rate constant derived from the crystallization exotherm at 313 K will be proportional to the number of nuclei produced at the lower nucleation temperature.

The crystallization process may be described mathematically as

$$X(t)=1-\exp\left\{-S\int_0^t \dot{N}(\tau,T)\left[\int_\tau^t G(z,T)\,\mathrm{d}z\right]^D \mathrm{d}\tau\right\} \tag{2}$$

where $X(t)$ is the degree of crystallinity, S is a shape factor, $\dot{N}(\tau, T)$ is the nucleation rate at time τ and temperature T, $G(z, T)$ is the growth rate at time z and temperature T, and D is the dimension of growth. For isothermal crystallization, equation (2) is often simplified to the Avrami equation

$$X(t)=1-\exp(-kt^n) \tag{3}$$

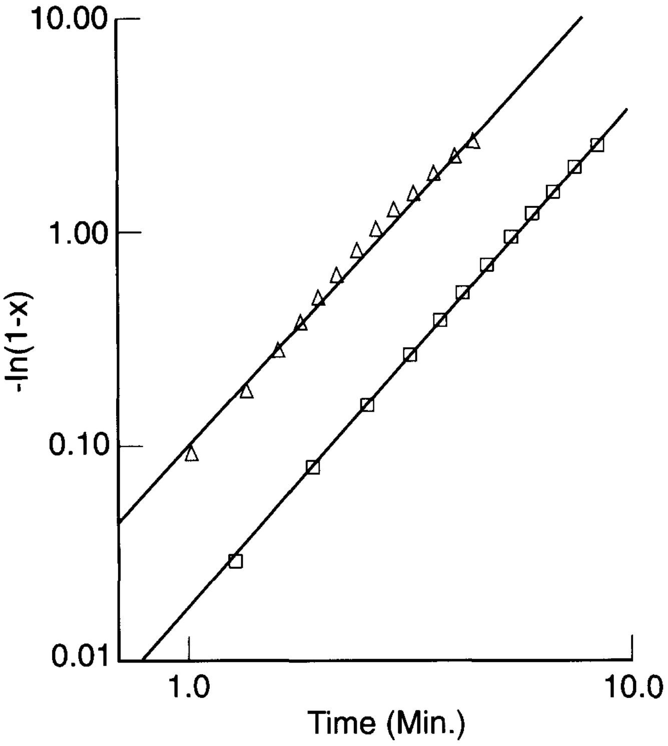


Figure 5 Plot of $\log[\ln(1-X)]$ against $\log(t-t_1)$ for 85/15 wt VDC/wt VC copolymer at two different nucleation conditions: (□) $T_1=293$ K and $t_1=3$ min and (△) $T_1=283$ K and $t_1=25$ min

where k is the crystallization rate constant and n is related to the dimension of growth.

Equation (2) can be expanded to describe the two-step crystallization model:

$$X(t)=1-\exp\left\{-S\int_0^{t_1}\dot{N}_1(\tau)\left[\int_\tau^{t_1}G_1(z)\,dz+\int_{t_1}^{t}G_2(z)\,dz\right]^D d\tau-S\int_{t_1}^{t}\dot{N}_2(\tau)\left[\int_\tau^{t}G_2(z)\,dz\right]^D d\tau\right\} \qquad (4)$$

$$\dot{N}_1(\tau)=\dot{N}(\tau,T_1) \qquad G_1(z)=G(z,T_1)$$

$$\dot{N}_2(\tau)=\dot{N}(\tau,T_2) \qquad G_2(z)=G(z,T_2)$$

Assume $\dot{N}_2(\tau)\sim G_1(z)=0$:

$$X(t)=1-\exp\left\{-S\int_0^{t_1}\dot{N}_1(\tau)\left[\int_{t_1}^{t}G_2(z)\,dz\right]^D d\tau\right\} \qquad (5)$$

Assume the growth rate is linear (G_2 is a constant):

$$X(t)=1-\exp\left\{-SG_2^D(t-t_1)^D\int_0^{t_1}\dot{N}_1(\tau)\,d\tau\right\} \qquad (6)$$

For simplicity, the equation may be rewritten as

$$X(t)=1-exp\{-k(t-t_1)^D\} \qquad (7a)$$

where

$$k=SG_2^D\int_0^{t_1}\dot{N}_1(\tau)\,d\tau \qquad (7b)$$

The integral is the number of nuclei formed up to time t_1.

During any one crystallization experiment at temperature T_2 and $t>t_1$, G_2 and the integral in equation (7b) are constant, thus k is a constant and may be considered the rate constant for that crystallization experiment. The data from each experiment were analysed by plotting $\log[-\ln(1-X)]$ as a function of $\log(t-t_1)$, which should be a straight line with an intercept equal to $\log(k)$, as illustrated in *Figure 5*.

For this work T_2 was constant for all two-step crystallization experiments. Thus k is only a function of the integral in equation (7b) and this integral depends only on the values of T_1 and t_1. *Figure 6* is a plot of the rate constant, k, as a function of T_1 for various times t_1. All the curves have a maximum occurring around 283 K, indicating that the nucleation is the greatest at ~283 K. As expected, the nucleation rate drops off rapidly as the glass transition temperature is approached.

Nucleation rate – time dependence

If the nucleation rate is independent of time, then

$$\int_0^{t_1}\dot{N}_1(\tau)\,d\tau=\dot{N}_1t_1 \qquad (8)$$

and k as a function of t_1 should be a straight line. *Figure 7* is a plot of k as a function of t_1 for various temperatures T_1. None of the curves in *Figure 7* are straight lines; they all appear to approach an asymptotic value at longer values of t_1, indicating that the nucleation rate is decreasing with time. Thus the nucleation rate is not linear but some function of time. Each of the curves is approaching a different maximum value, indicating that the maximum number of nuclei formed is a function of the nucleation temperature.

The time dependence illustrated in *Figure 7* has been observed for a variety of polymers, including polyethylene oxide[6] and poly(decamethylene terephthalate)[7]. This behaviour may be explained by assuming there to be a number of pre-existing nucleating centres (potential nuclei) in the melt and that the centres display a distribution of behaviour such that the transformation

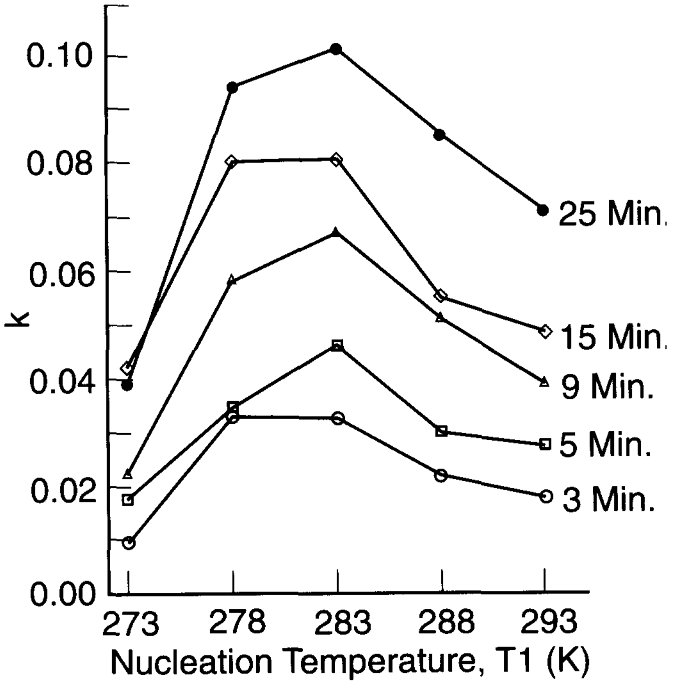


Figure 6 Plot of rate constant, K, against nucleation temperature, T_1 (K) for 85/15 wt VDC/wt VC copolymer at various nucleation times: (○) 3 min, (□) 5 min, (△) 9 min, (◇) 15 min and (●) 25 min crystallized at 313 K

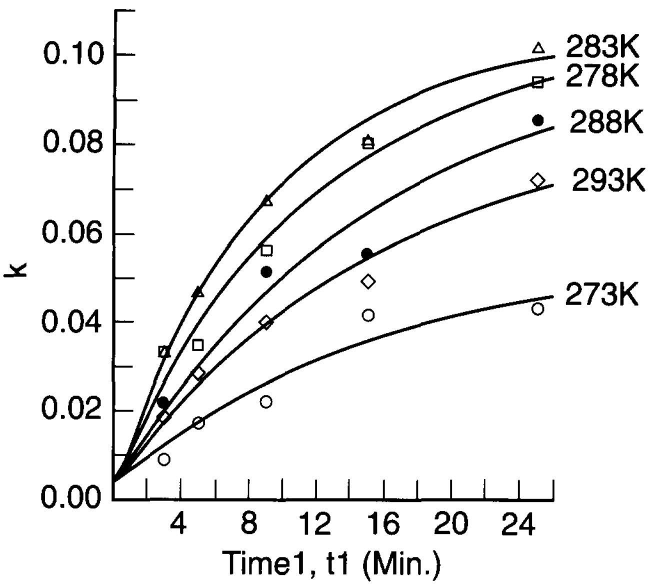


Figure 7 Plot of rate constant, K, against nucleation time, t_1, for 85/15 wt VDC/wt VC copolymer at various nucleation temperatures: (○) 273 K, (□) 278 K, (△) 283 K, (●) 288 K and (◇) 293 K crystallized at 313 K

of a particular group of centres into stable nuclei requires a critical value of undercooling. More centres come into play as the temperature is decreased from the equilibrium melting temperature. Thus, the maximum number of nuclei that can form is dependent on the nucleation temperature.

The above explanation may be described mathematically by allowing the rate of transformation to follow a first-order rate law with a specific rate constant v. The time dependence of the nucleation rate is then given by

$$\mathrm{d}N/\mathrm{d}t = v(\bar{N} - N) \tag{9}$$

where $\bar{N}$ is the maximum number of potential nuclei possible at the specified temperature. Solving equation (9) for a constant nucleating temperature and allowing for the presence of pre-existing nuclei results in the following equation for the number of nuclei:

$$N = N_0 + \bar{N}_1[1\text{-}\exp(-vt_1)] \tag{10}$$

where N_0 is the number of pre-existing nuclei, t_1 is the time the sample is allowed to nucleate at temperature T_1, and $\bar{N}_1$ is the maximum nuclei that can form during the supercooling. Pre-existing nuclei may result from unmelted crystallites or may form during the quench step. The number of pre-existing nuclei in the system is independent of the nucleation and crystallization temperatures, but does depend on the thermal history of the melt.

Substituting equation (10) into equation (6) gives the following expression for the degree of crystallinity as a function of time:

$$X(t) = 1 - \exp\{-SG_2^D(t - t_1)^D[N_0 + \bar{N}_1(1 - \exp(-vt_1))]\} \tag{11}$$

and

$$k = SG_2^D\{N_0 + \bar{N}_1[1 - \exp(-vt_1)]\} \tag{12a}$$

At time $t_1 = 0$, the rate constant is

$$k = SG_2^D N_0 \tag{12b}$$

Thus, k at $t_1 = 0$ is independent of temperature T_1. It was found that the rate constant k, at $t_1 = 0$ and $T_2 = 313$ K, is 2.81×10^{-3} min$^{-2.3}$. *Figure 7* gives the curves for the following equation fit to each data set:

$$k = 2.81 \times 10^{-3} + SG_2^D\bar{N}_1[1 - \exp(-vt_1)] \tag{13}$$

The values for $SG_2^D\bar{N}_1$ and v are given in *Table 4* and the resulting curves are shown in *Figure 7*. Although the uncertainty in the data precludes a conclusive fit, it appears from *Figure 7* that equation (12a) describes those experimental data well enough to provide a conceptual framework.

Nucleation rate – temperature dependence

The variations in the asymptotic limit that each curve in *Figure 7* approaches illustrate the temperature dependence of $\bar{N}_1$. In order to use a meaningful mathematical expression to describe the temperature dependence of $\bar{N}_1$, it was assumed that it follows the same functionality as the nucleation rate[5]

$$\bar{N}_1 = N_0 \exp[-B/R(T - T_\infty)] \exp[-k_n T_m^2/T(\Delta T)^2] \tag{14}$$

where N_0 is a constant and T_m is the equilibrium melt temperature. The first term, as in the growth equation (equation (1)), represents the energy of transport across the melt/solid interface. The second term is the free energy of formation of a stable nucleus. The fit of equation (14) is shown in *Figure 8*. It appears to fit the data, although

Table 4 Values of constants $SG_2^D\bar{N}_1$ and v from equation (13)

Temperature 1 (K)	$SG_2^D\bar{N}_1$ (min$^{-2.3}$)	v (min^{-1})
273	0.05608	0.05921
278	0.10481	0.08490
283	0.10432	0.10641
288	0.10177	0.06260
293	0.08701	0.06046

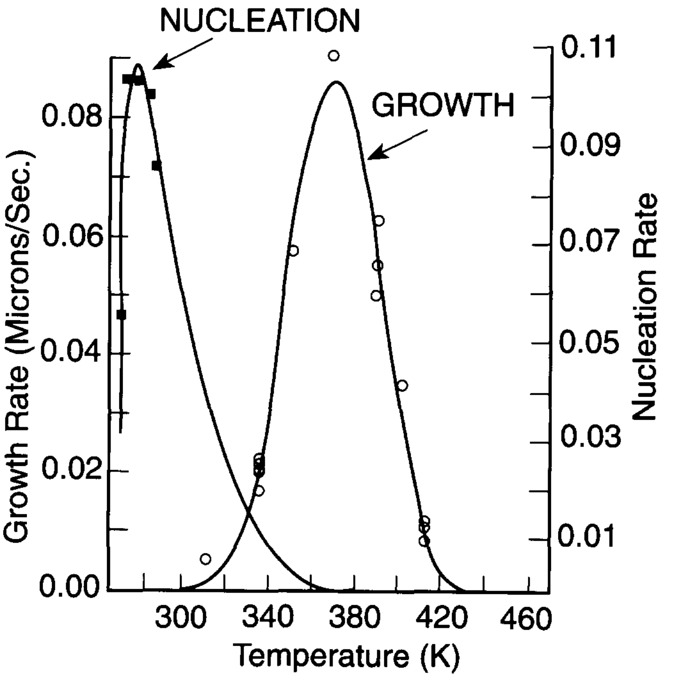


Figure 8 Plot of growth rate and nucleation rate against temperature for 85/15 wt VDC/wt VC copolymer. Equation (14) was fit to the nucleation data: $B = 370$ cal mol^{-1} and $k_n = 616$ K

the data set is not large enough to confirm the uniqueness of the fit. The temperature dependence of the growth rate is also shown in *Figure 8*. As can be seen, the temperature dependence of the growth rate and that of the nucleation rate are quite different.

CONCLUSIONS

The crystallization kinetics of vinylidene chloride/vinyl chloride copolymers were studied using differential scanning calorimetry and hot stage/optical microscopy. The nucleation rate and the growth rate exhibit different maxima as a function of temperature. The growth rate maximum is around 373 K, which is typical of polymers in that it occurs at around two-thirds of the melting temperature. The nucleation rate maximum was found to be around 283 K. The time dependence of the nucleation rate was modelled using a first-order rate law. Decomposition of the polymer must be considered when studying the crystallization kinetics for two major reasons: (1) the growth rate decreases as decomposition occurs since decomposition causes defect sites to be formed and (2) due to the high rate of decomposition above the melting point, a sample cannot be obtained which is free from pre-existing crystallites. Thus it is necessary to control rigorously the premelting conditions so that sample-to-sample variations are minimized.

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