

The Influence of Phthalocyanin Blue on the Crystallization Behaviour of Polypropylene

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ABSTRACT

The crystallization kinetics from the melt of isotactic polypropylene either unpigmented or containing the organic pigment phthalocyanin blue (at concentrations of 0.1, 0.2 and 0.3%) have been studied using a combination of calorimetry and optical microscopy.

The results show that the pigment acts as a nucleating agent, dramatically changing the crystallization behaviour of the polypropylene. At concentrations of 0.1% the pigment substantially reduces the size of spherulites and significantly increases their number. Non-isothermal measurements show that the onset of crystallization for samples containing this concentration of pigment occurs some 16°C higher than in the unpigmented material. The overall level of crystallization is unaffected by the addition of the pigment although the morphology of the spherulites changes from 2-d discs to 3-d spheres. The activation energy required for crystallization is essentially unaffected by phthalocyanin blue but the overall surface energy of the spherulites is lowered. This behaviour is consistent with that expected of a good nucleating agent.

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1 INTRODUCTION

The progressive phasing out of many environmentally unacceptable products has resulted in the loss of a number of inorganic pigments that contain heavy metals¹. In particular sales of cadmium and lead based pigments continue to decline, recent figures suggest that the sales of the latter are decreasing by 5-7% per annum². These inorganic pigments posed few problems to either the design engineer or plastics processor being thermally stable and having little effect on the dimensional stability of mouldings. In contrast the substitute organic pigments are less thermally stable and can increase shrinkage and warpage of mouldings compared with those manufactured from unpigmented semicrystalline materials^{3,4}. These changes in dimensional stability could be due to morphological differences between pigmented and unpigmented materials. It is well known that some organic pigments behave as nucleating agents raising the temperature at which crystallization begins to occur in a cooling melt². Furthermore it is known that changing the size and number of spherulites can change the properties of the product because the spherulite boundaries represent discontinuities in the matrix^{5,6}.

It is possible to predict changes in shrinkage and warpage behaviour using injection moulding simulation software but only if the pigmented material has been specifically characterised. This is a time-consuming and potentially endless exercise given the infinite number of combinations of polymer type, grade, pigment type, pigment concentration and potential interactions that can occur. This study forms part of a programme that may considerably reduce this potential workload by deriving quantitative relationships between different pigment types and changes in their crystallization behaviour.

The crystallization behaviour of polypropylene⁷ has been studied many times. These investigations have tended to focus on the characterization of different morphological forms of the pure material⁸⁻¹¹ or the behaviour of fibre filled polypropylene^{12,13}. There is surprisingly little published information on the influence that pigments have on crystallization kinetics given the size of the world wide market for these materials.

The blue pigment copper phthalocyanin that is the focus of this investigation has a reputation for causing unacceptable levels of dimensional instability in articles moulded from polyolefins^{3,14}. Despite this problem the pigment is still widely used as a colourant as it possesses good thermal stability and resistance to ageing.

2 EXPERIMENTAL

2.1 Materials and Sample Preparation

Copper phthalocyanin blue (kindly supplied by Ciba Specialty Chemicals) was mixed with a polypropylene homopolymer powder (Solvay Eltex PHV001P) at concentrations of 0.1, 0.2 and 0.3%. These mixtures were then extruded, pelletised and injection moulded by Gabriel-Chemie UK Ltd to form small rectangular injection moulded plaques. The polypropylene is approximately 97% isotactic based on quantitative solvent extraction using n-heptane. This material has a polydispersity of 6.0 where $M_w = 181500$ Daltons and $M_n = 30450$.

2.2 Thermal Analysis

Thermal analysis was carried out using a Perkin-Elmer Differential Scanning Calorimeter, DSC-2 interfaced to a PC. Isothermal temperatures were calibrated using a stepwise procedure and thermal lag was estimated from individual dynamic curves¹⁵; the

instrument was operated in the specific heat mode using alumina as a calibrant¹⁶. Samples weighing 11-13mg were cut from the central regions of the injection moulded plates and held within crimped aluminum pans. Nitrogen was used as purge gas. A common heating or cooling rate of 10 K.min⁻¹ was used throughout.

All the samples were heated to 450K and allowed to equilibrate for approximately three minutes to ensure that any crystalline structures formed during the manufacture of the plates were removed. Optical microscopy studies showed at that at this temperature any remnants of the initiation sites for previous crystal growth had been erased. The molten material was then cooled to the crystallization temperature. The rate of data collection was one point per second. At the cessation of crystallization each sample was returned to 450K and the melting endotherm recorded. Wherever possible a single specimen was used for successive isothermal runs. Sample stability was monitored by comparing the weight of the specimens before and after a series of measurements and by comparing the heats of fusion from duplicate runs at the start and end of a series. Heats of fusion were calculated as previously described¹⁶.

2.2.1 The determination of baselines and fractional areas

Figure 1 shows three isothermal DSC curves for samples containing increasing amounts of phthalocyanin blue. The heat flow is in arbitrary units, the data having been normalized by dividing by the appropriate sample mass. The figure shows an initial period of cooling from the annealing temperature of 450K to the crystallization temperature (413K). The crystallization temperature was always approached at a controlled rate rather than by 'quenching' to ensure that the instrument remained in control. The overall enthalpy change can then be resolved into contributions from specific heat alone and from subsequent crystallization. This was accomplished by running all crystallization experiments in the 'specific heat' mode that requires data for the empty sample pan and the pan and calibrant (synthetic sapphire in the present case). The specific heat in the molten state is a linear function of temperature and the value at T_{cryst} can be estimated from experiments that terminate at temperatures above that at which crystallization begins. Following this procedure eliminates any problems due to overshoot and subsequent overlap when crystallization is rapid. Baselines defining the limits of the crystallization endotherm were obtained by connecting the region of maximum heat flow at the onset of crystallization to a point where it was deemed that the process had reached completion i.e. a state of constant heat flow as shown in Figure 2A.

In a DSC curve such as that shown in Figure 2A the relative degree of crystallinity X_r shown in Figure 2B is defined according to the ratio

$$X_r = \frac{\Delta H_t}{\Delta H_\infty} \quad (1)$$

where

$$\Delta H_t = \int_0^t (dQ / dt) dt \quad (2a)$$

and

$$\Delta H_\infty = \int_0^\infty (dQ / dt) dt, \quad (2b)$$

dQ/dt is the heat flow. In practice ΔH_t corresponds to a partial area of the DSC curve between the onset of crystallization and a time t . The melting enthalpy ΔH_∞ is defined by equation (2b) integrated between the onset and completion of crystallization.

2.3 Polarised Light Microscopy (PLM)

The crystallization behaviour of thin films of molten polymer was observed using a Leitz Orthoplan microscope under polarized light. The films were prepared by melting small samples sandwiched between coverslips under light pressure on a microscope hot stage (Linkam THMS 600). A compensator was used to enhance the contrast between the growing (birefringent) spherulites and the isotropic melt. Snapshots of the growing spherulites were captured and stored on a PC using a colour video camera (JVC 3-CCD) and capture card (Integral Technologies, Flashpoint card Vs 2.70). The images were analysed using Image Pro-Plus (Vs 3.0.01) software. The hot stage was calibrated over the temperature range 341 - 436K using the melting points of five different sharply melting reference materials determined at heating rates of 0.1 K/min. A micrometer slide mounted on the microscope stage was used to provide a length scale for the image analysis software.

Films of both virgin and pigmented polypropylene were annealed at 445 K for a period of three minutes to erase all traces of previous thermal history. This procedure ensured that spherulites did not appear at the same position between successive melting and crystallization cycles. After annealing in the melt the films were cooled at a rate of 40 K min⁻¹ to set temperatures at which the growth of the spherulites was monitored. Snapshots of growing spherulites were typically recorded at intervals of 30s. The time dependence of the radii of the growing spherulites were derived from the circumference of the objects as measured by image analysis software.

3 RESULTS

3.1 Measurement of Spherulitic Growth Rates by Optical Microscopy

Figures 3A and B show a comparison of typical spherulitic structures that are found in unpigmented polypropylene with those in pigmented samples. Clearly the pigment has a dramatic effect on the size and number of spherulites. This behaviour appears to be independent of both the temperature at which the material is crystallized and the pigment concentration. Harkin-Jones et al¹⁷ also observed a reduction in the size of polypropylene spherulites after the addition of 0.5% titanium dioxide although the change in dimensions is less than that observed here. This behaviour is typical of materials containing nucleating agents and can be commercially exploited to manufacture products with improved clarity and toughness^{18,19}.

The growth of spherulites in the unpigmented material can be easily followed by microscopy. Images of the growing spherulites before they impinge on each other can be analysed to give a plot of the increase in the mean radius with time at different crystallization temperatures as shown in Figure 4. The slope of these linear plots yields the growth rates (Table 1) that are shown in Figure 5 together with a linear least squares fit of the data. As discussed later linearity is only valid over a limited temperature range. Figure 5 confirms that the radial growth rate increases with decreasing isothermal temperature²⁰. This behaviour reflects the increase in the driving force for crystallization that occurs as the crystallization temperature is reduced. Unfortunately these data cannot

be compared with that derived from pigmented materials as the spherulites are too small to be accurately measured by optical microscopy.

Isothermal temperature (K)	Mean spherulitic growth rate ($\mu\text{m/s}$)
404	0.130
405	0.120
406	0.087
407	0.079
409	0.052
410	0.038

Table 1: Mean spherulitic growth rates as a function of crystallization temperature.

3.2 Analysis of Calorimetric Data

Figure 6 shows cooling curves for as-received polypropylene and samples containing two different concentrations of phthalocyanin blue. The figure clearly shows that the presence of the pigment causes the polypropylene to crystallize about 16°C higher than the virgin material. Increasing the concentration of pigment from 0.1 to 0.3% causes an additional small shift in the onset of crystallization towards higher temperatures (~1°C). This observation is in agreement with the inference from the microscopy results that the pigment is acting as a nucleating agent. The DSC results suggest that the pigment essentially saturates the melt with potential initiation sites for crystal growth at a concentration of only 0.1%. The practical consequences of this are that;

- The morphology of pigmented mouldings will be different to those of the virgin material.
- Isothermal measurements of crystallization have to be made over different temperature ranges.

Figures 7, 8, 9 and 10 show fractional crystallization curves for polypropylene containing different concentrations of phthalocyanin blue. These figures that are discussed in detail below mirror the results obtained by optical microscopy in that the rate of crystallization increases on lowering the crystallization temperature.

The influence of phthalocyanin blue on the crystallization kinetics of polypropylene can be illustrated by comparing the crystallization half times for virgin and pigmented materials. The crystallization half time is defined as the time at which half the crystallization is complete. The half times derived from figures 7 - 10 have been plotted as a function of temperature in Figure 11. The dependence of the half times on temperature seen in the figure suggest that there is a concentration dependence of the pigment. This is shown more clearly in Figure 12 where a comparison of $\log t_{1/2}$ at constant temperature for different pigment concentration is shown. This behaviour has also been observed for fibre filled and other pigmented systems in which the fibres or pigments behave as nucleating agents ^{17,21}.

3.2.1 The determination of absolute crystallinity.

Table 1 shows the absolute level of crystallinity for both pigmented and unpigmented polypropylenes. These data were calculated using the total enthalpy method of Richardson²². Although the heat of fusion of perfect polypropylene crystals²³ varies with temperature it is essentially 165 J/g over the region of interest.

Pigment concentration (%)	Temperature (K)	H _f (Jg ⁻¹)	Absolute crystallinity (%)
0	395.4	96.9	0.59
	397.4	96.3	0.58
	399.4	96.8	0.59
0.1	413.2	91.6	0.56
	414.2	92.5	0.56
	415.2	94.4	0.57
0.2	413.2	93.4	0.57
	414.2	91.5	0.55
	415.2	91.6	0.55
0.3	413.2	92.5	0.56
	414.2	93.5	0.57
	415.2	96.1	0.58

Table 2: The dependence of absolute crystallinity on both temperature and concentration of phthalocyanin blue.

Table 2 shows that the unpigmented material is typically 59% crystalline and this value is independent of both the crystallization temperature and of pigment concentration. These results imply that the process of crystallization at each isothermal temperature was complete at the end of each DSC measurement.

3.2.2 Derivation of kinetic parameters

Many of the published functions for modelling isothermal crystallization are derived from those derived by Kolmogoroff²⁴, Johnson and Mehl²⁵, Avrami²⁶ and Evans²⁷ and has the form

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

X_t is the degree of crystallinity at some time t with respect to that which finally develops over a long period of time. The rate constant, k contains information about the rates at which nuclei form and crystals grow. The parameters in equation 3 can be derived from plots of $\log(-\ln(1-X_t))$ versus $\log t$ as shown in Figure 13. The shape parameter n is then given by the slope of the plot whilst the intercept yields $\log k$. The derivation of these parameters can be difficult as often the double log plots are non-linear showing gentle curvature at both low and high levels of crystallization. The literature contains many explanations of the origin of this non-linearity²⁸. At low levels of crystallinity it may be due to the behaviour of the logarithmic function itself which tends to minus infinity as (1-

X_c) tends to unity. Secondary crystallization is often cited as the cause of non-linearity at high crystallinity. In addition it should be noted that the shape of the crystallization curve is sensitive to the position of the baseline used to define the envelope of the crystallization envelope. This is particularly true at high levels of conversion (in excess of 0.9) for the broad shallow exotherms that are obtained at high temperatures.

The applicability of the Avrami model to crystallizing polymers has been discussed at some length by Hay²⁹. It has been suggested that the ‘best way’ to fit the model to fractional crystallization data is to fit the derivative of the function to the data^{3,30}. Whilst this approach has its merits the act of differentiating the fractional crystallization curve can introduce ‘noise’ in to the data degrading the accuracy of the derived parameters. In this study we have chosen to use a non-linear least squares procedure to fit the fractional crystallinity curves shown in figures 7 - 10. This direct approach to fitting equation 3 to the data that has been used before³¹ overcomes many of the problems associated with interpreting double log plots.

In the first stage of fitting both n and k were allowed to vary to give values for the ‘best fit’ to the data. In the second phase of fitting the shape parameter was fixed and new values for k were generated. The purpose of this second phase of fitting is to explore the potential for deriving empirical shift factors for modeling the influence of pigment on crystallization kinetics. Both sets of parameters are listed in Table 3. Plots of the optimum fits to the fractional crystallization data are shown in Figures 7 - 10. The fit is excellent implying that crystallization occurs through a single mechanism. This in itself is an interesting observation as there is evidence to suggest that crystallization occurs in two morphological forms during continuous cooling³².

From Table 3 it is apparent that the shape factor n changes from approximately 2 to 3 due to the presence of the phthalocyanin blue. n appears to be independent of the pigment concentration. This behaviour has been observed by other authors after the addition of nucleating agents to polypropylene²⁸. The spherulitic morphologies associated with these n values are 2-d discs and 3-d spheres respectively²⁹. This interpretation seems to agree with the optical microscopy results that show the virgin material crystallizing as large thin spherulites and supports the hypothesis that the pigment affects spherulitic morphology. Values of $n = 2$ are typical of those found for virgin polypropylene^{12,28,33}. It could be argued that the difference in n between pigmented and unpigmented polypropylene is due to co-crystallization of the two different crystal habits in the virgin material. To some extent this argument can be countered by looking at the shape of the melting curves obtained as the material is re-heated to the annealing temperature of 450K. Figure 14 shows a comparison between melting endotherms of pigmented and unpigmented material. This figure shows that the pigment causes the melting exotherm to broaden suggesting a more complex morphology than for the virgin material. Broadening of the C_p curves during reheating may be due to crystal reorganization although it does not provide hard evidence for the presence of α and β phases¹¹.

k can also be derived from experimental values of $t_{1/2}$ ³⁴, where $t_{1/2}$ is the time taken for 50% of the total crystallization to occur according to

$$k = \frac{\ln 2}{t_{1/2}^n} \quad (4)$$

Values of k calculated using this expression are in excellent agreement with those determined from the Avrami analysis. This suggests that the model which only strictly

applies prior to the spherulites impinging on each other is valid to a level of at least 50% fractional crystallinity

Pigment concentration (%)	Temp. (K)	Optimum values for k and n		Fixed n		t _{1/2} (mins)
		k	n	k	n	
0	395.4	0.0502	2.02			1.81
	397.4	0.0102	2.23			3.64
	399.4	0.0101	2.05			6.61
	400.0	1.92E-3	2.15			7.77
	403.0	0.2553	1.66			16.05
0.1	413.0	0.0100	2.86	8.22E-3	3.0	4.37
	413.2	0.0074	2.88	6.09E-3	3.0	4.86
	414.2	0.0031	2.98	2.99E-3	3.0	6.14
	415.2	0.0011	3.07	1.25E-3	3.0	8.23
	416.0	4.14E-4	3.26	7.70E-4	3.0	9.67
	418.0	1.82E-4	3.06	2.15E-4	3.0	14.75
	418.2	3.31E-4	2.83	2.04E-4	3.0	15.0
0.2	412.0	0.0417	2.81	0.0339	3.0	2.72
	412.4	0.0762	2.78	0.0639	3.0	2.21
	413.0	0.0164	2.91	0.0145	3.0	3.62
	413.2	0.0152	2.85	0.0124	3.0	3.83
	414.2	5.94E-3	2.95	5.50E-3	3.0	5.01
	415.2	2.28E-3	3.05	2.50E-3	3.0	6.52
	416.0	1.15E-3	3.24	1.88E-3	3.0	7.19
	416.0	1.25E-3	3.13	1.65E-3	3.0	7.50
	420.0	6.46e-5	3.12	9.49E-5	3.0	21.90
0.3	413.0	0.0265	2.93	0.0247	3.0	3.02
	413.2	0.0241	2.85	0.0200	3.0	3.27
	414.2	9.60E-3	2.93	8.60E-3	3.0	4.31
	415.2	6.69E-3	2.80	4.76E-3	3.0	5.24
	416.0	2.72E-3	2.98	2.67E-3	3.0	6.34
	418.0	6.06E-4	3.01	6.06E-4	3.0	10.32
	418.2	6.18E-4	2.91	4.96E-4	3.0	11.18

Table 3: Optimum values for n and k were obtained by directly fitting the Avrami model to isothermal data. In a second round of fitting n was constrained to a value of 3 and values of k were re-determined.

3.2.3 Activation energy for crystallization

Assuming that the process of crystallization is thermally activated the temperature dependence of the crystallization rate parameter k is approximately^{35,36}

$$k^{1/n} = k_0 \exp(-\Delta E / RT) \tag{5}$$

The coefficient k_0 is a temperature independent factor. ΔE is the activation energy, R the universal gas constant (8.314 J.mol^{-1}) and T the absolute temperature. Values for $-\Delta E / R$ can be obtained from the slopes of the Arrhenius plots shown in Figure 15. The data shown in Table 4 illustrate that the activation energy required for crystallization is essentially independent of the concentration of pigment. However figure 15 clearly shows that the intercept k_0 is affected by the pigment. These findings are contrary to those obtained for the crystallization behaviour of poly (ether ether ketone) (PEEK) by Tan et al³⁷ who observed that the activation energy depended on the type of nuclei present.

Pigment concentration (%)	Activation energy (kJ mol^{-1})
0	5383
0.1	4853
0.2	5010
0.3	5063

Table 4: Crystallization activation energy as a function of pigment concentration.

The Arrhenius approach assumes an increase in the rate constant with increasing temperature³⁸. This topic has received some attention in the literature although a widely accepted theory remains to be found³⁹⁻⁴⁴.

3.2.4 The influence of pigments on the surface energies of spherulites

In practice melt or cold crystallization data for most polymers can only be obtained over limited temperature ranges. To extend this range extrapolation procedures have been employed^{45,46} that use Hoffman et al.'s⁴⁷ relationship between the linear growth rate of spherulites G_r and the temperature at which the material crystallizes i.e.

$$G_r = G_0 \exp\left(-\frac{U^*/R}{T - T_\infty}\right) \exp\left(-\frac{K_g}{T \Delta T f}\right) \quad (6)$$

where G_0 is a pre-exponential factor. Equation (6) has been modified by both Chan and Isayev⁴⁸ and Patel and Spruiell⁴⁵ such that the growth rate G_r is replaced by $(1/t_{1/2})$ and G_0 by $(1/t_0)_{1/2}$ where $1/t_{1/2}$ is the reciprocal of the time taken for 50% of the crystallinity to occur.

The first exponential term in the model (equation 6) accounts for the increase in melt viscosity and hence lowering of molecular mobility that occurs as the crystallization temperature approaches T_∞ . T_∞ is a hypothetical temperature where chain motion due to viscous flow or reptation ceases and is assumed to be equivalent to $T_\infty = T_g - 30 \text{ K}$. The second exponential term represents the driving force for crystallization. This term is dominated by the degree of supercooling given by $\Delta T = T_m^\circ - T$ where T_m° is the melting point at equilibrium. The opposing temperature dependencies of these two exponential terms gives rise to a peak in a plot of crystal growth rate against temperatures. This peak

is typical of nucleation controlled processes. The location of the maximum growth rate is midway between the thermodynamic melting point, T_m^0 and T_g . U^* is the activation energy for segmental jump rate in polymers that Hoffman has assigned a value of 6300 J mol^{-1} ($1500 \text{ cal mol}^{-1}$) and R is the gas constant. The parameter $f = 2T / (T + T_m^0)$ is a corrective term⁴⁸ that approximately describes the decrease in the latent heat of fusion that occurs on lowering the crystallization temperature.

An estimate of the equilibrium melting point T_m^0 can be obtained by using the nucleation theory approach of Hoffman and Weeks⁴⁹⁻⁵¹. Here the melting points T_m of crystals formed at different isothermal crystallization temperatures are plotted as a function of crystallization temperature T_c following

$$T_m = T_m^0 \left(1 - \frac{1}{\beta}\right) + \frac{T_c}{\beta} \quad (7)$$

In this equation β is the ratio of the crystal thickness to that of the nucleus. Under equilibrium conditions $\beta = 1$. A line drawn through these data can then be extrapolated to a second line corresponding to $T_m = T_c$ as shown in Figure 16. Melting temperatures in this case were taken as those corresponding to the peak positions in the C_p curves as shown in Figure 14. There is no discernible difference within experimental error in the equilibrium melting point of crystals formed from pigmented or unpigmented material as shown in Figure 16. A value of $T_m^0 = 480 \text{ K}$ has been assumed. This value is within the range reported in the literature for this variable ($459 - 493 \text{ K}$)^{52,53}. The value of T_m^0 chosen is not that important as Galante et al⁵² have shown that changes in T_m^0 do not affect the slope or the linearity of Hoffman - Lauritzen plots. T_g was assumed to be 270K ⁵³.

The nucleation constant K_g in equation (6) is a function of the surface free energy of the crystals and the heat of crystallization and is defined⁵¹ by

$$K_g = \frac{4b\sigma\sigma_e T_m^0}{\Delta H_f k_b} \quad (8)$$

where b is the layer thickness i.e. the distance between two adjacent fold planes. σ and σ_e represent the free energies per unit area of the surfaces of the crystalline lamellae that run parallel and perpendicular to the chain direction respectively. ΔH_f is the heat of fusion and k_b is the Boltzman constant. The nucleation constant reflects the change in the interfacial free energy that occurs whenever crystalline material adsorbs on to the surface of a foreign body, in this case a pigment particle. The reduction in energy that occurs depends on both the geometry and chemistry of the nucleating agent.

Figure 17 shows plots of $\ln(1/t_{1/2}) + U^*/[R(T-T_\infty)]$ versus $1/(T\Delta)$ for both unpigmented and pigmented polypropylene. It is clear from this figure that the slope of the linear fits to these plots is lower for the pigmented materials than for the virgin plastic and essentially independent of the pigment concentration. The slopes of these plots represent the product of the interfacial energies ($\sigma\sigma_e$) and are given in Table 5.

Pigment concentration (%)	$K_g \times 10^{-5} \text{ K}^2$	$\sigma\sigma_e$ ($\times 10^{-3} \text{ J}^2 \text{ m}^{-4}$)
unpigmented (DSC)	-10.83	2.38
unpigmented (Microscopy)*	-6.29	1.38
0.1	-5.39	1.19
0.2	-5.72	1.26
0.3	-5.61	1.23

Table 5: Crystal growth kinetic data generated from nucleation theory. $b = 6.26 \times 10^{-10} \text{ m}$, $K_b = 1.35 \times 10^{-23} \text{ J K}^{-1}$, $\Delta H_f = 165 \text{ J gm}^{-1}$, $T_m^0 = 480 \text{ K}$, $T_\infty = T_g - 30$, $T_g = 269 \text{ K}$, $U = 6300 \text{ J mol}^{-1}$.

It is possible to resolve the product of $\sigma\sigma_e$ in to the free energy components, however since σ is constant ($\sim 0.1\Delta H_f$) there seems little point in performing the calculation. What is apparent from Table 5 is that the surface interfacial free energy of polypropylene is lowered by the presence of the pigment. These findings show that according to Beck’s criteria⁵⁴ the pigment is behaving as a good nucleating agent. The reduction in surface energy of the spherulites due to the addition of a nucleating agent has been discussed elsewhere⁵⁵.

Figure 18 shows a Hoffmann - Lauritzen plot for virgin material obtained by replotting the data presented in figure 5 using the same parameters as used to generate figure 17. Although the y scale is different to that of Figure 17 , k_g obtained from the slope of the plot is broadly in agreement with that derived from calorimetric data.

3.2.5 Are spherulitic growth rates affected by pigmentation?

Whilst it is difficult to experimentally determine spherulitic growth rates for pigmented samples due to their small size comparisons of relative growth rates can be made by comparing Avrami rate constants. Flory^{56,57} and generalized the rate constant to account for different morphologies such that $G \propto k^{1/n}$, hence

$$\ln G = \frac{1}{n} \ln k + \text{constant } t \tag{9}$$

Figure 6 shows a plot of $1/n \ln k$ versus crystallization temperature. From this figure it is evident that spherulitic growth rates increase on lowering the crystallization temperature as expected. Due to the nucleating effect of the pigment direct comparisons of the growth rates between virgin and pigmented samples are not possible except by large extrapolations. Direct comparisons of the growth rates of samples containing different concentrations of pigment shows that increasing the amount of pigment has a small influence on the rate of crystallization at a given temperature. This can also be seen in Table 6. Since it appears that this difference is not due to differences in the amount of supercooling i.e. T_m^0 is constant then this small increase in rate is probably due to the increased density of nucleation sites.

	Pigment concentration (%)		
	0.1	0.2	0.3
Crystallization Temperature (K)	$k^{1/n}$	$k^{1/n}$	$k^{1/n}$
413.0	0.200	0.243	0.290
413.2	0.182	0.230	0.270
414.2	0.144	0.176	0.205
415.2	0.109	0.136	0.167
416.0	0.092	0.124	0.138
418.0	0.060	-	0.085

Table 6: The concentration and temperature dependence of $k^{1/n}$

4 DISCUSSION

The addition of the organic pigment phthalocyanin blue to isotactic polypropylene has a profound affect on its crystallization behaviour during cooling from a melt. Polarised light microscopy shows melts containing pigment crystallize as a myriad of small spherulites in contrast to the large plate like structures characteristic of unpigmented material. The radial growth rate of these large spherulites although independent of time increases as expected on lowering the crystallization temperature. Unfortunately these results cannot be compared with those of pigmented samples as the small size of the spherulites is beyond the reliable measurement range of the optical microscope.

Non-isothermal calorimetric measurements of melts crystallizing during cooling show that the presence of a small quantity of phthalocyanin blue (0.1%) is enough to raise the temperature at which crystallization occurs by approximately 16K. Increasing the pigment concentration from 0.1% to 0.3% results in a further increase in crystallization temperature of approximately 1K. These findings are confirmed by isothermal measurements of crystallization which show that the time taken for 50% of the material to crystallize at a particular temperature falls as the amount of pigment contained within a sample is increased. Despite the changes in crystallization behaviour that occur when pigment is added to polypropylene the overall level of crystallinity remains essentially constant at approximately 59%. The equilibrium melting temperature for polypropylene spherulites also remains constant at approximately 480 K.

Interpretation of the isothermal calorimetric measurements using Avrami's model suggest that the morphology of the spherulites changes in the presence of the pigment from a 2-d disc to a 3-d sphere. This may affect the mechanical properties of, for example, pigmented mouldings. Changes in morphology of this nature have been observed elsewhere, Parrini and Corrieri⁵⁸ observed by electron microscopy that small amounts of nucleating agents seems to induce the development of fibrils which subsequently did not organise themselves into spherulites. Similar results were also obtained using isotactic polypropylene crystallized by heterogenous nucleation.

A consequence of n changing with the addition of the pigment means that it is not possible to use an empirical shift factor to account for the influence of both temperature and pigment concentration on a crystallization curve obtained from virgin material. However the influence of changing the concentration of pigment can be modelled. Table 3 contains values of the rate constant k when the shape parameter n is kept constant at 3. These k values do not differ significantly from the optimum values obtained when n is allowed to be a variable. Data generated using equation 3 with both optimum and ‘forced’ parameters shows that the quality of the fit is relatively unaffected by forcing n to have a value of 3. The linear temperature dependence of $k^{1/n}$ (figure 15) is also unaffected by assuming n is constant. It is possible to derive an empirical relationship to describe both the concentration and temperature dependence of k however this is beyond the scope of the current paper.

The activation energy required for crystallization appears to be unaffected by the presence of the pigment as is the overall level of crystallinity. These findings coupled with the decrease in surface interfacial free energy that occurs when pigment is added to polypropylene imply that it is acting as a nucleating agent.

In practical terms these results suggest that the morphology of pigmented mouldings will be different to those manufactured from virgin material. This may affect their mechanical properties and will influence dimensional stability. This has been demonstrated in a recent study of high density polyethylene⁵⁹ where the shrinkage and warpage behaviour of square plates injection moulded from virgin and pigmented high density polyethylene. The ability of phthalocyanin blue to act as a nucleating agent will raise the crystallization temperature of a cooling melt. This should enable a shorter cooling time to be used during injection moulding. However the potential saving in cycle time is likely to depend on the mould geometry and on the processing conditions used. Warner and Holt⁶⁰ found that phthalocyanin green accelerated crystallization of PET under quiescent conditions but observed no difference in the crystallization behaviour of spun PET. These findings suggest that in PET orientation effects exceed nucleation effects, this may also be the case for polypropylene.

5 CONCLUSIONS

Calorimetric and microscopic studies of the crystallization behaviour of polypropylene suggest that the organic pigment phthalocyanin blue is an effective nucleating agent for this material. The presence of the pigment has a profound affect on the crystallization behaviour of isotactic polypropylene as it is cooled from a melt. The morphology of polypropylene containing small amounts (up to 0.3%) of pigment is a myriad of very small spherulites typically less than 10 μm in diameter. This is in marked contrast with the large plate-like spherulites with diameters greater than 100 μm characteristic of the unpigmented material. Modelling of isothermal crystallization data using a single stage Avrami model shows that the 2-d plates seen in the virgin material give rise to 3-d spherical spherulites in the presence of the pigment. Non-isothermal calorimetric measurements show that phthalocyanin blue (at a concentration of 0.1%) raises the crystallization temperature of the melt by approximately 16°C. Increasing the pigment concentration to 0.3% results in a smaller increase in crystallization temperature of approximately 1°C. Despite these morphological differences the overall level of crystallinity remains constant.

The practical implications of this work are that:

- The morphology of pigmented mouldings will be different to those manufactured from virgin material which may affect their mechanical properties and dimensional stability.
- It should be possible to reduce the cycle time when injection moulding polypropylene containing phthalocyanin blue as less supercooling will occur during the cooling phase of the cycle.

6 ACKNOWLEDGEMENTS

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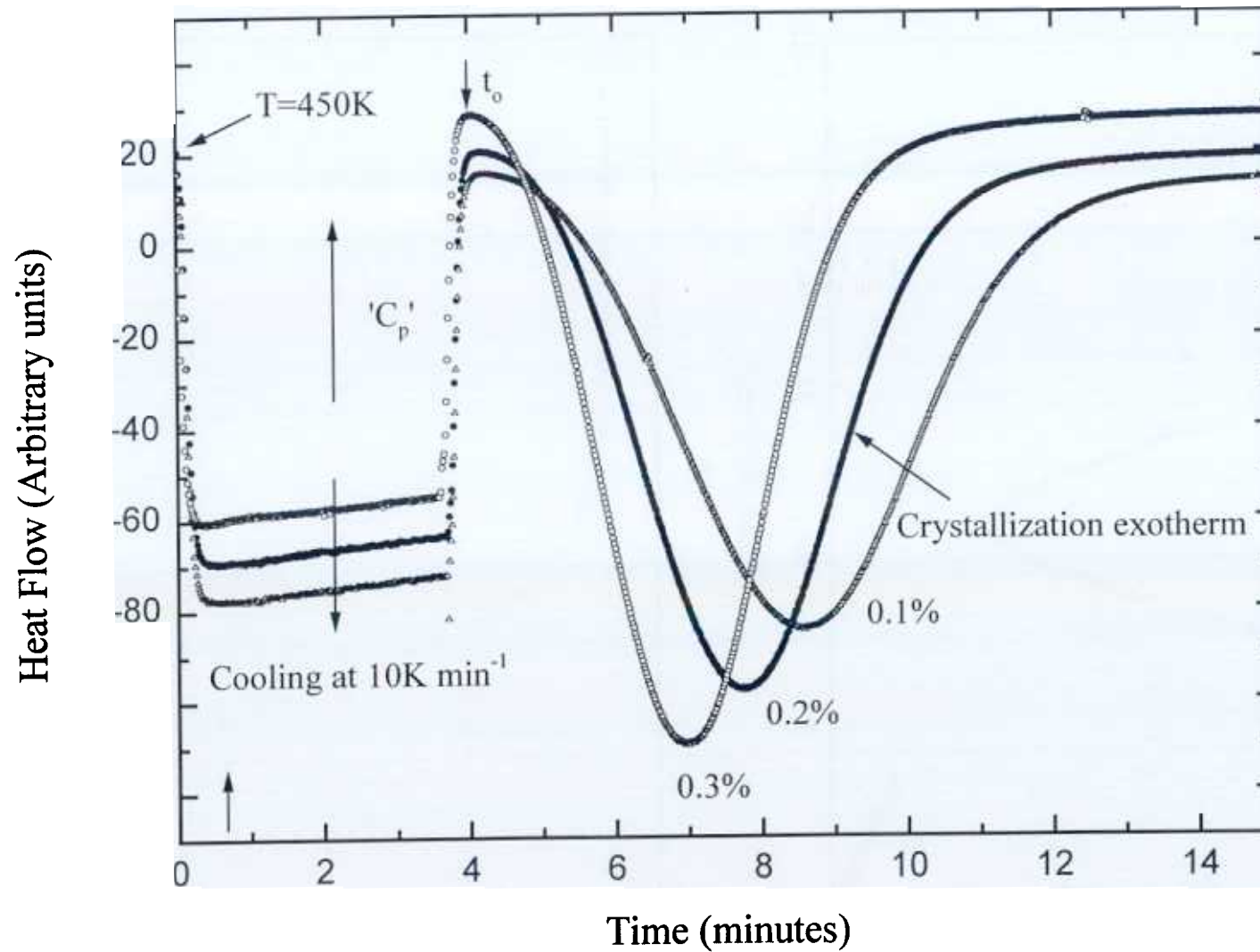
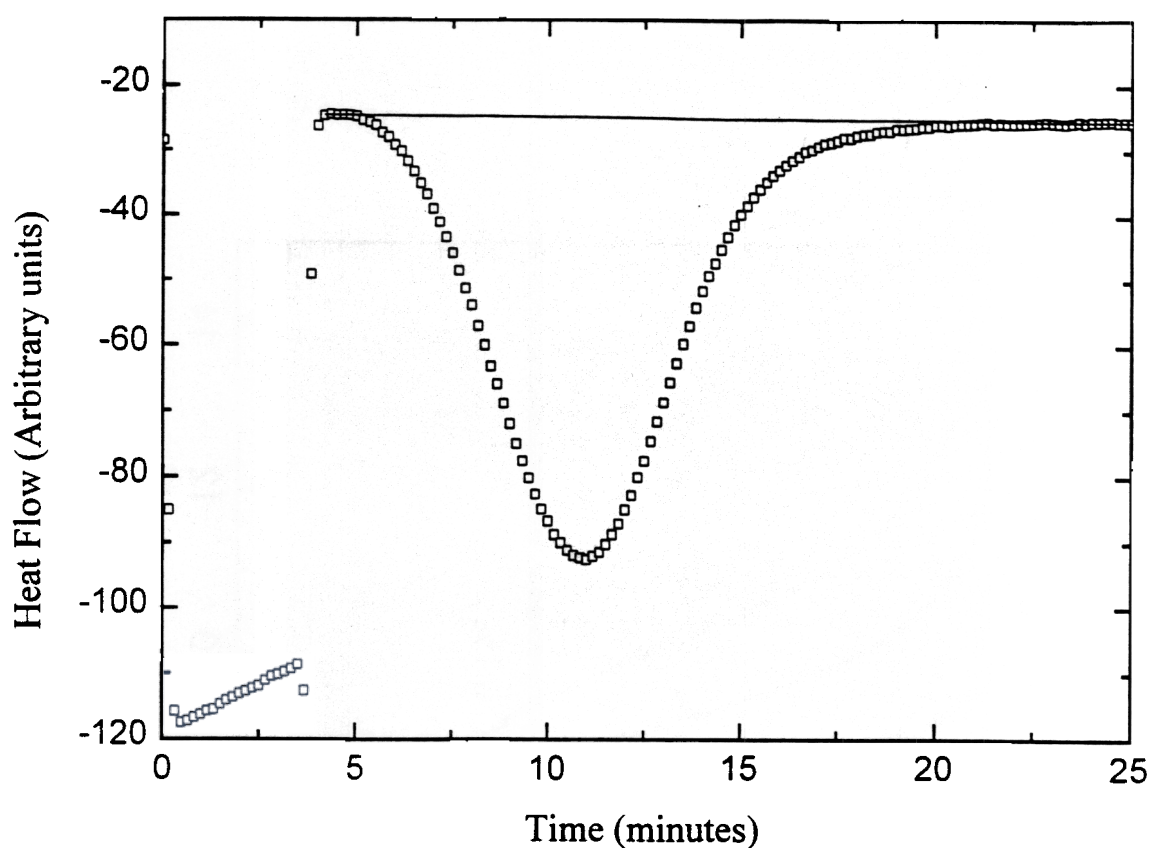


Fig. DSC curves of polypropylene containing different concentrations (0.1, 0.2 and 0.3%) of phthalocyanin blue. The samples were cooled at a rate of 10K min⁻¹ from an annealing temperature of 450K to an isothermal temperature of 413K. (Note that the curves have been shifted in Y to facilitate the understanding of the figure.)

A



B

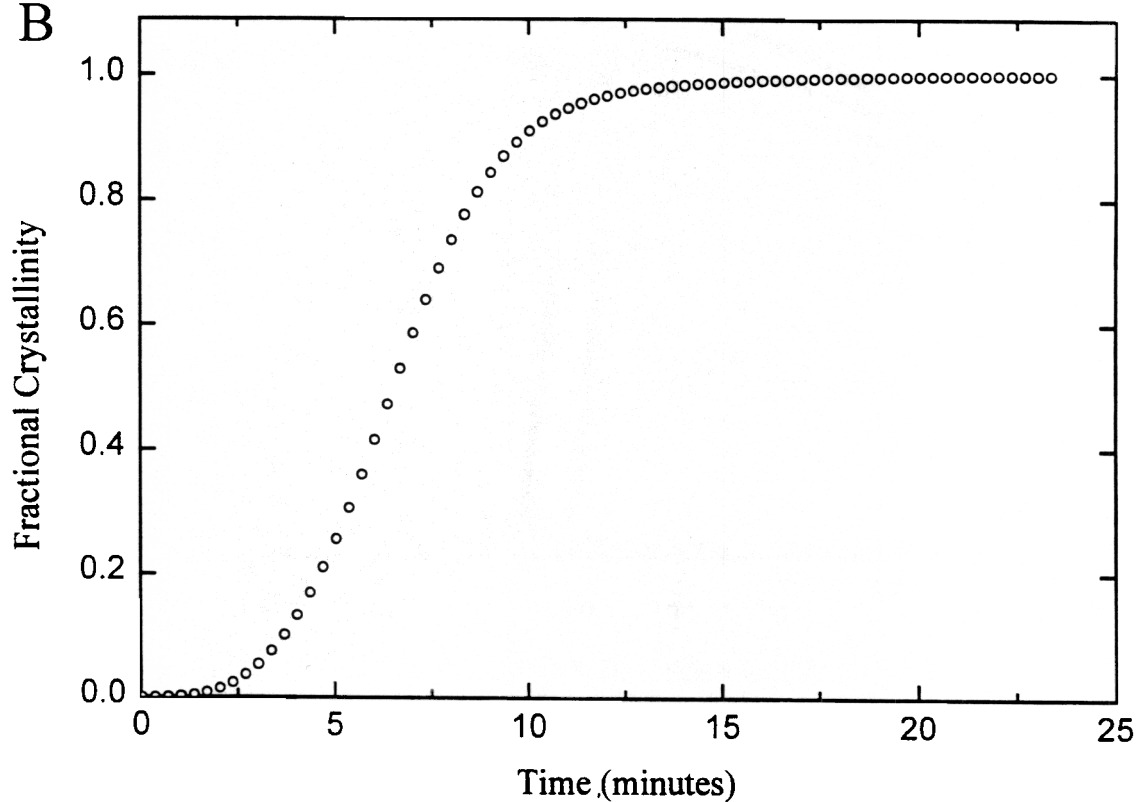
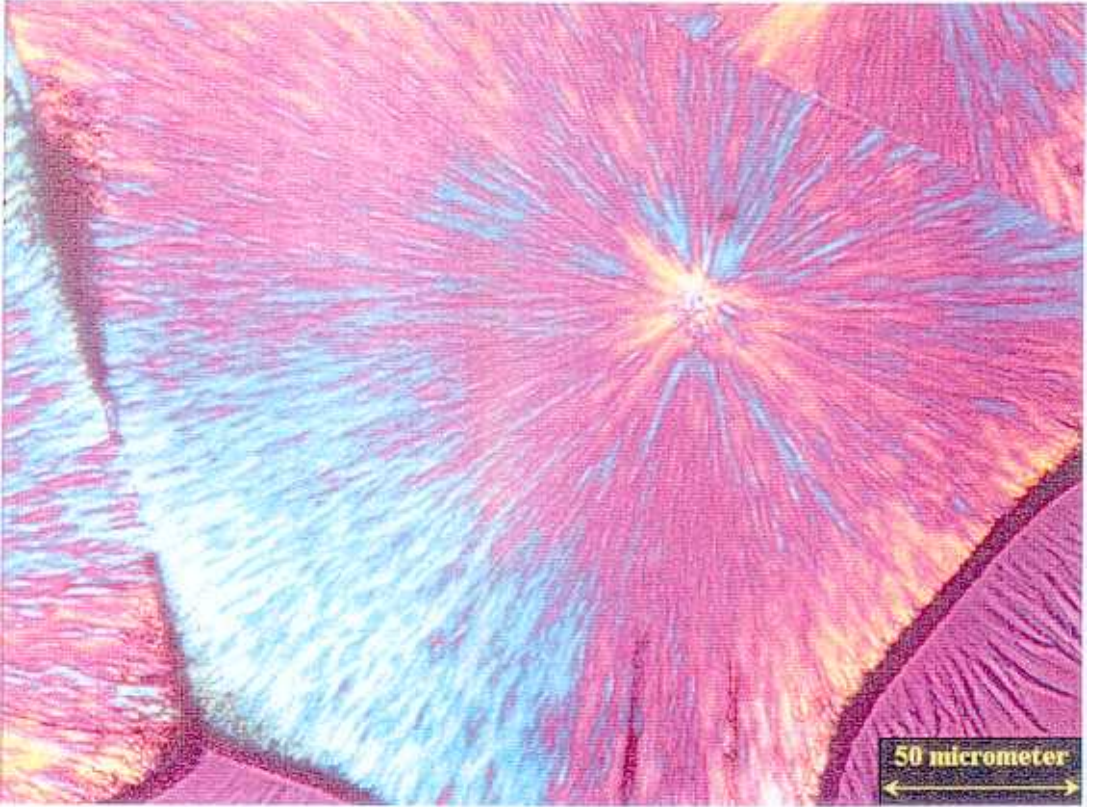


Fig. 2. A) The crystallization endotherm for a sample containing 0.1% phthalocyanin blue at 413K. The baseline drawn connects points corresponding to the onset and completion of crystallization.

B) The development of crystallization with time is obtained from the ratio of equations 2a and 2b.

A



B

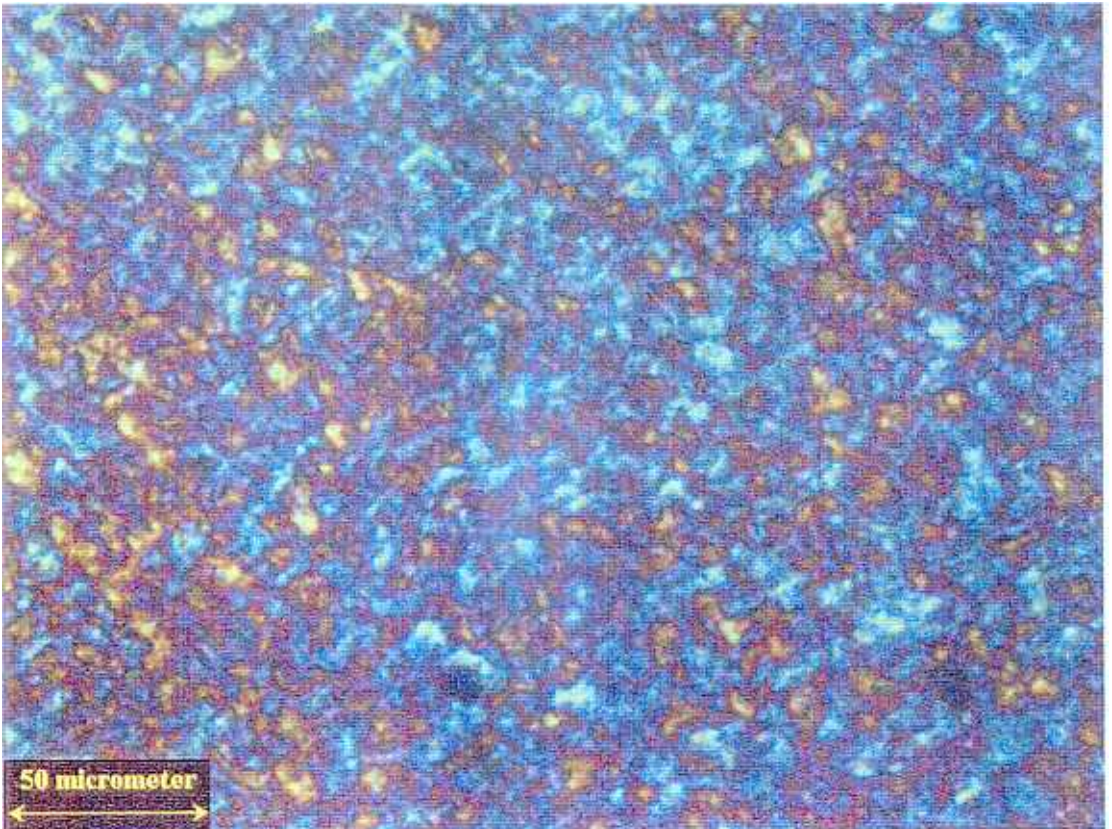


Fig. 3. The presence of phthalocyanin blue has a very pronounced effect on the size and number of spherulites in polypropylene. (A) shows the structure of unpigmented material whilst (B) shows the influence of 0.3% phthalocyanin blue.

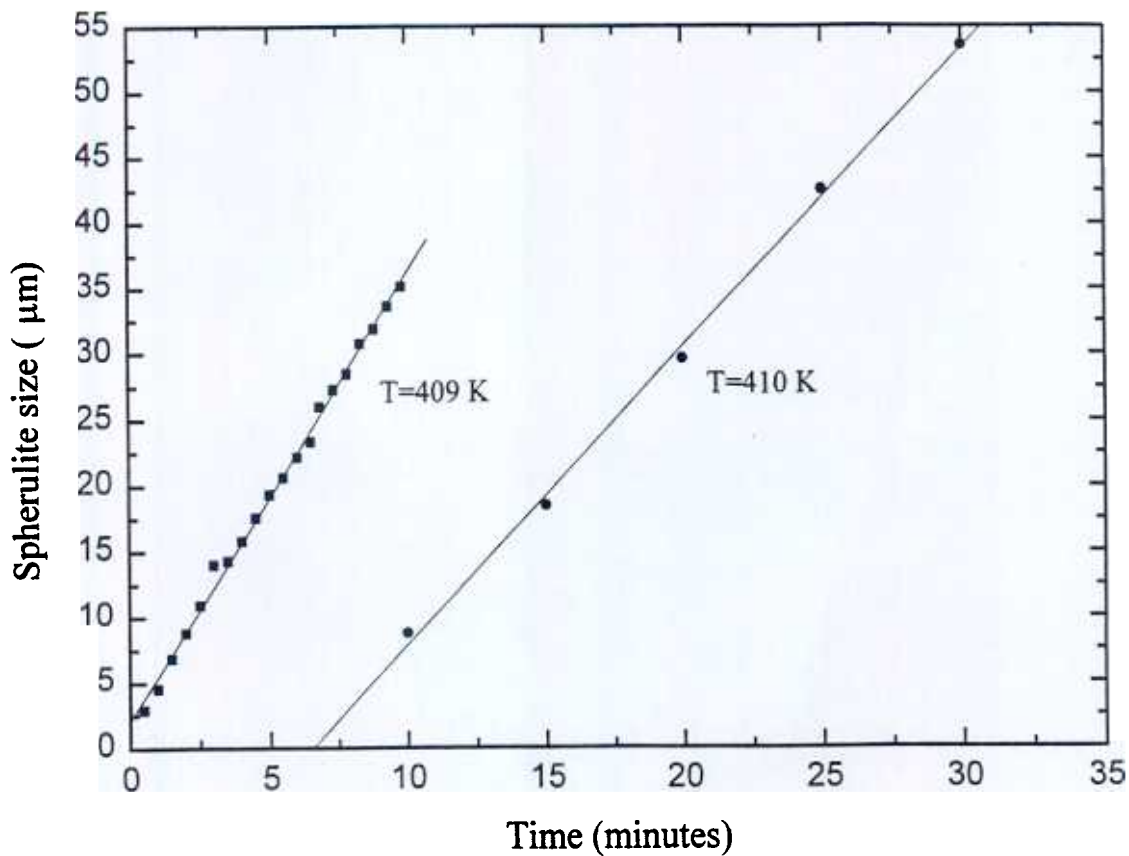


Fig. 4. The linear growth rate of spherulites of unpigmented polypropylene depends on temperature.

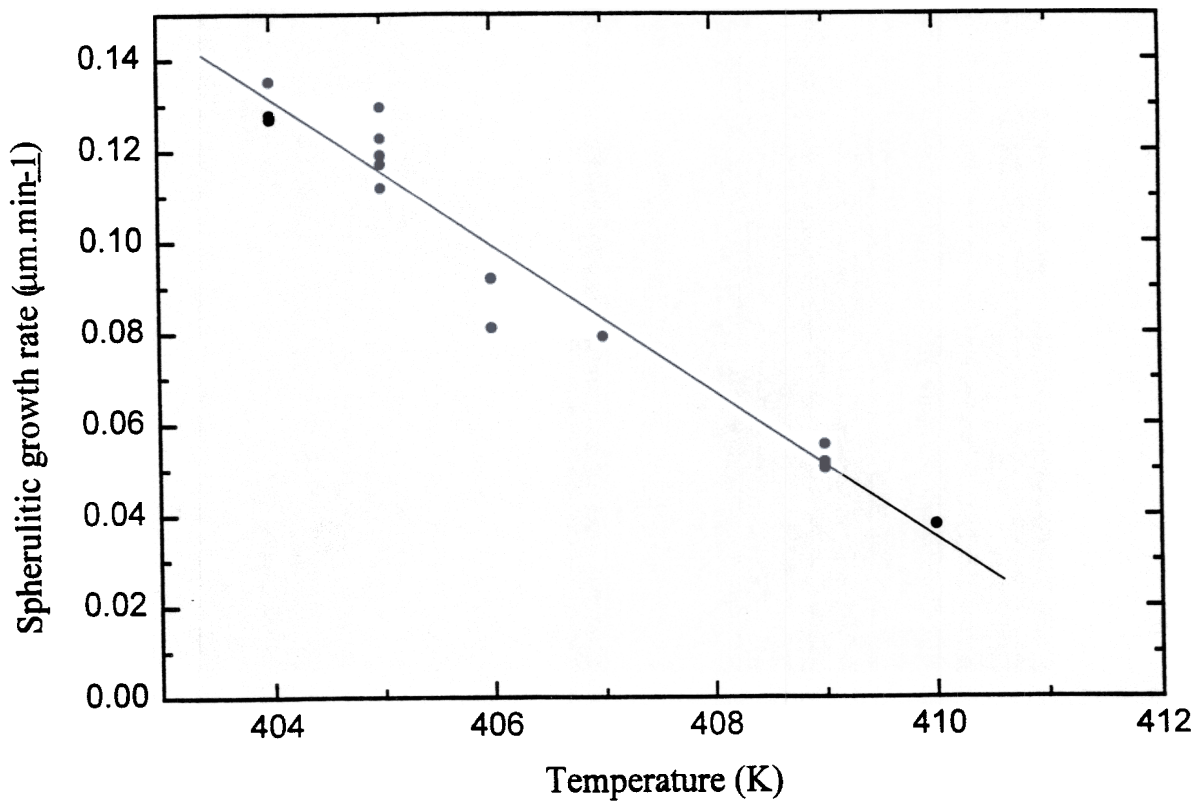


Fig. 5. The temperature dependence of the growth rates of spherulites of unpigmented polypropylene can be described over a limited temperature range by a straight line.

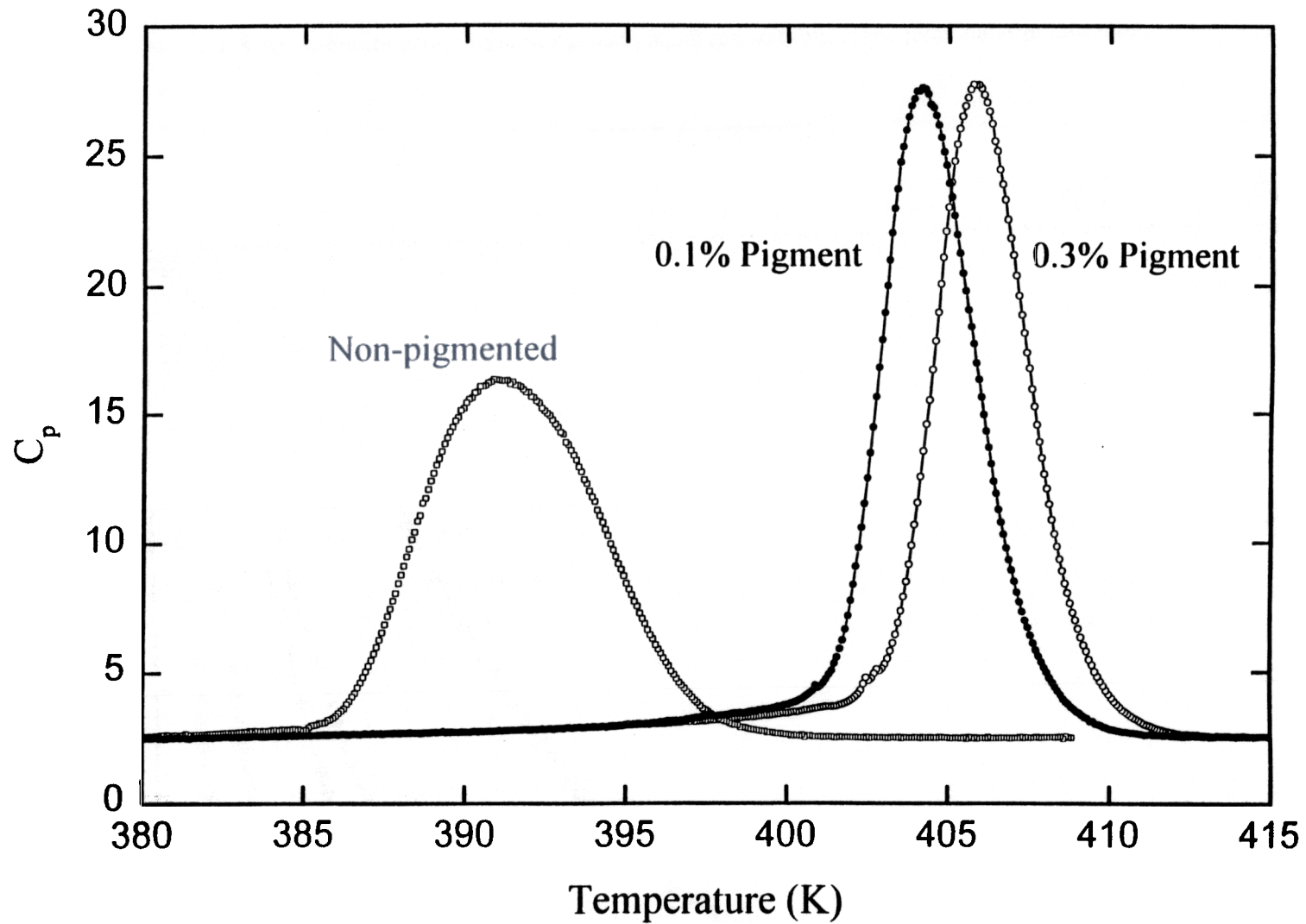


Fig. 6. Observing the temperature at which the onset of crystallization begins shows that phthalocyanin blue has a substantial affect on the crystallization behaviour of polypropylene. These non-isothermal DSC curves were obtained by cooling a melt from an annealing temperature of 450K at a rate of 10 K.min⁻¹.

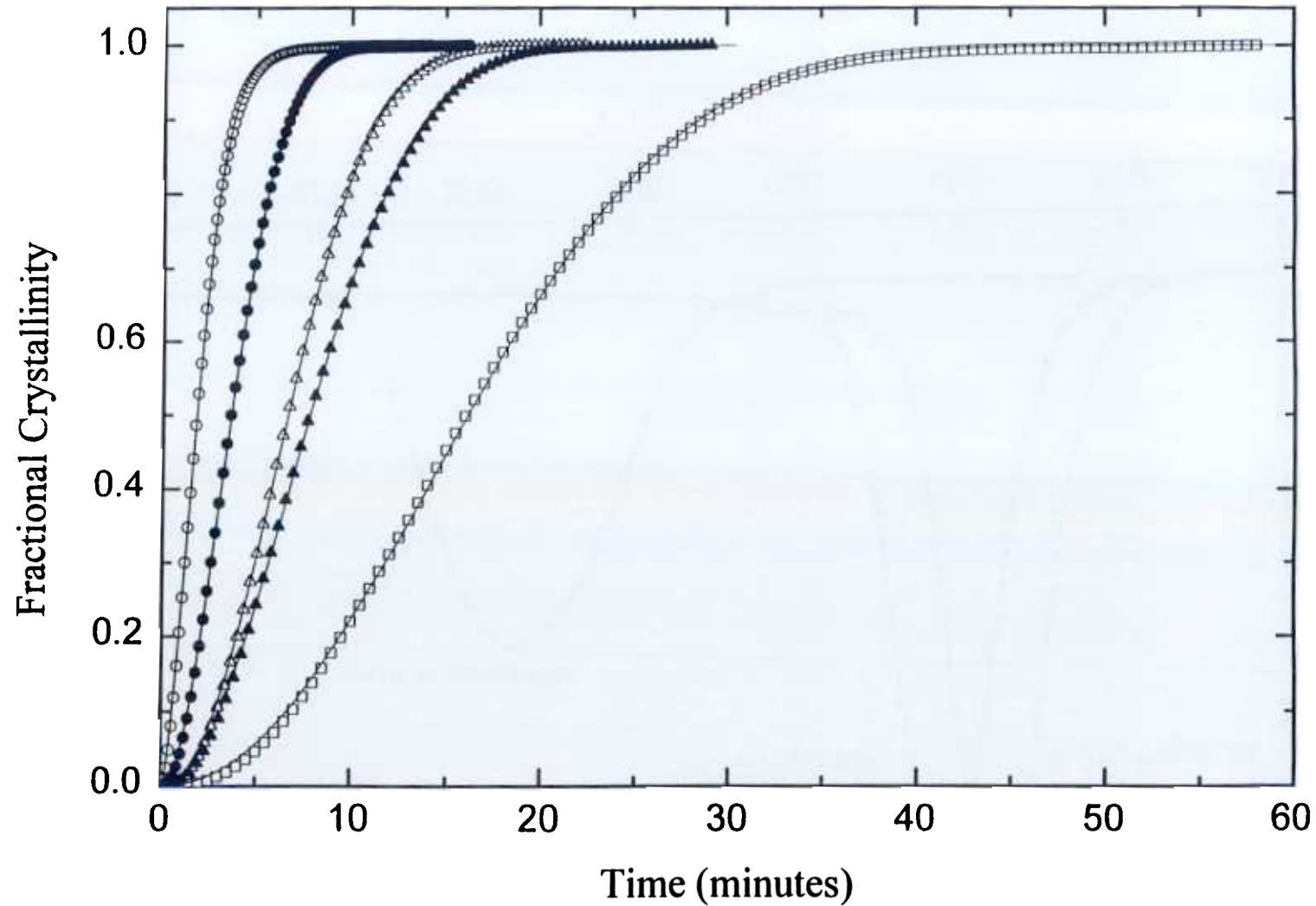


Fig. 7. A comparison of the fit obtained using the Avrami/Evans function with measured data for unpigmented polypropylene at the following temperatures: ○ = 395.4K, ● = 397.4K, △ = 399.4K, ▲ = 400K, □ = 403K.

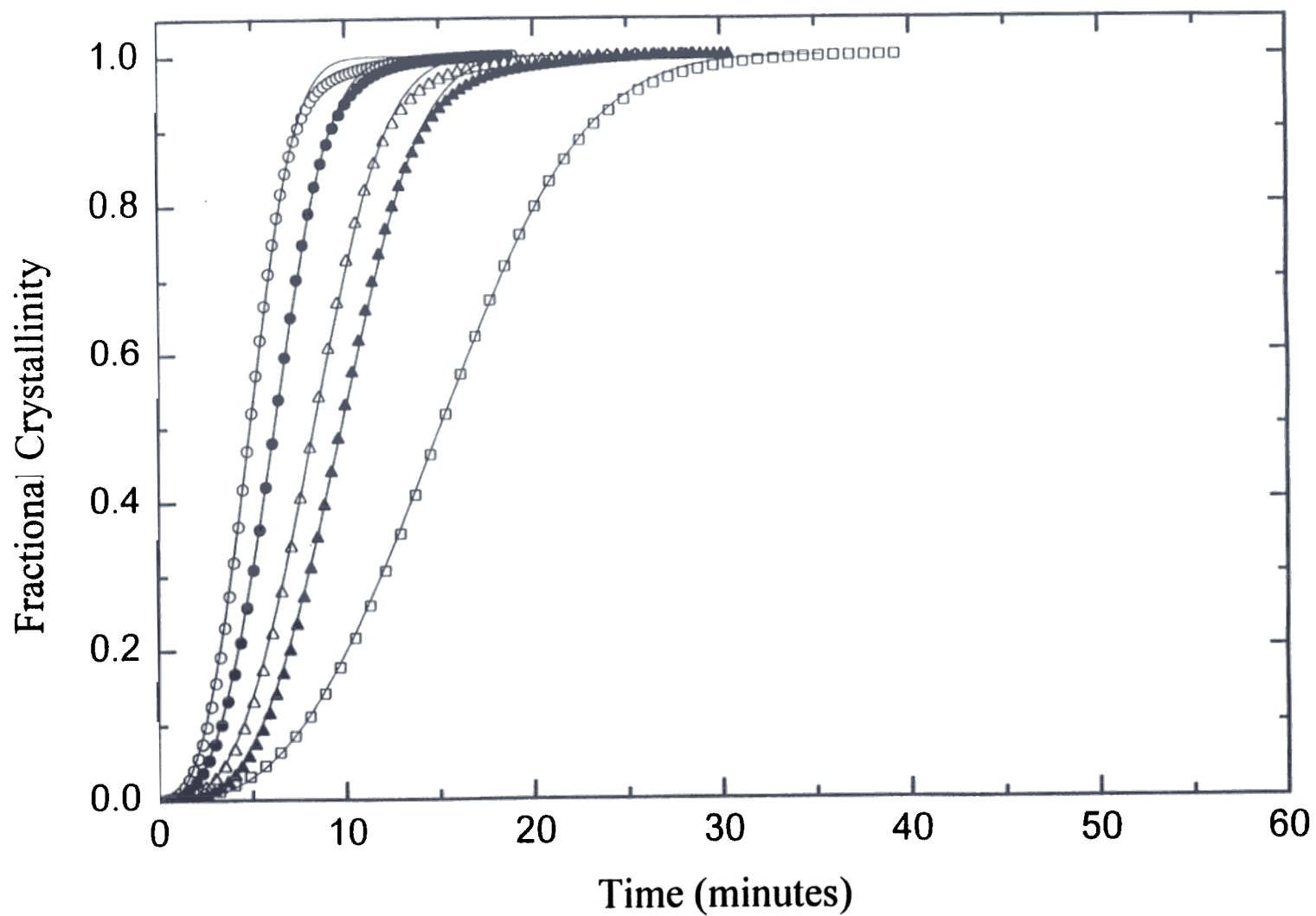


Fig. 8. A comparison of the fit obtained using the Avrami function with measured data for samples containing 0.1% phthalocyanin blue at the following temperatures: ○ = 413.2K, ● = 414.2K, △ = 415.2K, ▲ = 416K, □ = 418.2K.

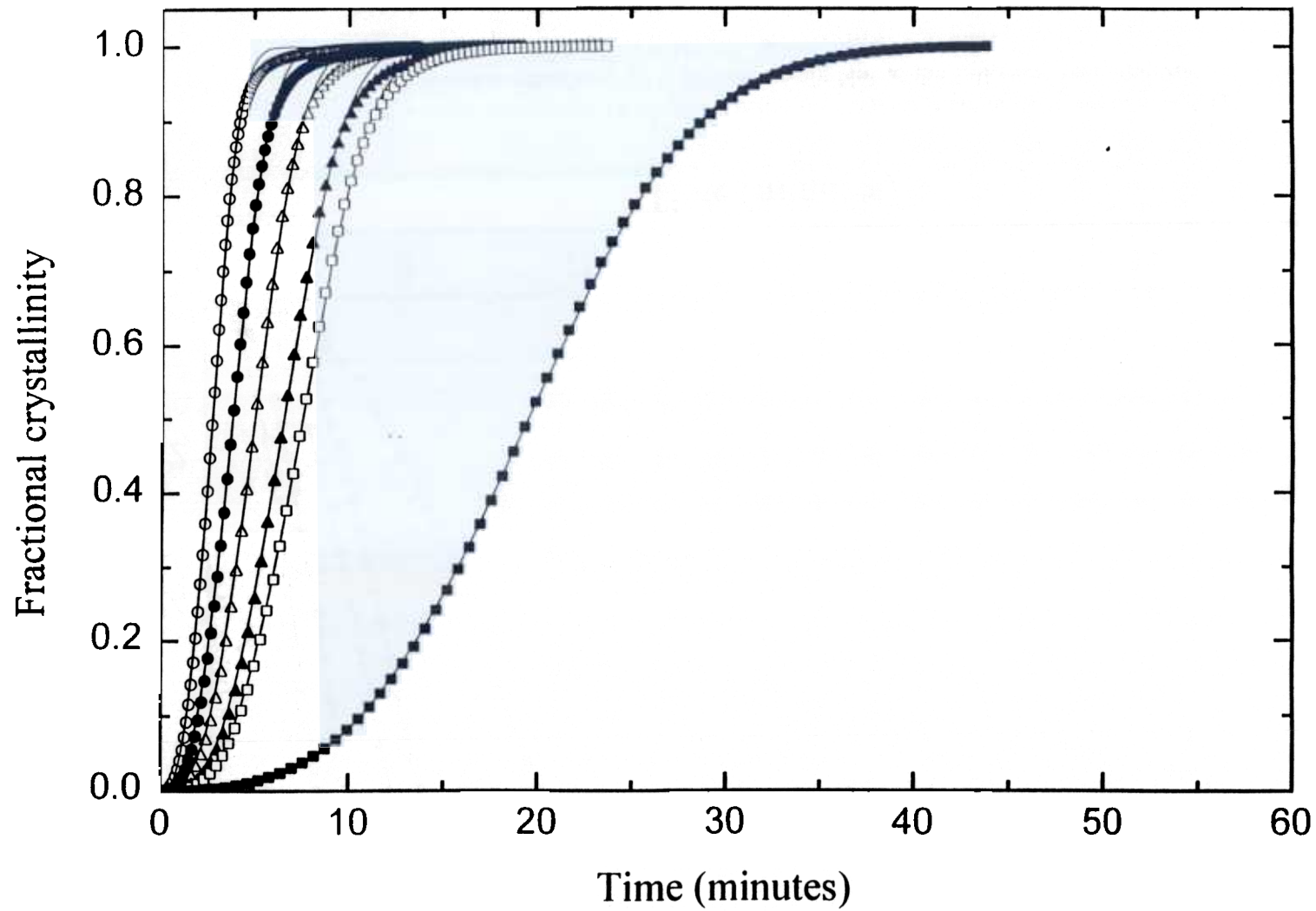


Fig. 9. A comparison of the fit obtained using the Avrami/Evans function with measured data for samples containing 0.2% phthalocyanin blue at the following temperatures: $\circ$ = 412K, $\bullet$ = 413K, Δ = 414.2K, $\blacktriangle$ = 415.2K, $\square$ = 416K, $\blacksquare$ = 420K.

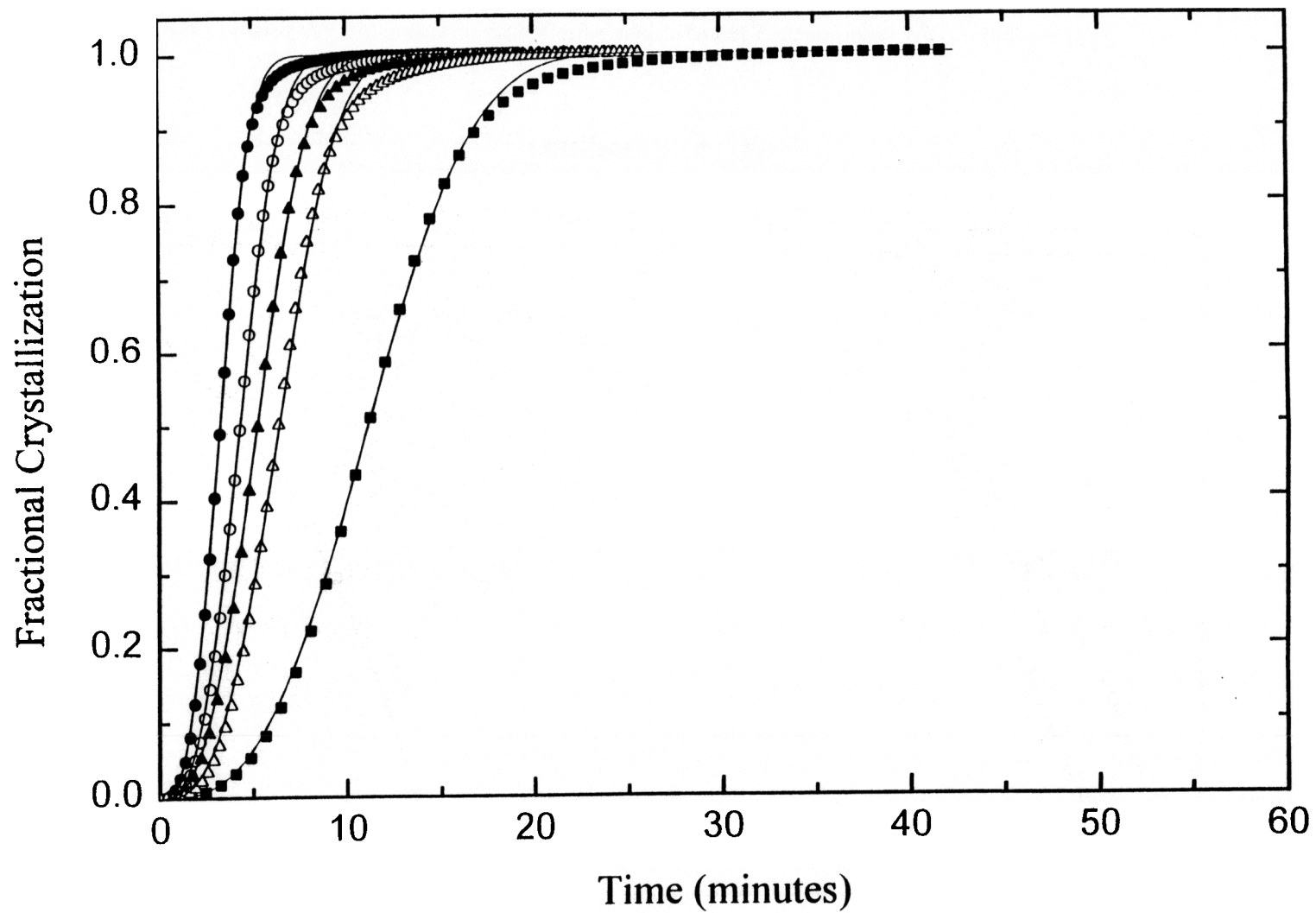


Fig. 10. A comparison of the fit obtained using the Avrami/Evans function with measured data for samples containing 0.3% phthalocyanin blue at the following temperatures: ● = 413.2K, ○ = 414.2K, ▲ = 415.2K, △ = 416K, ■ = 418.2K

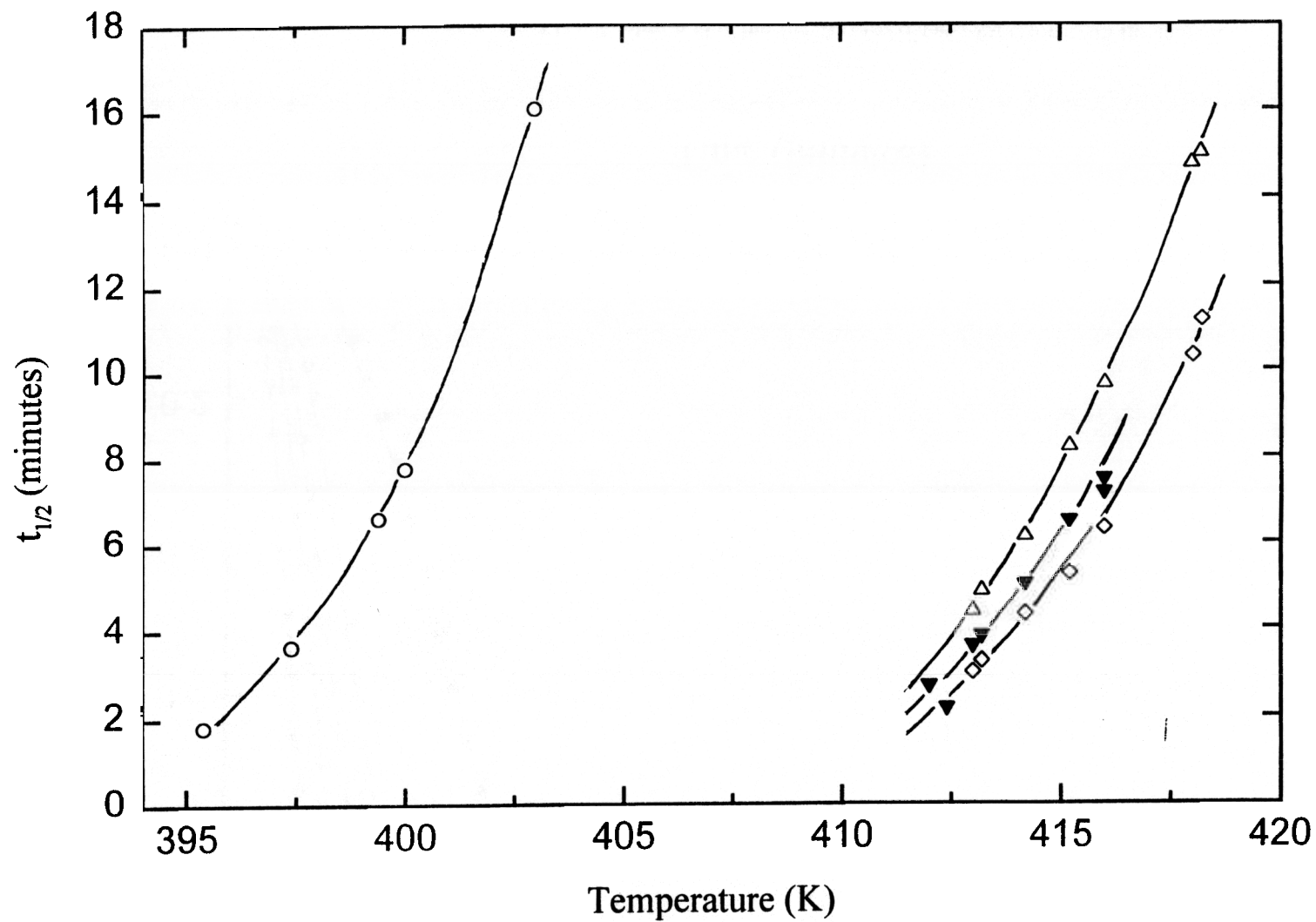


Fig. 1 $t_{1/2}$ as a function of temperature and pigment concentration ($\circ$ = unpigmented polypropylene, Δ = 0.1%, $\blacktriangledown$ = 0.2% and $\diamond$ = 0.3%).

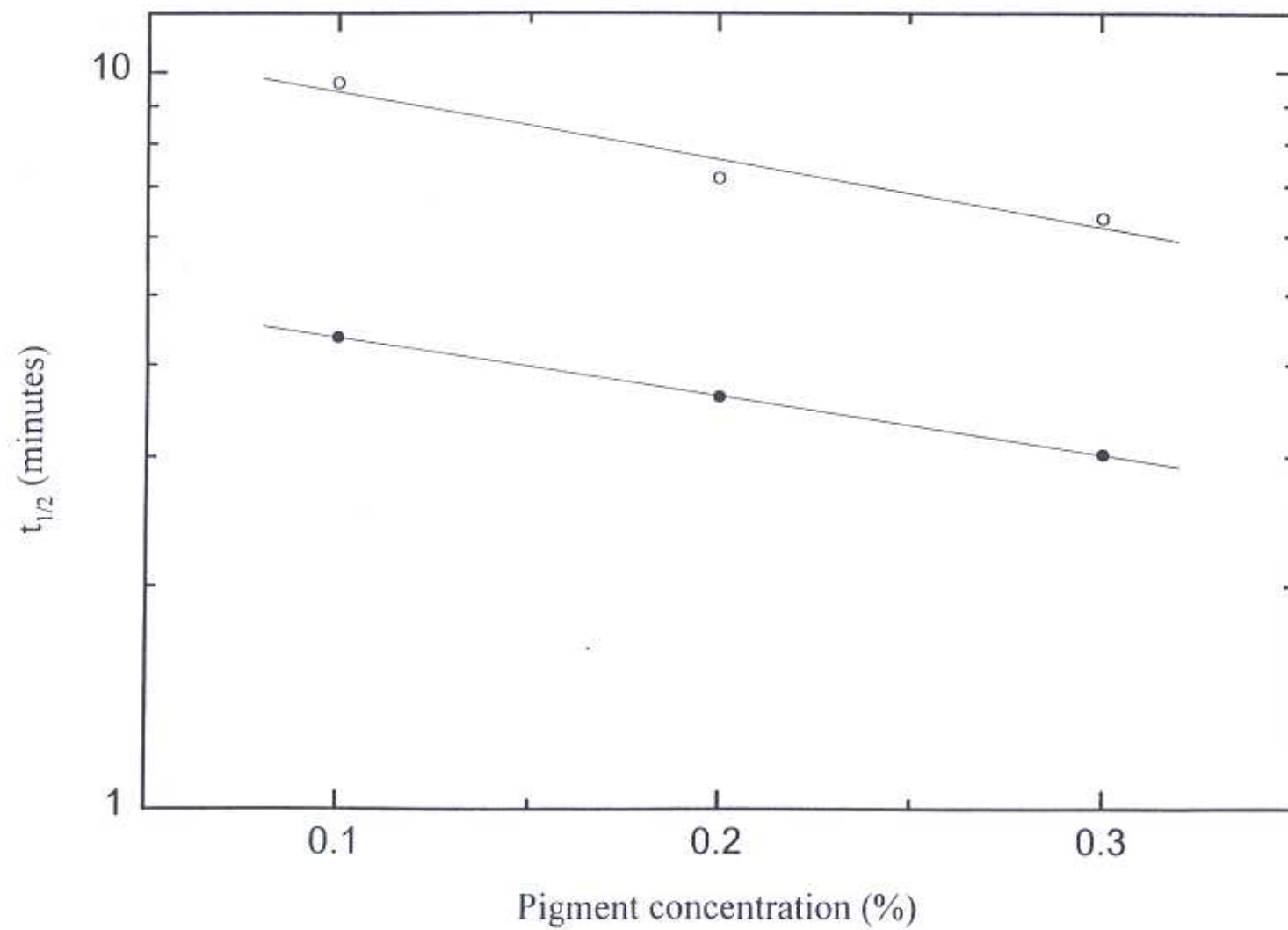


Fig. 12. Log $t_{1/2}$ as a function of pigment concentration at temperatures of 413 K (●) and 416 K (○).

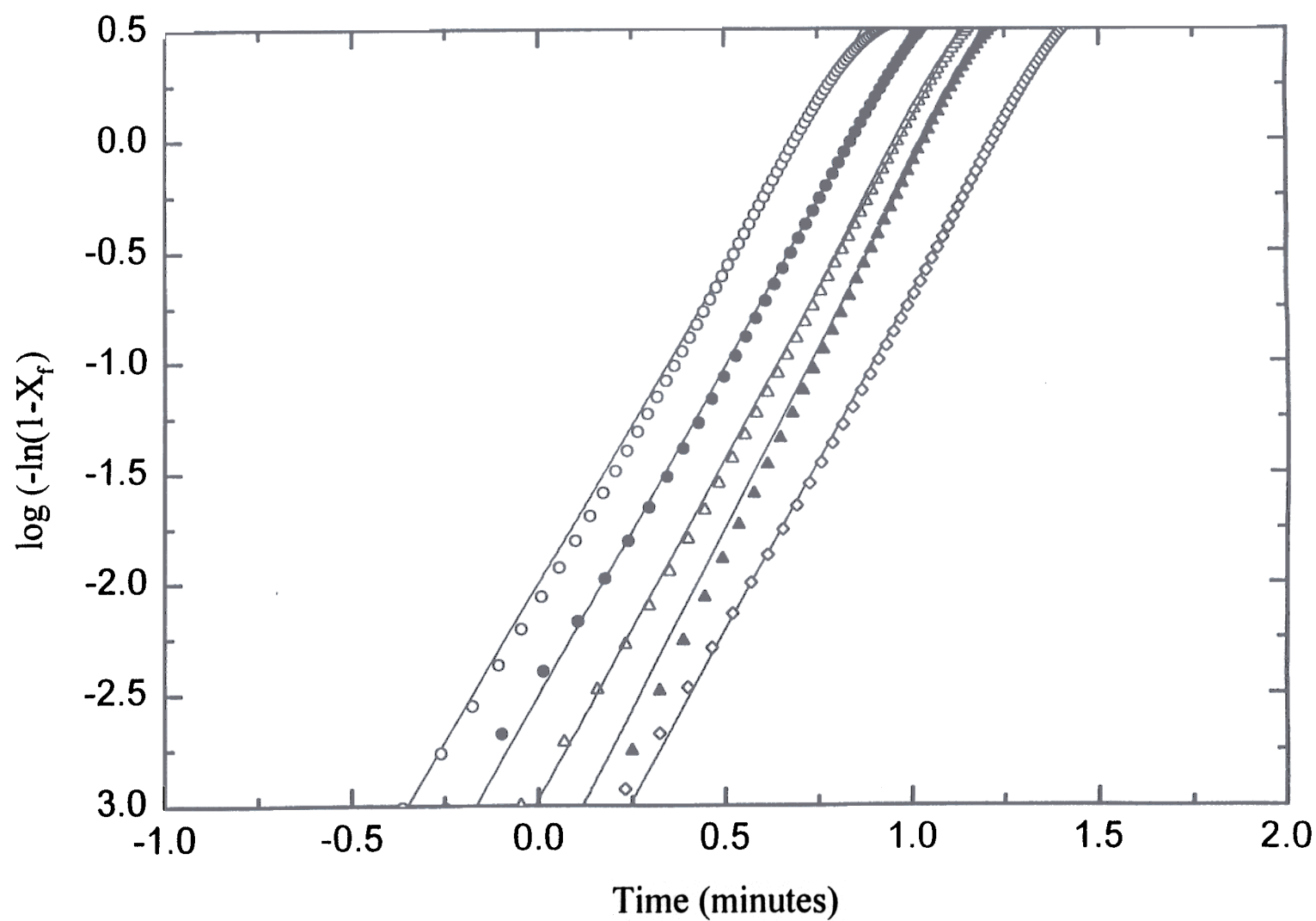


Fig. 13. Linear double logarithmic plots of the rearranged Avrami function yield a slope n and intercept $\log k$. These data are for a sample containing 0.1% phthalocyanin blue at temperatures of: $\circ = 413\text{K}$, $\bullet = 414.2$, $\Delta = 415.2\text{K}$, $\blacktriangle = 416\text{K}$, $\diamond = 418\text{K}$

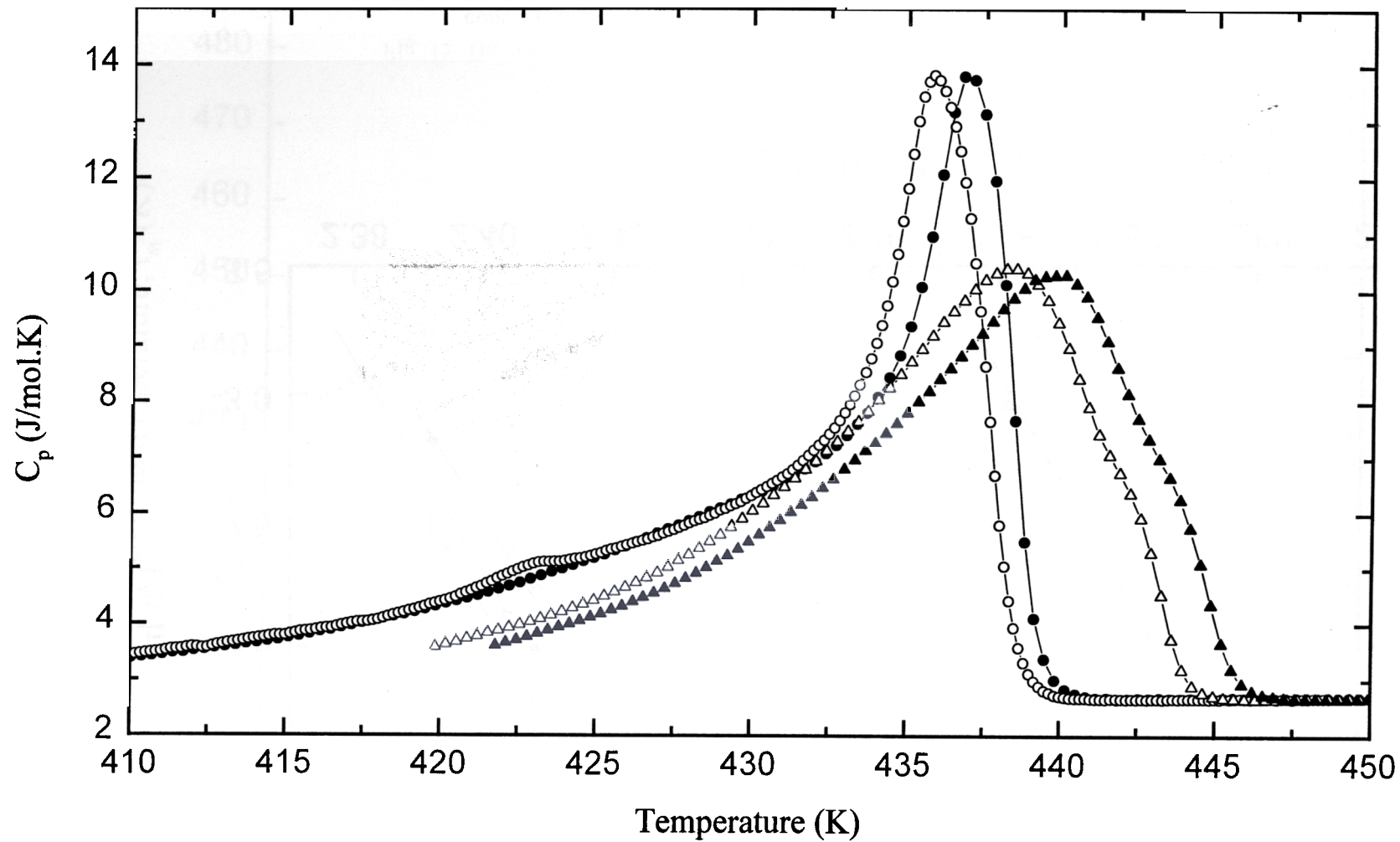


Fig. 14. C_p curves for polypropylene containing 0.2% phthalocyanin are broader than those obtained for unpigmented material. The curves are obtained by reheating samples that have been crystallized at the following temperatures: *virgin*, $\circ$ = 400K, $\bullet$ = 401.4K, 0.2% *pigment*, Δ = 413.2K, $\blacktriangle$ = 415.2K.

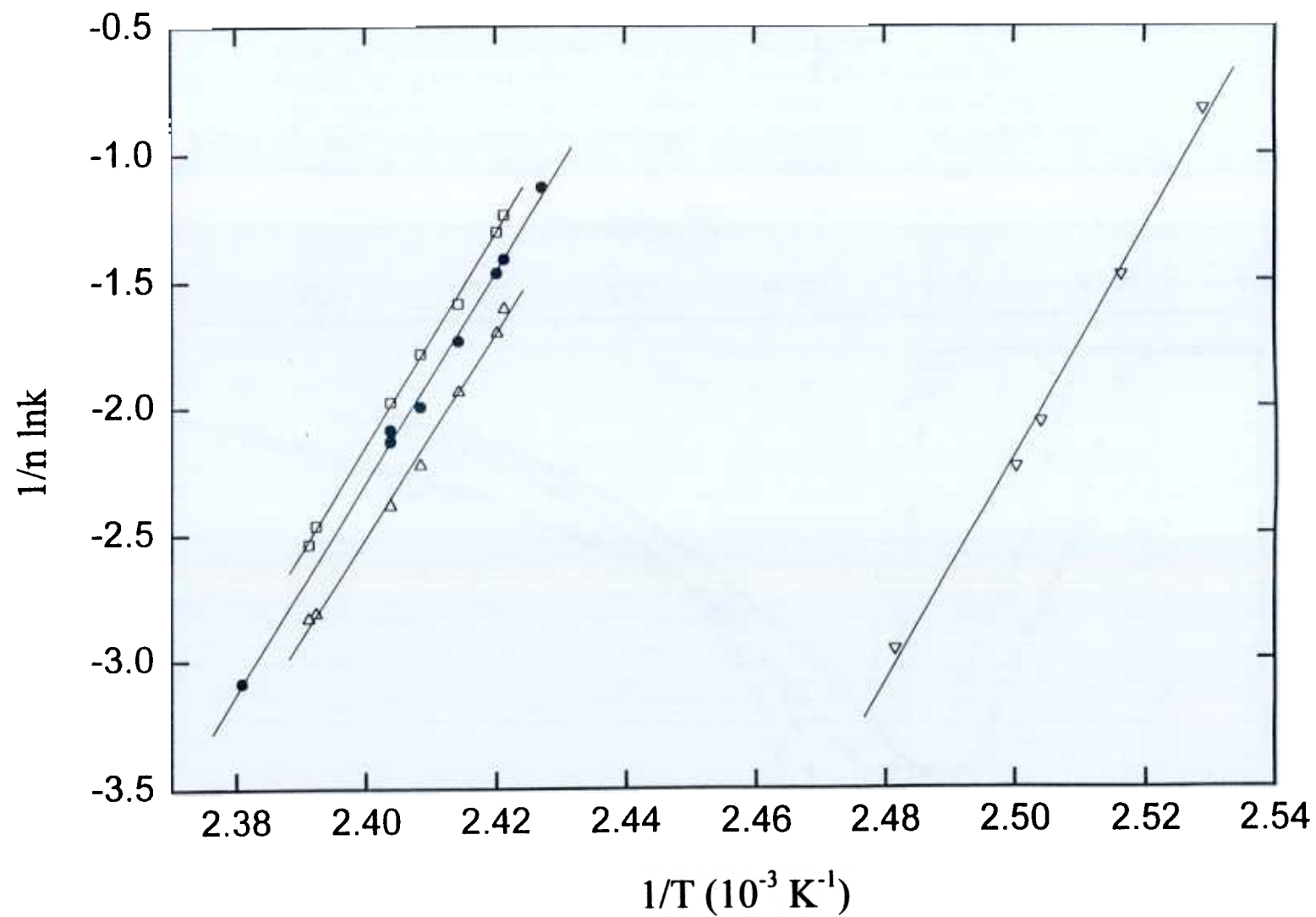


Fig. 15. The slopes of the Arrhenius plots for polypropylene containing the following concentrations of pigment $\nabla = 0\%$, $\Delta = 0.1\%$, $\bullet = 0.2\%$, $\square = 0.3\%$ yields the activation energy required for crystallization.

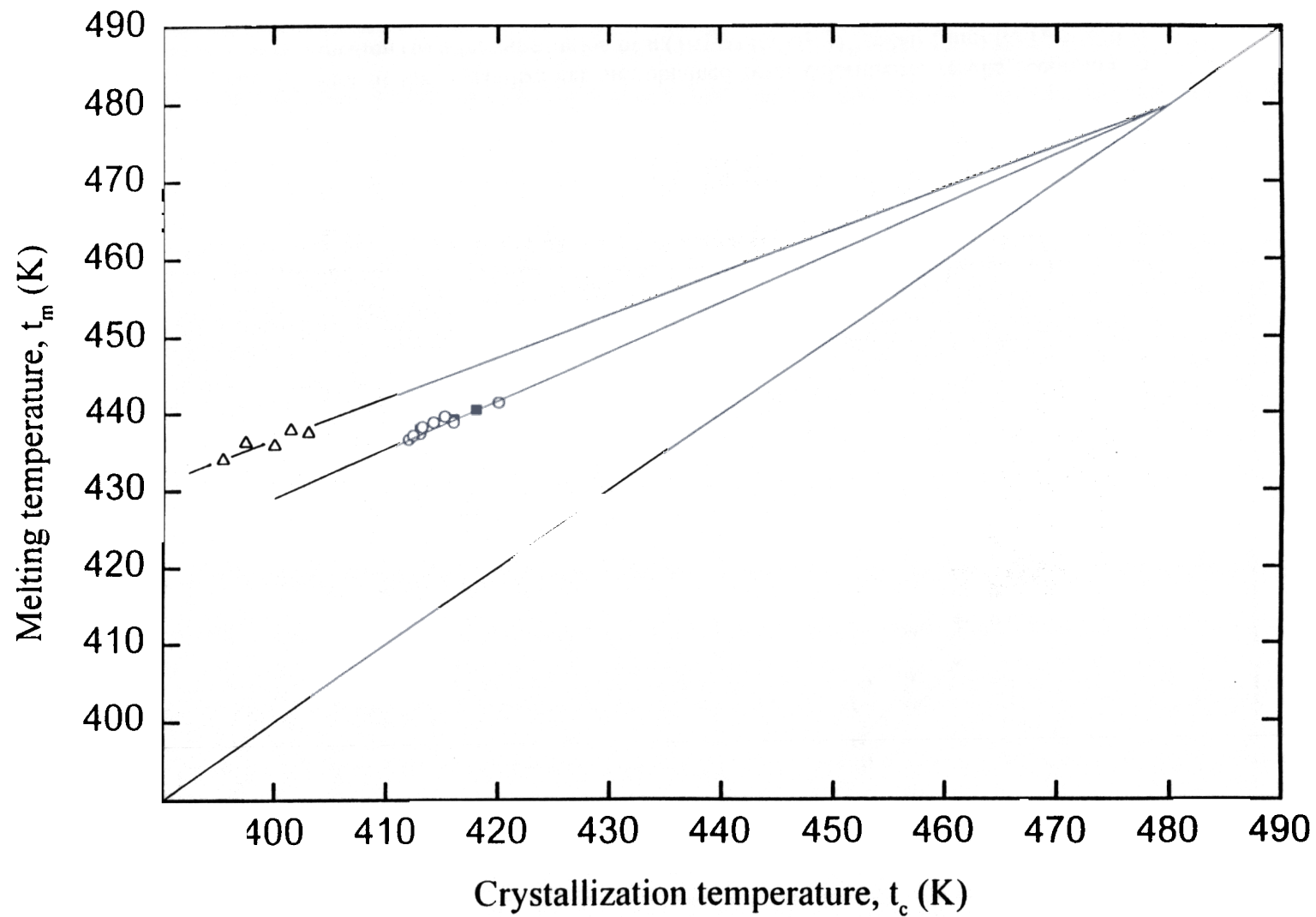


Fig. 16. The variation of melting point with isothermal crystallization temperature for polypropylene containing the following concentrations of phthalocyanin blue; Δ = 0%, $\blacksquare$ = 0.1%, $\circ$ = 0.2%.

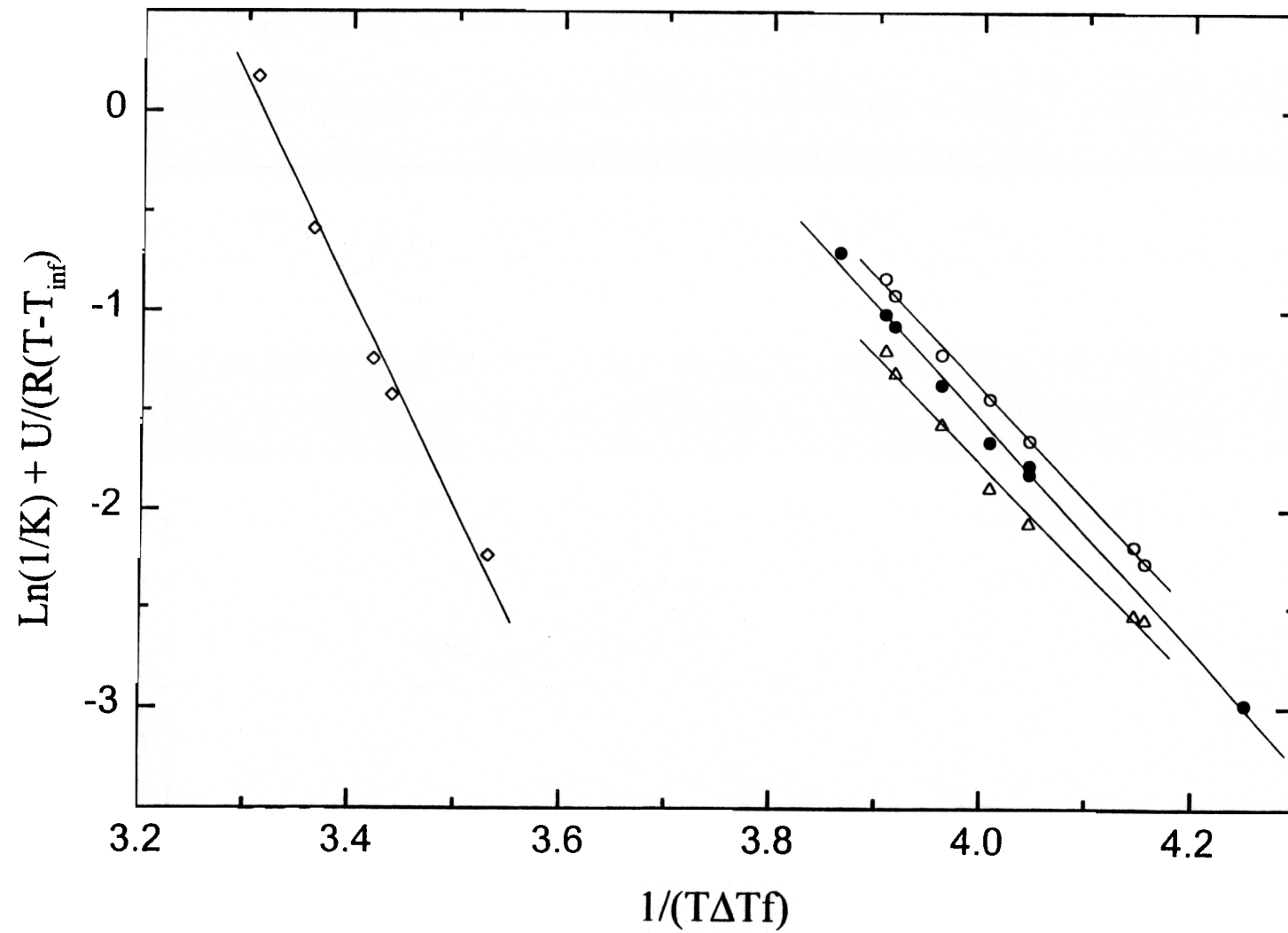


Fig. 7. Plot of the crystallization rate obtained from calorimetric results according to equation (6) after substitution of $\ln(1/t_{1/2})$ for G_r . $U^*=6280$ J/mol.K, $T_g = 270$ K and $T_m^0 = 480$ K.

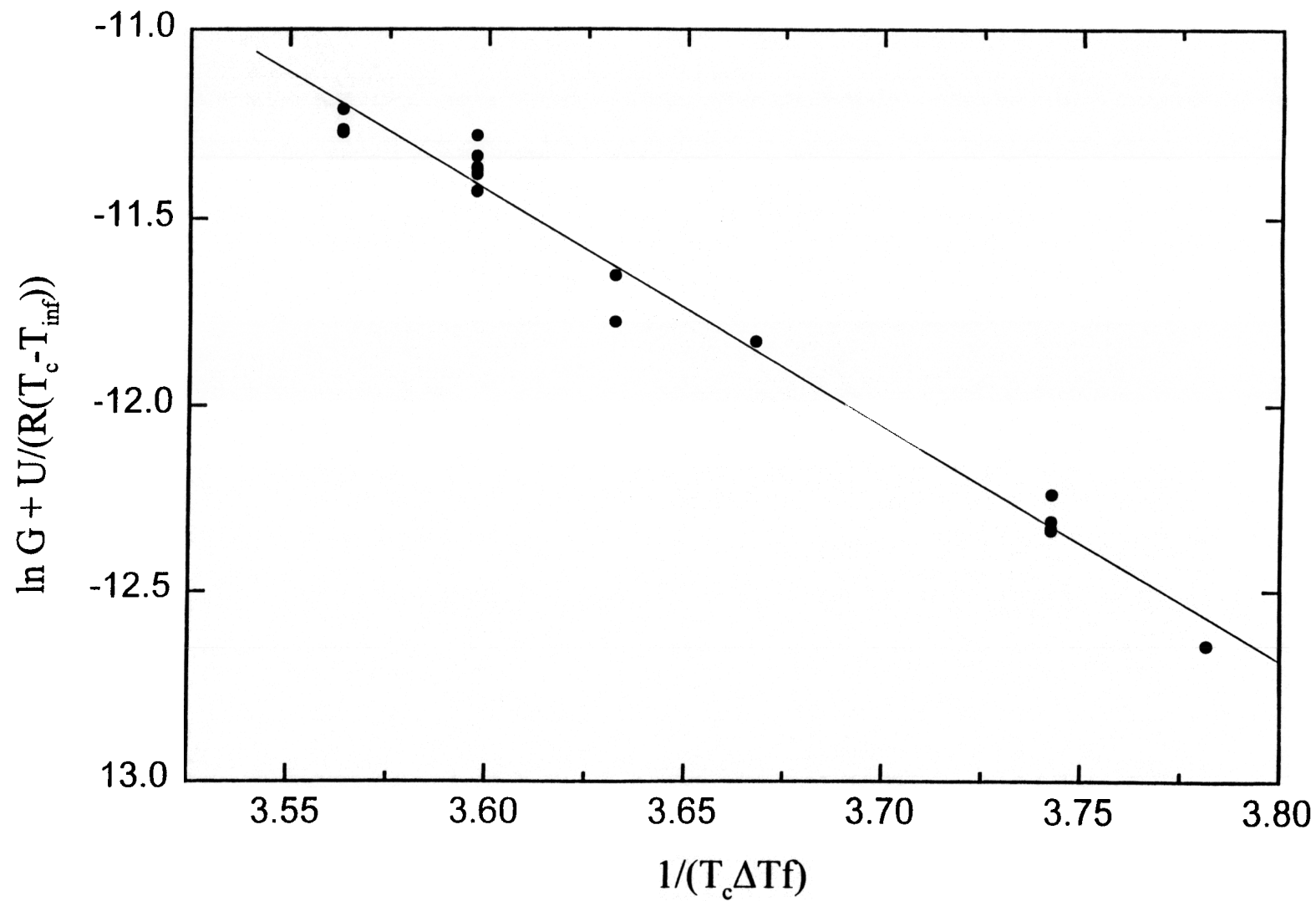


Fig. 18. Plot of the crystallization rate obtained from optical microscopy results according to equation (6). $U^*=6280$ J/mol.K, $T_g = 270$ K and $T_m^0 = 480$ K.