

The Influence of Pigments on the Crystallization Behaviour, Morphology and Dimensional Stability of Plates Injection Moulded from HDPE.

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ABSTRACT

Certain organic pigments such as phthalocyanine blue are renounced within the moulding industry for causing problems of dimensional instability. In this study we examine how phthalocyanine blue and other organic pigments affect the crystallization behaviour of high density polyethylene through isothermal calorimetric measurements. These data are interpreted using a two stage parallel model based on coupled Avrami functions.

All of the pigments considered in this investigation affect the morphology of melt crystallized high density polyethylene to some extent as revealed by transmission electron micrographs of microtomed permanganically etched specimens. These morphological differences can arise from a combination of the processing conditions used to mould the material and or the nucleating effect of the pigments themselves. To distinguish between these two influences the morphology of samples melt crystallized under controlled cooling conditions are compared with those cut from injection moulded plates. These comparisons allow us to not only assess the relative importance that processing and pigments have on morphology and to identify the driving forces that are probably responsible for causing excessive shrinkage and warpage.

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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 metals. Historically, inorganic pigments presented few problems either to the design engineer or to plastics processor being thermally stable and having little effect on the dimensional stability of mouldings. In contrast, environmentally acceptable organic pigments, e.g. phthalocyanine blue, quinacridone,¹⁻⁴ are less thermally stable and can increase shrinkage and warpage of mouldings. This unsatisfactory situation has been attributed to changes in the supramolecular structures formed by the host polymer as a result of heterogeneous nucleation^{4,5}. A number of organic pigments are active nucleating agents as shown by their ability to raise the temperature at which crystallization occurs in supercooled melts^{4,6}. In polypropylene, containing only 0.1% phthalocyanine blue, for example melt crystallization occurs some 16 °C higher than in the un-pigmented material⁴.

In this paper, we show how organic pigments affect the melt-crystallization behaviour and morphology of high density polyethylene (HDPE). The links between the morphology of the HDPE, pigment type and the shrinkage and warpage behaviour of plate injection moulding are discussed⁵. One of the pigments, phthalocyanine blue, acts as a nucleating agent that dramatically modifies the lamellar morphology of the HDPE spherulites that determine the physical properties of this material.

2 EXPERIMENTAL METHODS

2.1 MATERIALS

The pigments listed in Table 1 were added to high density polyethylene (DSM Stamylan HD) as a masterbatch. The yellow 62 and yellow 93 are both mono-azo calcium salts (C.I. numbers 13940 and 20710 respectively). The blue pigments are both forms of Cu-phthalocyanine (B) with a colour index of 74160. The modified phthalocyanine blue is a commercial product that has been tailored to produce a 'low' distortion pigment. The concentration of each pigment together with the composition of the masterbatch are given in Table 1. Linear low density polyethylene (LLDPE) was used as a carrier for the pigments and wetting agents.

Pigment	Masterbatch composition				Concentration of pigment in feedstock (%)
	% Pigment concentration	% Zinc stearate	% Polyethylene wax	% LLDPE	
Yellow 62	6.7	1	3	89.3	0.13
Yellow 93	6.7	1	3	89.3	0.13
Mod. phthalocyanine blue	6.7	-	-	93.3	0.13
Phthalocyanine blue	6.7	1	3	89.3	0.13

Table 1: The composition of the masterbatches used to colour HDPE feedstocks.

Pellets of the masterbatches prepared by Addcolour Plastics Ltd were tumble mixed with small quantities (3 Kg) of similarly sized granules of HDPE. This feedstock was then used to mould square plates using the processing conditions given in Table 2. Virgin material was used to flush the barrel between moulding different colours to ensure that all traces of the previous feedstock were removed.

Melt temperature	225 °C
Holding pressure time	7 s
Cooling time*	40 s
Injection time	2.64 s
Cycle time	77 s
Holding pressure*	33 bar

*Table 2: The processing conditions used to mould plates using a Demag 150 tonne injection moulding machine from HDPE. * Machine settings.*

After processing, the plates were allowed to slowly cool in air at room temperature (17–18 °C). Samples used for both calorimetric measurements and morphological studies were cut from these mouldings.

In a separate series of moulding trials² square plates were manufactured from feedstocks containing either virgin HDPE or material coloured with yellow 62 or phthalocyanine blue. A range of different processing conditions used to determine the influence of different pigments on both shrinkage and warpage behaviour are presented in Section 4.

2.1.1 Mould Geometry

Figure 1 shows the geometry and cooling circuit of the square plate moulding used in this investigation. This simple edge-gated plate has been designed to maximise the amount of anisotropy in properties such as Young's modulus⁷. This is achieved by forcing the melt to flow through the domed region that precedes the gate which ensures that a uniform flow front progresses through the cavity as it fills. The dimensions of the mouldings produced by the cavity are 150 mm x 150 mm and either 2.2 mm or 4.0 mm thick (an insert is used to manufacture thinner plates).

2.2 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Measurements were made using a Perkin-Elmer DSC2 interfaced to a PC. Isothermal temperatures were calibrated using a stepwise procedure and the thermal lag was derived from individual dynamic curves⁸. The instrument was operated in the specific heat mode and calibrated using alumina⁹. Samples weighing between 11 – 14 mg were contained within crimped pans. Nitrogen was used as a purge gas and common cooling/heating rates of 10 K/min were used throughout.

To erase the effects of any previous thermal history all samples were annealed for 3 minutes at 430 K. This ensured that a homogenous melt was produced that did not contain any remnants of previous crystals and subsequent recrystallization in isolated regions. This temperature was chosen on the basis of optical microscopy studies (using polarized light) where all traces of previously grown spherulites were erased, at least to within the resolution of the microscope. After the annealing period, melt crystallization was monitored after

cooling to some isothermal crystallization temperature, T_c . After crystallization at T_c samples were reheated back to 430 K. The melting endotherms were recorded during this period and subsequently used to compare heats of fusion from measurements made at the beginning and end of a series. Sample variability was limited by using a single specimen for successive crystallization kinetics measurements wherever possible.

2.2.1 The determination of baselines and fractional areas

Figure 2 shows three isothermal DSC curves for HDPE containing yellow 93 measured at three different temperatures. The heat flow is in arbitrary units. The figure shows an initial region (A) where the sample is being cooled from the initial melt temperature of 430 K to T_c . The cooling rate was kept deliberately low so that the instrument remained in control at all times.

The overall enthalpy change can then be resolved into contributions from specific heat alone and from subsequent crystallization by running the calorimeter in 'specific heat' mode. This requires data for both an empty pan and a calibrant i.e. sapphire. Since the specific heat of the melt has a linear dependence on temperature the value at T_{cryst} can be estimated from measurements over a range of temperatures in excess of that at which crystallization occurs. Following this procedure eliminates problems due to overshooting and subsequent overlap that can occur in rapidly crystallizing materials.

The time, t_0 is that at which the sample is predicted to have reached the set isothermal temperature. A baseline drawn from t_0 to a point at longer times where crystallization was apparently complete served to define the crystallization exotherm as shown in Figure 3(A). In a DSC curve such as that shown in Figure 3(A), the relative degree of crystallinity X_t shown in Figure 3(B) can be defined according to the ratio

$$X_t = \frac{\Delta H_t}{\Delta H_\infty}$$

where

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

and

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

dQ/dt is the heat flow. ΔH_t corresponds to a partial area of the DSC curve between the onset of crystallization, t_0 and a time t . The melting enthalpy ΔH_∞ is defined by equation (2b) integrated between the onset and completion of crystallization i.e. at the points where the heat flow departs from and returns to a constant value. Crystallization in samples of HDPE begins almost immediately on reaching the isothermal temperature although the process can take considerable time to complete. The time at which crystallization begins serves to define a low temperature limit below which it is not possible to measure the entire crystallization exotherm.

2.3 ELECTRON MICROSCOPY

Electron microscopy was used to study both samples that had been subjected to a known thermal history and those cut from the central regions of injection moulded plates.

Comparisons of the results of these two studies allowed us to distinguish between changes in morphology due to the presence of particular pigments and those attributable to processing.

Transmission Electron Microscopy (TEM)

A Philips 400T with EDS capability was used to examine carbon replicas in bright field mode under an accelerating voltage of 80 kV. Specimens were mounted in a rotating goniometer stage capable of *xy* movement in the plane of the specimen as well as in and out-of-plane tilt. Tilting of replicas with respect to the electron beam was used occasionally to enhance resolution and to improve the clarity of complicated microstructural details.

Specimen Preparation

The procedure used to examine the morphology of the moulded plates was as follows. Triangular samples were cut from the central region of an injection moulded plate as shown schematically in Figure 4. The face lying perpendicular to the flow direction was then microtomed at room temperature using a rotary microtome to cut successive slices approximately 5 μm thick. An optical microscope with interference contrast was used to monitor this process. These slices were then etched for 3 hours in a mixture of 1% w/v solution of potassium permanganate dissolved in a blend of 2:1 sulphuric and dry ortho-phosphoric acids¹⁰. The etching process was monitored by temporarily arresting it and examining the specimen under an optical microscope. A standard two-stage indirect carbon replica was made of the etched specimen (using cellulose acetate film moistened with acetone). These replicas, which were several tens of nanometers in thickness, were then transferred to copper grids for examination. The use of carbon replicas enables the electron microscope to be used at maximum resolution without running the risk of radiation damage or generating artefacts that are usually associated with morphological studies of plastics.

Thin films (50 μm) of un-pigmented HDPE and those containing either phthalocyanine blue or yellow 62 were heated in a nitrogen atmosphere to 430 K to erase any structures formed as a result of an unknown thermal history. These melts were subsequently cooled at a rate of 10 K/min to room temperature, etched and carbon replicated.

3 RESULTS AND DISCUSSION

3.1 INTERPRETATION OF KINETIC DATA

Most of the published models for describing the time dependence of isothermal crystallization are based on the original work of Kolmogoroff¹¹, Avrami¹² and Evans¹³. This basic function is of the form

$$X_t = 1 - \exp(-kt^n) \quad (3)$$

where 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 rate at which crystals are nucleated and grow. n is a parameter that reflects the shape of the crystals, when $n = 1$ (fibrillar growth), $n = 2$ (lamellar growth) and $n = 3$ (spherulitic growth). Optimal values for k and n can be obtained by fitting equation 3 to the time dependent fractional crystallinity data using a non-linear least squares approach. However as Figure 5 shows, the match between the model and the experimental data is poor, and this behaviour was common

to all specimens examined. This finding reinforces earlier studies¹⁴⁻¹⁶ which have shown that the crystallization behaviour of polyethylene cannot be described by a simple function shown in equation 3. This disparity between the data and prediction has been attributed to secondary crystallization and has been observed in a number of semicrystalline polymers including poly (ether ether ketone)¹⁷⁻¹⁹ and poly (butylene terephthalate)²⁰.

The current view of melt crystallization in these materials assumes that primary spherulitic structures grow as a result of heterogeneous nucleation within the melt. These spherulites rapidly grow forming three-dimensional lamellar structures during *Stage 1* crystallization. With time these spherulites will begin to make contact with each other thus reducing their growth rate. The composition of the melt at this stage can be thought of as a sea of amorphous chains containing a substantial number of poorly packed spherulites. Further 'secondary' (*Stage 2*) in-filling crystallization can occur in those areas between dominant lamellae within spherulites. However the growth of these minor lamellae develops whilst the material is strained because of the limited space in which they have to grow. A higher melting point can be associated with these infilling secondary crystalline lamellae²¹⁻²⁴.

3.1.1 Modelling of two stage crystallization processes.

Essentially two approaches have been adopted to model two stage crystallization processes using either series - parallel^{25,26} or parallel models^{17,21}. The series-parallel model assumes that stage 1 crystallization can be accurately described by a single Avrami function (equation 3) up to a time t_d . For times less than t_d the primary crystal spherulites are not in contact and it is assumed that the growth of secondary crystals is minimal.

For times in excess of t_d the model must account for the additional secondary crystallization and for this an additional Avrami term is added to equation 3.

An alternative approach to modelling two stage crystallization is to assume that both primary and secondary crystallization processes occur simultaneously but at different rates^{19,21}. This approach is more likely to represent what actually happens during isothermal melt crystallization. In this parallel model it is assumed that;

$$X_r = w_1(1 - \exp(-k_1 t^{n_1})) + w_2(1 - \exp(-k_2 t^{n_2})) \quad (4)$$

Adopting this approach increases the difficulty of obtaining values for each of the parameters although some authors²⁰ have simplified this problem by assuming that n_1 and n_2 are 3 and 1 respectively. Estimates for each of the required parameters can be obtained directly by fitting equation 4 to fractional crystallinity data using a non-linear least squares algorithm.

Figure 6 shows how equation 4 behaves with time and the contributions from the two crystallization processes. It is evident from this figure that at short times any changes in the fractional crystallinity are dominated by the growth of stage 1 primary crystals. As this process reaches equilibrium so any further increase in crystallinity is attributable to the growth of the in-filling secondary crystals of stage 2 (bottom curve, dashed line). The solid line is the summation of contributions from the primary (dominant lamellar crystals) and the secondary (in-filling or subsidiary lamellar crystals) crystallization processes.

3.1.2 Interpretation of isothermal data based on the parallel model

A non-linear least squares approach was used to determine the parameters k_1 , k_2 , w_1 and n_1 . n_2 was assumed to be 1 following the work from previous investigators²⁰. The modelling of the fractional crystallization curves using equation 4 is not trivial. The success of the fitting is particularly sensitive to the starting set of parameters that are chosen and on the

Material	Temp. (K)	k_1	N_1	w_1	k_2	n_2	$t_{1/2}$ (mins)
Virgin HDPE	397.6	0.320	1.94	0.59	0.187	1.0	1.8
	398.6	0.022	2.41	0.70	0.129	1.0	4.8
	398.6	0.058	2.15	0.63	0.137	1.0	4.5
	399.6	0.005	2.23	0.73	0.066	1.0	8.2
Yellow 62 + HDPE	397.6	0.085	2.53	0.75	0.235	1.0	2.3
	398.6	0.012	2.79	0.68	0.122	1.0	4.4
	399.6	0.003	2.55	0.65	0.057	1.0	11.7
Yellow 93 + HDPE	397.6	0.161	2.34	0.71	0.155	1.0	2.0
	398.6	0.015	2.67	0.73	0.148	1.0	4.1
	399.6	0.006	2.35	0.62	0.089	1.0	10.6
Mod. Phth. Blue + HDPE	399.1	0.051	2.63	0.51	0.233	1.0	2.7
	399.6	0.026	2.72	0.46	0.119	1.0	4.2
	400.6	0.002	2.48	0.52	0.051	1.0	12.6
Phth. Blue + HDPE	398.6	0.211	2.01	0.54	0.183	1.0	2.1
	399.1	0.094	2.07	0.55	0.115	1.0	3.1
	399.6	0.021	2.56	0.47	0.104	1.0	4.4
	399.6	0.161	2.84	0.45	0.128	1.0	4.1
	400.6	0.0014	2.84	0.38	0.055	1.0	11.8

Table 3: Optimum values for n_1 , k_1 , w_1 and k_2 were found by fitting equation 4 directly to fractional crystallization curves, assuming that $n_2 = 1$.

precise location of the initial starting time t_0 . In practice t_0 was taken as the time at which the sample reached the isothermal temperature. Table 3 shows the results obtained from this curve fitting exercise and Figures 7 to 11 show how the fitted functions compare with measured fractional crystallinity curves.

The time taken for 50% of the crystallization to occur, $t_{1/2}$ can be obtained from plots of fractional crystallinity versus time as shown in Figure 6. These are also listed for each pigmented material in Table 3. Figure 12 shows a plot of $t_{1/2}$ versus the isothermal crystallization temperature. It is evident from this figure that there is a distinct difference in $t_{1/2}$ between HDPE pigmented with phthalocyanine blue and unpigmented or HDPE coloured with yellow pigments. This behaviour demonstrates that crystallization of the HDPE at a particular temperature occurs more rapidly in the presence of phthalocyanine blue.

w_1 and w_2 (equation 4) give the relative proportions of primary to secondary crystallization respectively. Figure 13 shows how w_1 for unpigmented and pigmented materials depends on the isothermal crystallization temperature. Again we note a distinct difference between the behaviour of HDPE containing phthalocyanine blue irrespective of whether it has been modified or not and that containing no pigment or yellows 62 and 93. The results show that the overall level of primary crystallization is lowered in the presence of phthalocyanine blue. This behaviour is to be expected as impingement will occur at an earlier stage of conversion

in a system composed of a large number of small spherulitic structures (discussed below). Figure 14 suggest that the shape of the spherulites grown under isothermal crystallization conditions were unaffected by pigmentation.

3.1.3 The determination of absolute crystallinity

Table 4 shows the absolute level of crystallinity for both pigmented and unpigmented HDPE. These data were calculated using the total enthalpy method of Richardson²⁷. The heat of fusion for perfect crystals of HDPE²⁸ was taken to be 293 Jg⁻¹.

Material	Temperature (K)	H _f (Jg ⁻¹)	Absolute crystallinity (%)
Virgin HDPE	397.6	203.0	0.69
	398.6	203.4	0.69
	399.6	201.3	0.69
Yellow 62 + HDPE	397.6	206.7	0.70
	398.6	205.3	0.70
	399.6	199.4	0.68
Yellow 93 + HDPE	397.6	206.6	0.70
	399.6	198.8	0.68
Mod. Phth. Blue + HDPE	398.6	192.3	0.66
	399.6	187.8	0.64
	400.6	183.5	0.63
Phth. Blue + HDPE	398.6	193.0	0.66
	399.6	187.1	0.64
	400.6	175.1	0.60

Table 4: The dependence of absolute crystallinity on both temperature and pigment type.

It is clear from table 4 that the overall level of crystallinity in HDPE is lowered by some 5% in the presence of phthalocyanine blue either on its own or as a modified form. The addition of either yellows 62 or 93 or changing the crystallization temperature has no little effect on the overall level of crystallization.

Plots of melting curves as a function of time for each of the pigmented materials listed in Table 4 are broad indicating that there is a wide spread of crystal melting points.

3.2 THE MORPHOLOGY OF VIRGIN AND PIGMENTED HDPE.

Analysis of the crystallization kinetics data shows that the pigmented samples fall into two distinct groups: virgin HDPE, together with that containing the two yellows, and HDPE + phthalocyanine blues. We have therefore only examined the morphology of three of these materials – virgin HDPE and samples containing yellow 62 and unmodified phthalocyanine blue.

3.2.1 The morphology of melt-crystallized materials

The un-pigmented HDPE was used as a reference material. It contained (Fig. 15) spherulites some 10 μm in diameter. There is evidence for dominant-subsidary lamellar structures, (highlighted by arrows) several microns in length that are close-stacked and contiguous. Lamellar thicknesses were relatively uniform and approximately 25 nm for both dominant and subsidiary varieties.

Figure 16 shows the morphology of a sample of HDPE containing 0.13% wt/wt of phthalocyanine blue. By contrast with Fig. 15 there is little large-scale orientation. The morphology is best described as one of non-spherulitic lamellar domain structures or mosaic blocks. Lamellar thicknesses were slightly reduced, varying from 22 nm to 18 nm depending on the relative populations of dominant to subsidiary lamellae respectively.

The structure of HDPE/0.13% wt/wt yellow 62 is shown in Fig. 17. The morphology is intermediate between those of Figs. 15 and 16. Pockets of ordered 10 μm long sheaf-like lamellar structures are present throughout. The growth of spherulites appears to be incomplete because those observed are relatively small. Lamellar thicknesses ranged from 18 nm and 23 nm and were very similar in size to those in samples containing phthalocyanine blue.

3.2.2 The morphology of mouldings

Figure 18 shows an etched section through a plate moulded from un-pigmented HDPE. This figure completely lacks the lamellar organisation shown in Fig. 15. By contrast, Fig. 18 shows densely populated lamellar domain structures no larger than 1 μm . One of the domains, which are circular in appearance, is shown highlighted by arrows, where each arrow marks the boundary of the domain. The example of Fig. 18 is non-spherulitic and poor in lamellar contrast relative to that of Fig. 15. There is evidence of orientation in isolated areas of parallel stacked lamellar structures which represent only a few percent of the overall morphology. There were systematic variations in lamellar thickness throughout the specimen but the lamellar thickness never exceeded 20 nm.

Orientation as prescribed by up to one dozen closely packed parallel stacked arrays of lamellae can be seen running along the long edge of Fig. 19. One type of circular object can also be seen. The small approximately circular dots embedded within the underlying matrix are probably pigment related. These spots are in excess of 50 nm in diameter, approximately twice as thick as the lamellae.

Moulded HDPE containing yellow 62 has the morphology shown in Fig. 20. Here there are spherulitic objects ranging in size from a few microns to an upper limit of approximately 10 μm . Some 1 μm to 2 μm lamellar domains were also observed. Within spherulites, the lamellae are approximately 25 nm thick although those at the spherulitic boundaries are slightly smaller.

3.2.3 Morphological comparisons between samples with known thermal history and 'as moulded'

Thin films made from melts cooled under controlled conditions are not influenced by the molecular orientation that is a feature of the process of injection moulding. There are obvious structural differences. Injection moulding erases the well-defined lamellar stack morphologies characteristic of melts crystallized under controlled conditions. Large spherulitic structures are barely visible in the moulded sample suggesting that the time allowed for structural development has been reduced. The effect is more noticeable when yellow 62 is present; here, circular lamellar domain patterns form where once spherulitic structures based on dominants and subsidiaries would have been. The greatest effect is, however, in HDPE/ phthalocyanine blue system where the morphology of the moulded system bares little resemblance to that formed by controlled cooling.

3.2.4 Raman Spectroscopy of mouldings

The Raman effect arises when a beam of intense monochromatic radiation (laser) is scattered because of a change in molecular polarizability. Part of the scattered radiation is inelastic and observed to have a different frequency from that of the incident radiation, this is known as the Raman effect. From the literature, the Raman band at 1416 cm^{-1} is assigned to bending vibrations of CH_2 units in only those polyethylene chains that are incorporated into the orthorhombic lamellar crystals. Another band of particular importance is the 1303 cm^{-1} which is specific to the amorphous phase and is assigned to CH_2 twisting. The integrated intensities of these bands can then be conveniently used to estimate the degree of crystallinity. From these measurements, we were also able to assess the degree of interfacial structure (so-called “rigid amorphous fraction”) in these materials. The results from this exercise are shown in Table 5.

	Crystalline Fraction	Amorphous Fraction	Interfacial Fraction
HDPE + Phthalocyanine blue	0.61	0.19	0.20
HDPE + Yellow 93	0.63	0.19	0.18
Virgin	0.66	0.19	0.15

Table 5: Raman spectroscopy identifies the amount of crystalline and amorphous material in differently pigmented samples.

The estimated degree of crystallinity is broadly in-line with the results from calorimetry for both pigmented and un-pigmented HDPE, the presence of phthalocyanine blue lowers the overall level of crystallinity. Interestingly, the greatest change is observed in the interfacial region (anisotropic amorphous phase) which increases with phthalocyanine blue. The relative errors associated in integrating the specific excited bands are less than 2%.

3.2.5 The dimensional stability of mouldings

There are a number of different ways in which dimensional instability can be measured. For a simple plate geometry we can consider the shrinkage that occurs in directions both parallel ($S_{\parallel}$) and perpendicular ($S_{\perp}$) to the direction of flow. Out-of-plane warpage (RW_z) can be used to measure the unevenness of the surface. Warpage can also occur within the plane of the plate which will look like it has wavy edges even though the distance between opposite edges is preserved. The angle formed by the intersection of the diagonals is also a measure of plate distortion.

Care must be taken in handling these measures to avoid ‘diluting’ or losing valuable information, for example, averaging can erase trends in the data. The methods that we used to characterise shrinkage, warpage and angular distortion have been published elsewhere^{1,2}, here we are only interested in the findings of this earlier study².

As described in section 2.1 plates were moulded using a range of different processing conditions from un-pigmented HDPE or material containing either yellow 62 or phthalocyanine blue. These moulding trials are an extension of a much earlier investigation where plates were moulded from differently pigmented HDPE’s using the same processing conditions². Whilst the results of the preliminary investigation are valuable they effectively represent a ‘snapshot’ of the link between processing, pigments and dimensional instability. The results of the extensive trials² provide a comprehensive view of the influence that these

organic pigments have on both shrinkage and warpage.

Shrinkage		In-plane warpage		Angle score	Out-of-plane warpage RW_z	
$S_{ }$	$S_{\perp}$	$W_{ }$	$W_{\perp}$			
Yellow 62	Phth. blue	Yellow 62	Phth. blue	Yellow 62	Yellow 62	less distortion $\uparrow\uparrow\uparrow$
Virgin	Yellow 62	Virgin	Yellow 62	Virgin	Virgin	
Phth. blue	Virgin	Phth. blue	Virgin	Phth. Blue	Phth. blue	
						more distortion

Table 6: The influence of pigment type on the dimensional stability of plate mouldings. The pigments are ranked with those causing most shrinkage or warpage at the bottom. Cells containing two or more pigments are equally ranked. (Redrawn from reference 2).

The co-ordinates of five plates taken from each batch of mouldings were determined by using shadow Moire interferometry as described elsewhere². From these co-ordinates the plates values for the shrinkages ($S_{||}$ and $S_{\perp}$) and both in-plane warpings ($W_{||}$ and $W_{\perp}$) and out-of-plane warpage (RW_z) were determined. These values were then ranked (following an analysis of means approach) to identify which colours caused most or least distortion as shown in Table 6.

This table suggests that phthalocyanine blue causes the most distortion as measured by both out-of-plane warpage and the angular score. Note the difference in the shrinkage behaviour of the plates as measured parallel and perpendicular to the flow direction. Phthalocyanine blue causes more shrinkage in a direction parallel to the flow than perpendicular to it when compared to both yellow 62 and virgin. The behaviour affect the ratio of $S_{\perp}/S_{||}$ changing it from ~ 1 (yellow or virgin) to ~ 0.5 i.e. plates containing phthalocyanine blue are more rectangular than those made from un-pigmented or HDPE containing yellow 62. The in-plane warpage is similarly affected. It is highly likely that this imbalance in shrinkage is responsible for both the in- and out-of-plane distortion.

4 DISCUSSION

Based on the experimental findings of this and previous investigations^{1,2,6} it appears that phthalocyanine blue behaves as a nucleating agent in polyolefins raising the temperature at which melt crystallization begins. There is also strong evidence from microscopy, calorimetry and Raman spectroscopy to support the thesis that phthalocyanine blue has a profound influence on the morphology of HDPE. The growth of the densely populated lamellar structures characteristic of spherulites during primary crystallization is short lived. The pigment by providing a plethora of nucleation sites causes a myriad of small diameter spherulites to grow. As a consequence of this these spherulites impinge within a comparatively short period of time which signals the end of stage 1 crystallization. However the growth of in-filling lamellae continues unabated until approximately 60 % of the available

polymer has been crystallized. Perhaps the apparent reduction in the overall level of crystallinity with the HDPE doped with phthalocyanine blue is a reflection of the lower density of dominant lamellae. The correlation between the morphology predicted by the Avrami analysis of the calorimetric data and direct observations by microscopy is not as strong as one might expect. The microscopic observations suggest that spherulites are formed during stage 1 crystallization which would be consistent with values of $n = 3$. These are not observed in practice, whether this disparity between the techniques is of significance remains to be seen. As expected the amount of interfacial contact between the spherulites and in-filling or subsidiary lamellae is greater for HDPE containing phthalocyanine blue. This result is entirely consistent with the increased number of small spherulitic structures characteristic of this material.

Perhaps the most significant feature that could be expected to affect the dimensional stability of mouldings is the difference in the ratio of shrinkages measured parallel and perpendicular to the flow direction between phthalocyanine blue and the other pigments. This anisotropy is probably the driving force responsible for out-of-plane warpage. Examination of the morphology of blue mouldings shows the existence of sheath like stacks of lamellae that could give rise to preferential shrinkage in one direction. Anisotropic shrinkage due to the presence of the pigment suggest that the only way of controlling warpage in mouldings made from phthalocyanine blue is to modify the chemistry of the pigment. This would ideally reduce its efficacy as a nucleating agent making it less compatible with apolar polymer systems.

5 CONCLUSIONS

Phthalocyanine blue is an effective nucleating agent for HDPE.

A two stage model is required to interpret the kinetics of melt crystallization under isothermal conditions.

The primary crystallization process reaches equilibrium at a lower overall level of crystallinity in HDPE containing phthalocyanine blue compared to both un-pigmented material and that containing yellows 62 or 93.

The shape parameter n used to model the primary crystallization process is independent of both pigment type and isothermal crystallization temperature.

The difference in the ratio of shrinkage measured in a direction parallel to the flow to that measured perpendicular to it in a simple moulding is probably the driving force for out-of-plane warpage.

The morphology of pigmented HDPE is quite different to that of virgin material, spherulites are less well defined with a greater percentage of in-filling relative to thicker dominant lamellae, particularly in moulded materials.

The differences in morphology that are attributable to the presence of different organic pigments are likely to affect the mechanical properties of HDPE.

6 ACKNOWLEDGEMENTS

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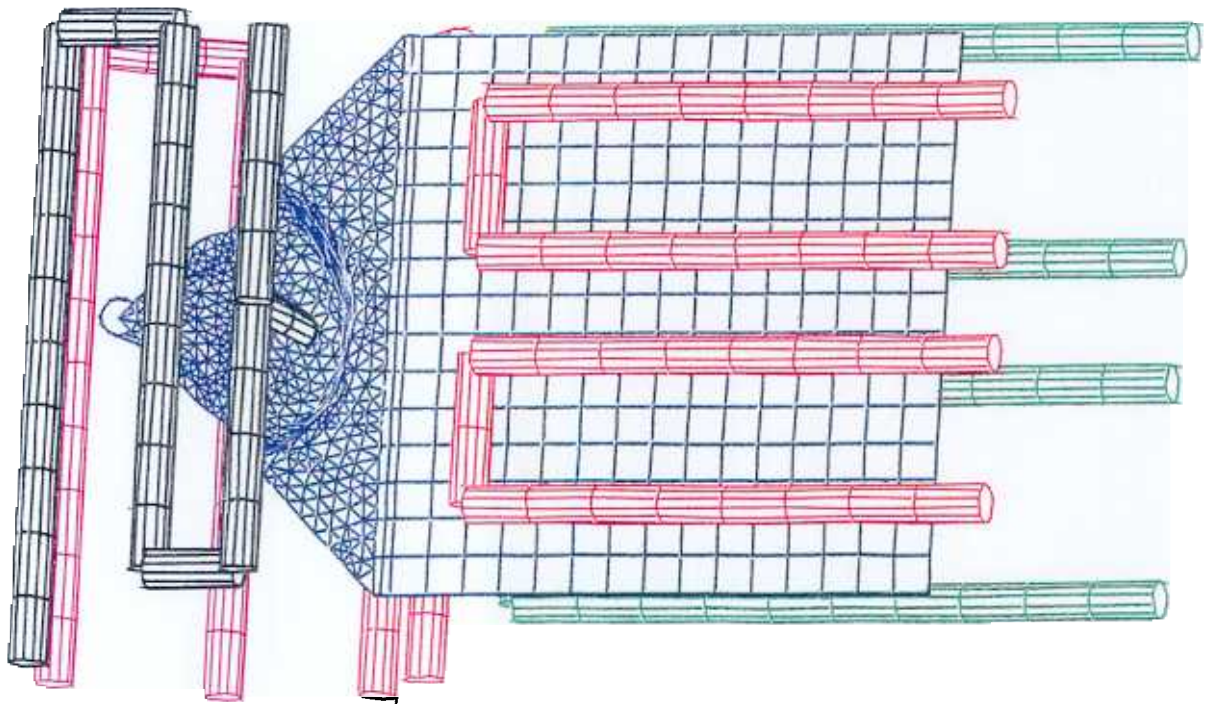
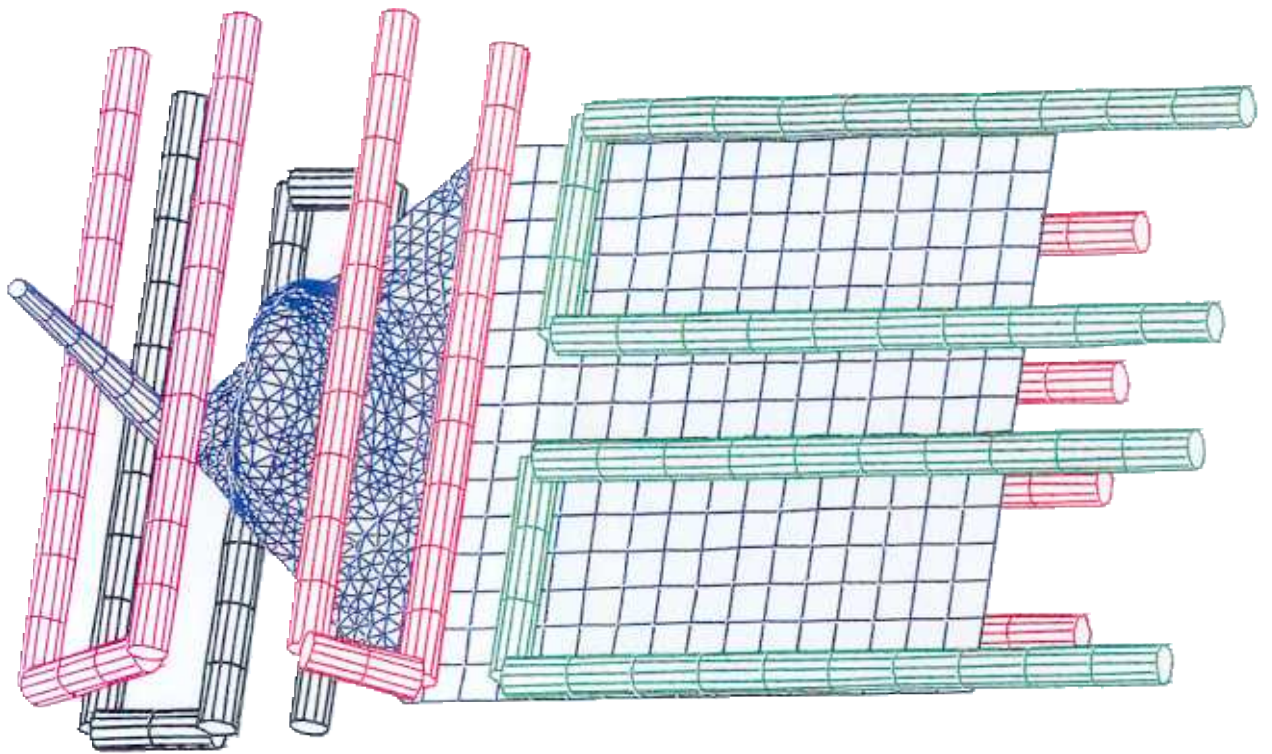


Fig. 1. Details of the cooling circuit and the geometry of the mould cavity. (a) upper surface of the cavity, (b) underside view.

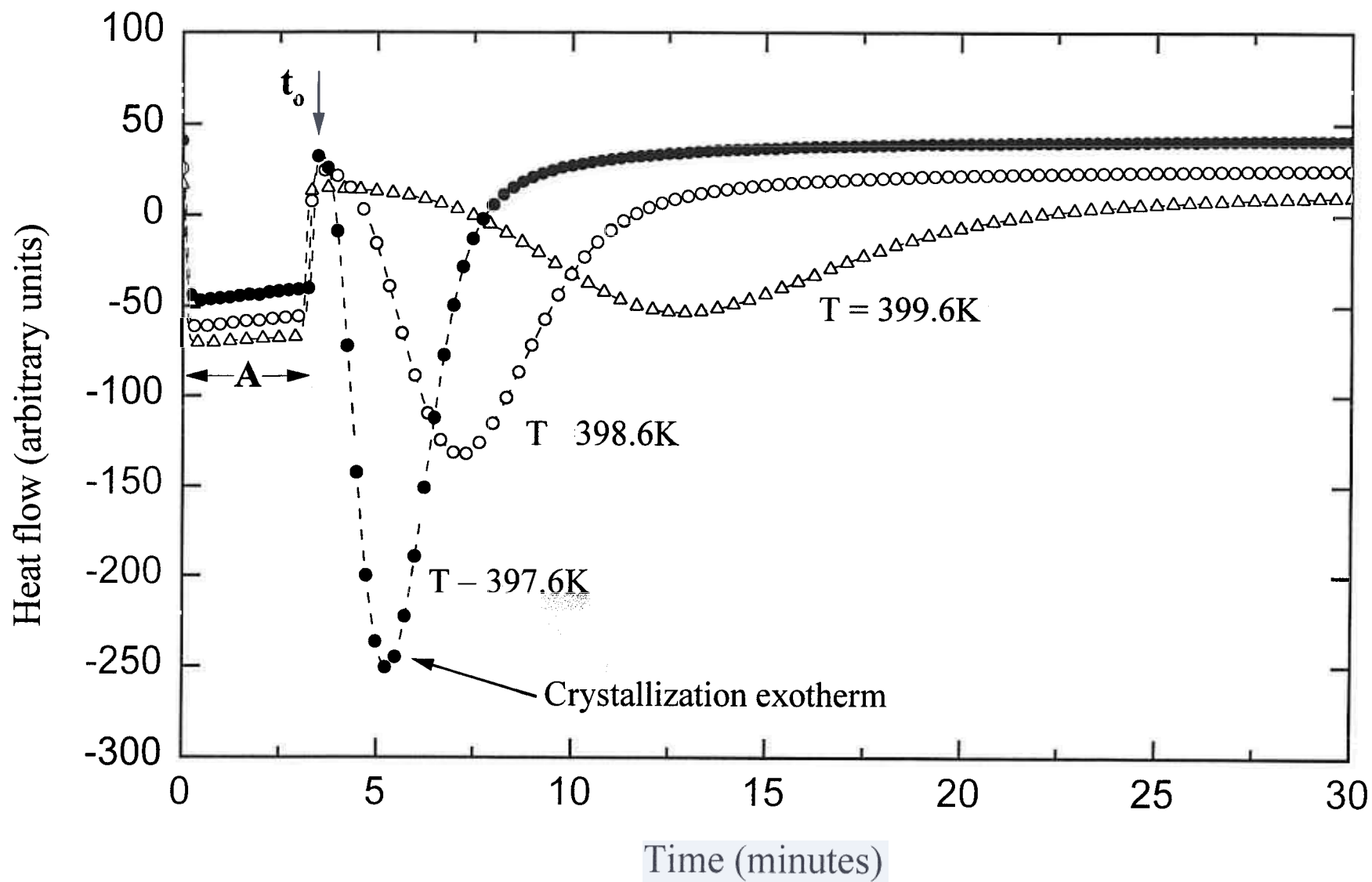


Fig. 2. DSC curves of HDPE containing yellow 93. Measurements at each isothermal temperature indicated in the figure (reached at time t_0) were made after cooling the sample at a rate of 10 K/min from the annealing temperature of 430 K (during period A). (Note that the curves have been shifted along the ordinate to improve the clarity of the figure).

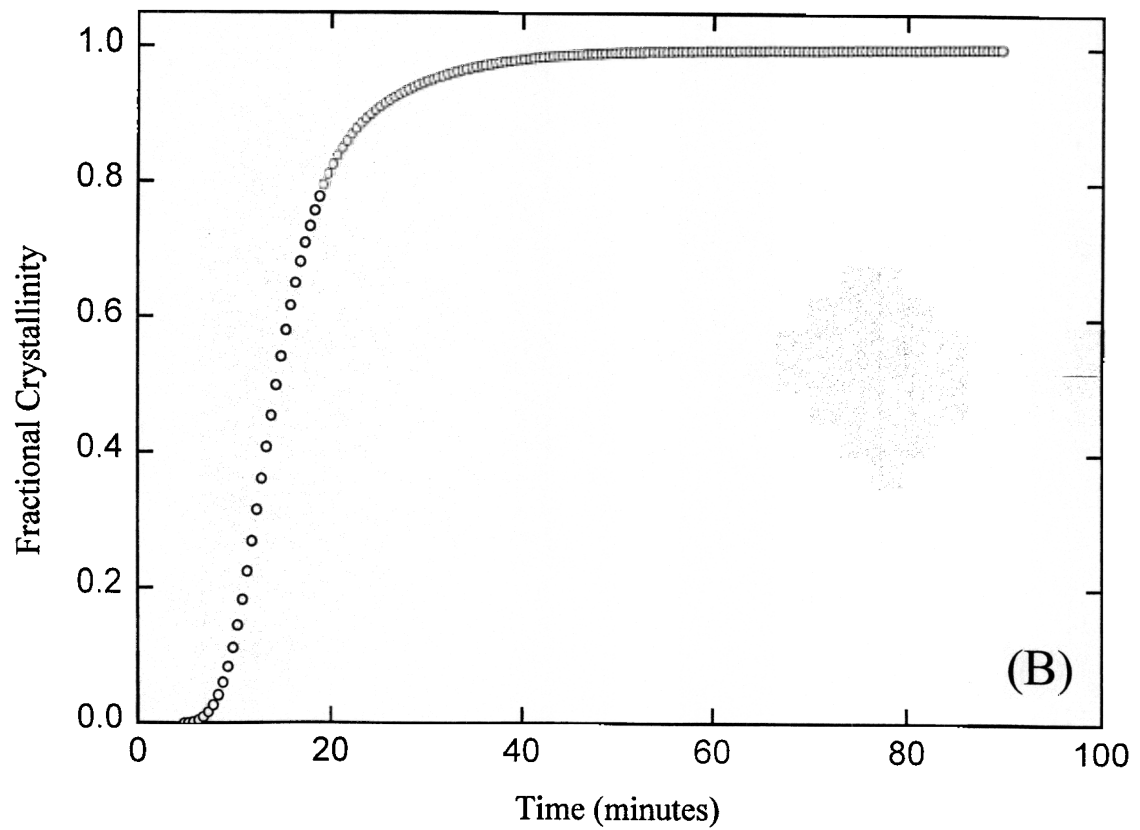
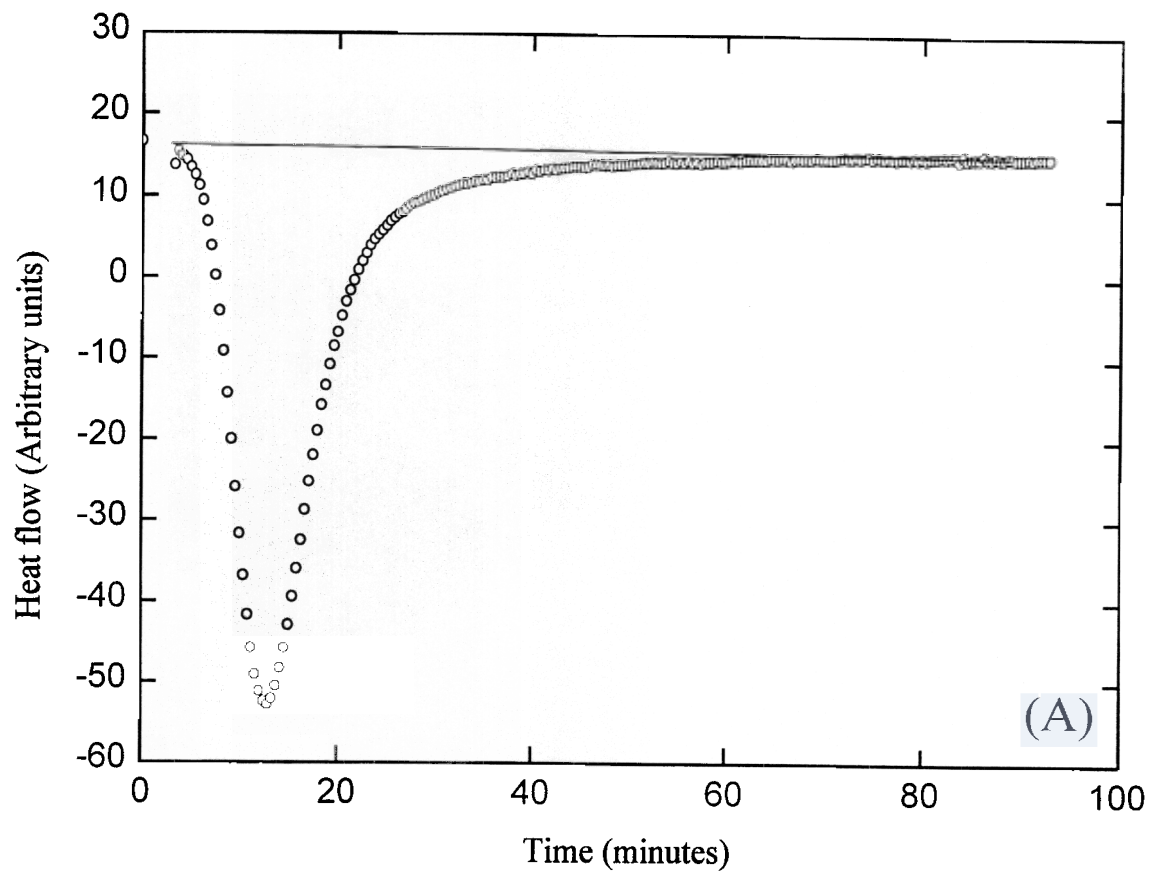


Fig. 3. A) A typical crystallization endotherm. The baseline connects points corresponding to the onset and completion of crystallization.

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

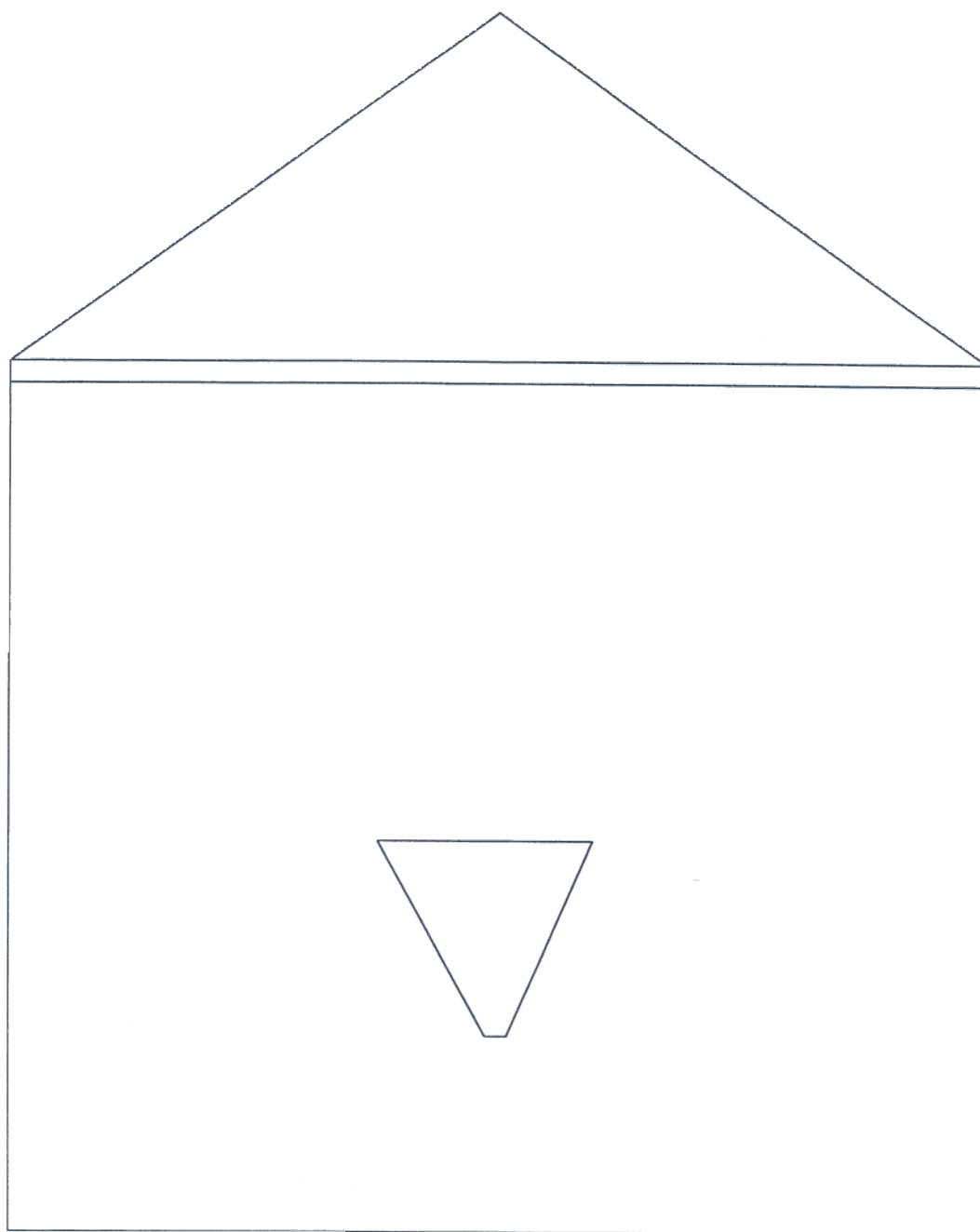


Fig. 4. Samples for electron microscopy were microtomed from the blunt tip of a triangular region cut from the central region of each moulded plate.

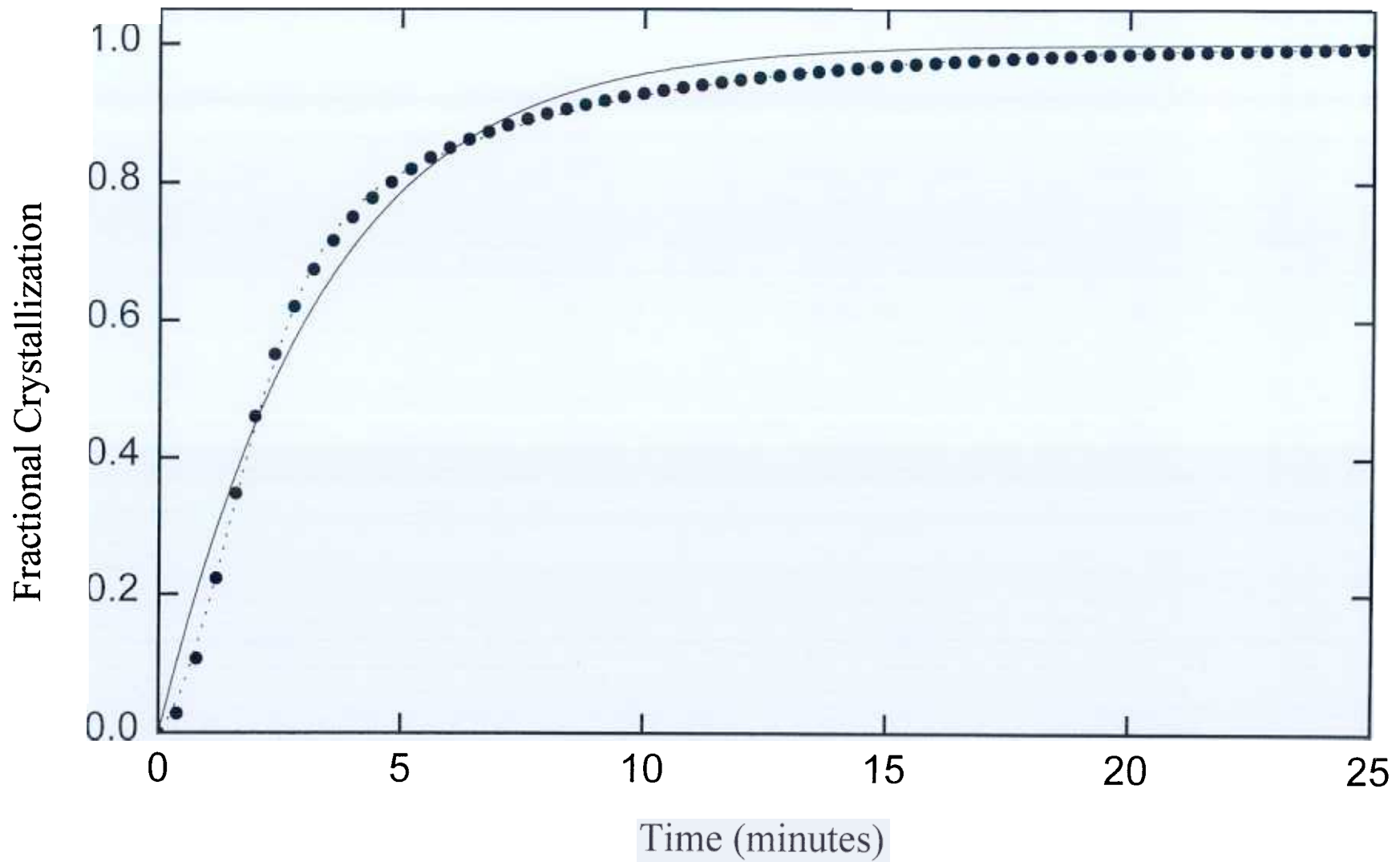


Fig. 5. The fit of a single stage Avrami function (solid line, $k = 0.295$, $n = 1.03$) to fractional crystallinity curve obtained from HDPE is poor as shown here for HDPE pigmented with phthalocyanine blue crystallized at 398.6 K. The dashed line is a fit of equation 4 which assumes that two crystallization processes occur simultaneously.

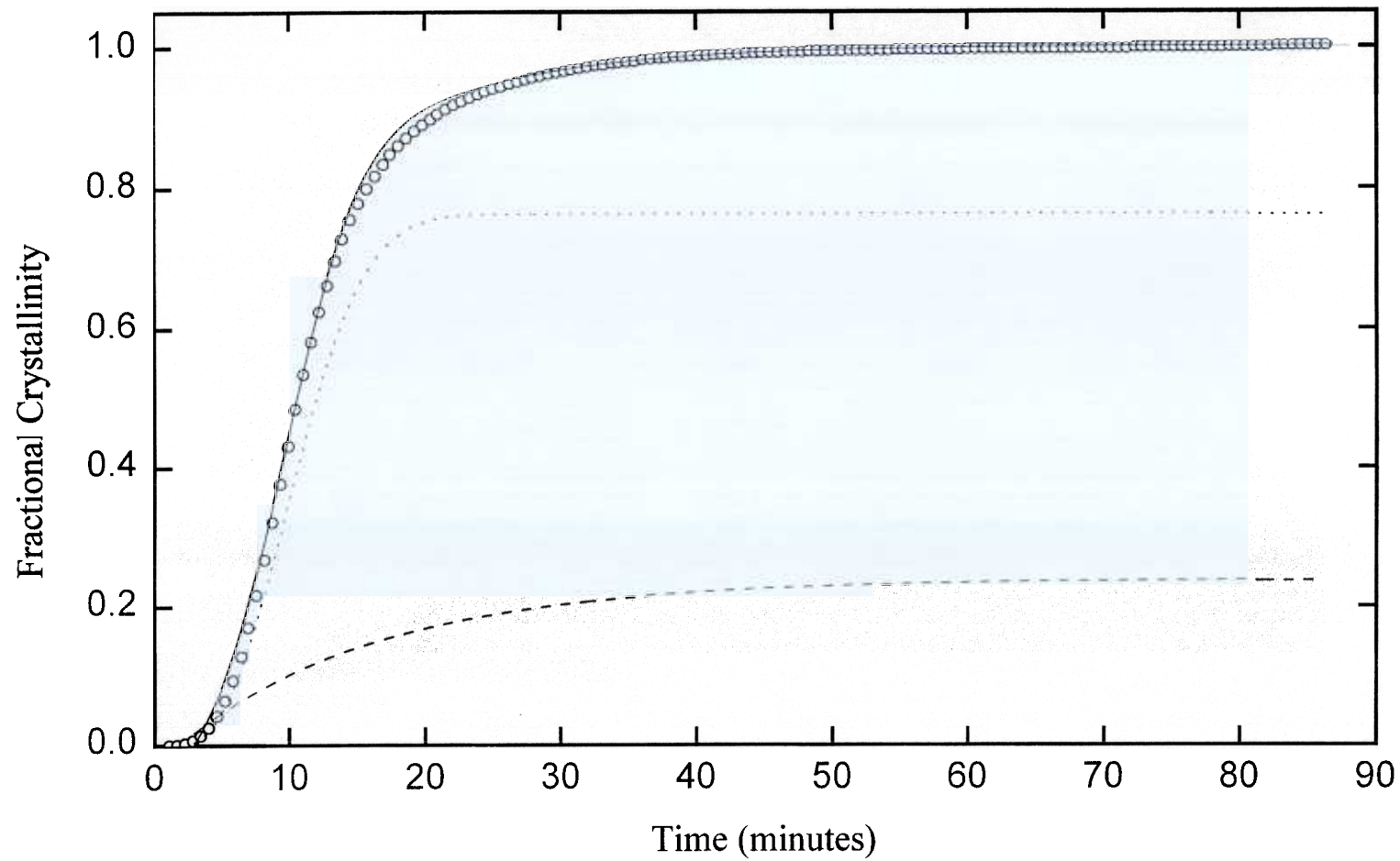


Fig. 6. Equation 3 was used to generate the solid line fit to the time dependent fractional crystallinity data shown in this figure (HDPE + yellow 93 crystallized at 399.6 K). The dotted line represents the contribution from primary crystallization and the dashed line from secondary crystallization. Note that the primary process is first to reach equilibrium.

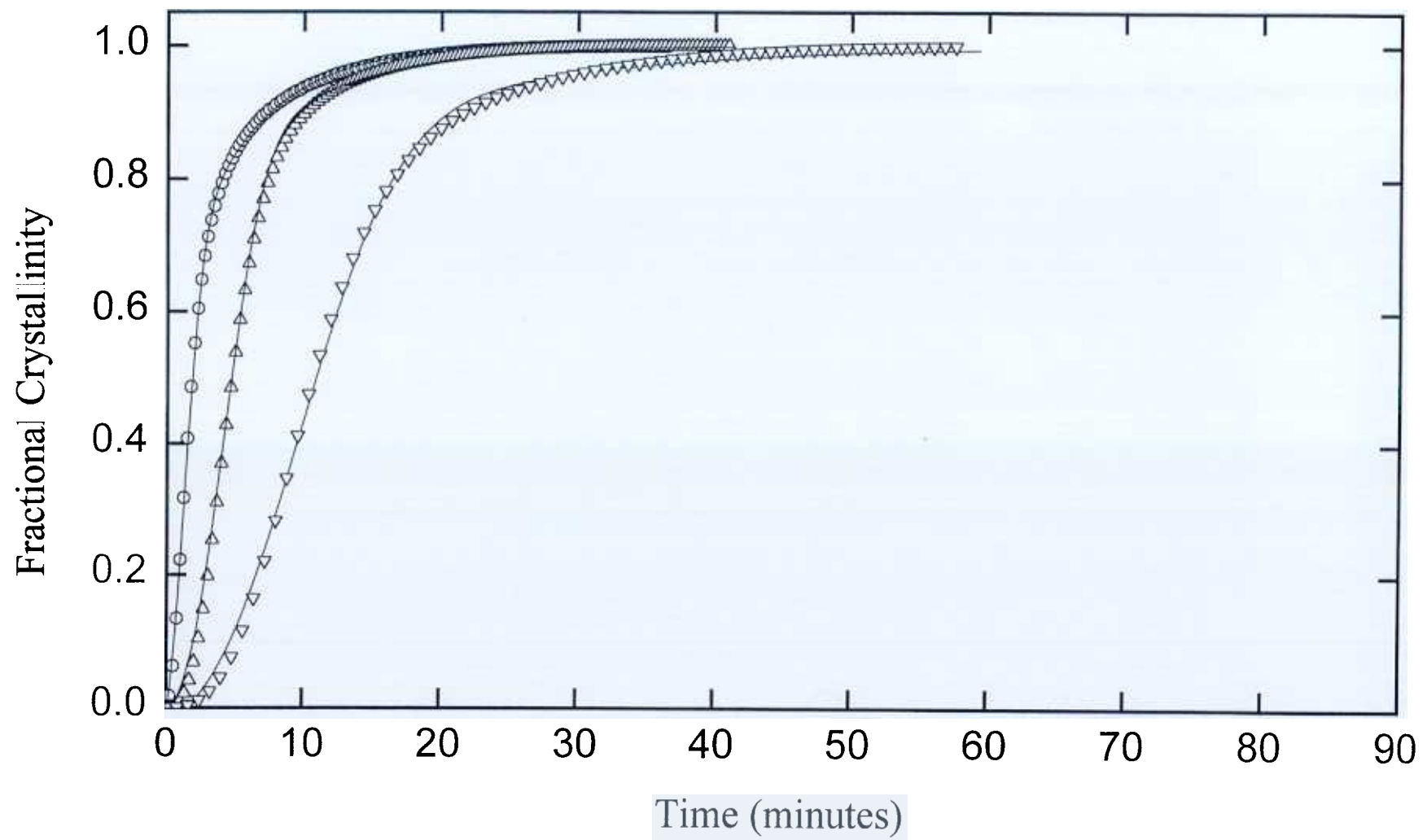


Fig. 7. A comparison of the fit obtained using equation 4 with measured data for un-pigmented HDPE at the following temperatures; $\circ$ = 397.6 K, $\triangle$ = 398.6 K and ∇ = 399.6 K.

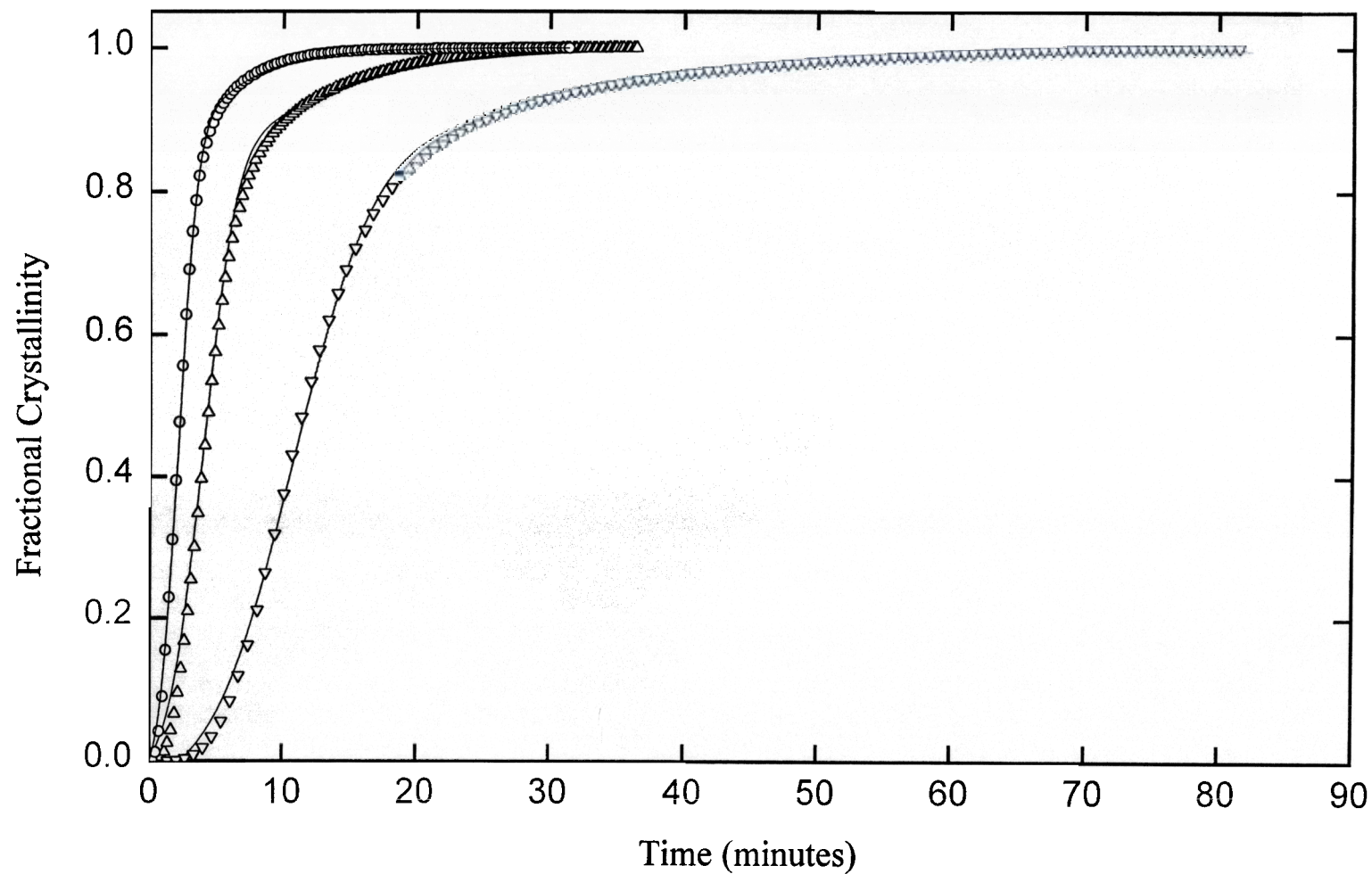


Fig. 8. A comparison of the fit obtained using equation 4 with measured data for samples containing 0.13% wt/wt yellow 62 at the following temperatures; $\circ$ = 397.6 K, $\triangle$ = 398.6 K and ∇ = 399.6 K.

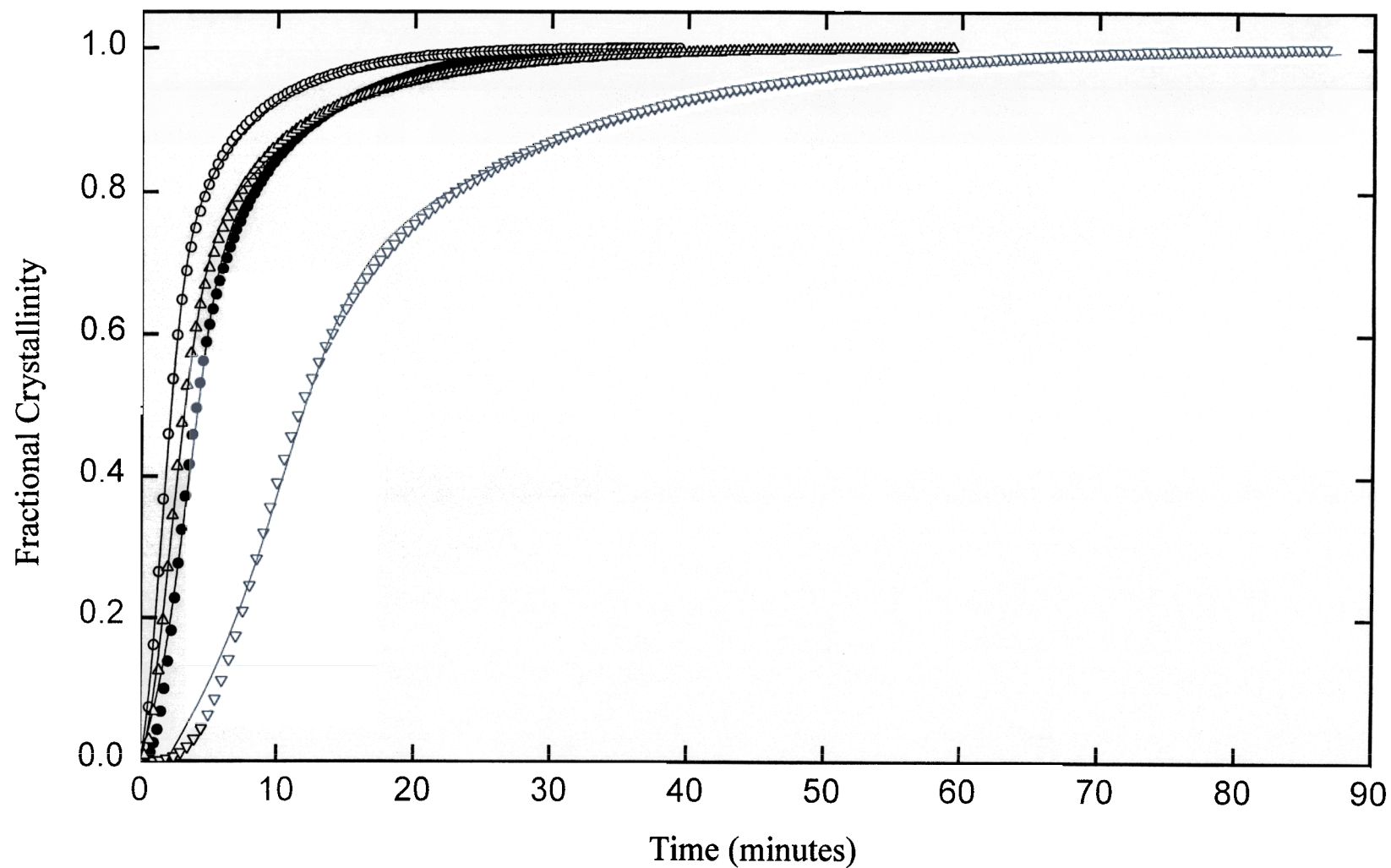


Fig. 9. A comparison of the fit obtained using equation 4 with measured data for samples containing 0.13% wt/wt yellow 93 at the following temperatures; $\circ$ = 397.6 K, $\triangle$ = 398.6 K and ∇ = 399.6 K.

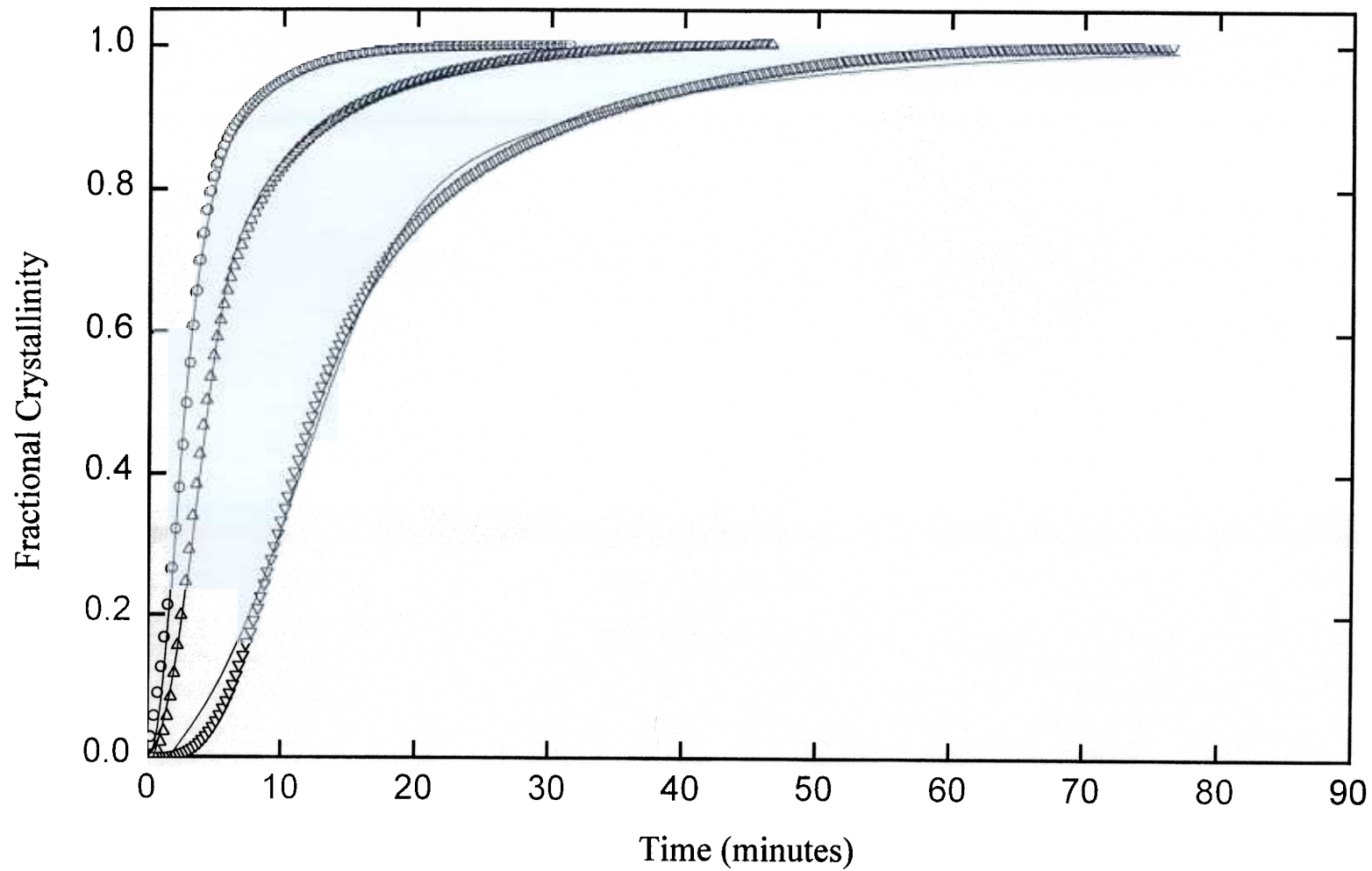


Fig. 10. A comparison of the fit obtained using equation 4 with measured data for samples containing 0.13% wt/wt modified phthalocyanine blue at the following temperatures; $\circ = 399.1$ K, $\triangle = 399.6$ K and $\nabla = 400.6$ K.

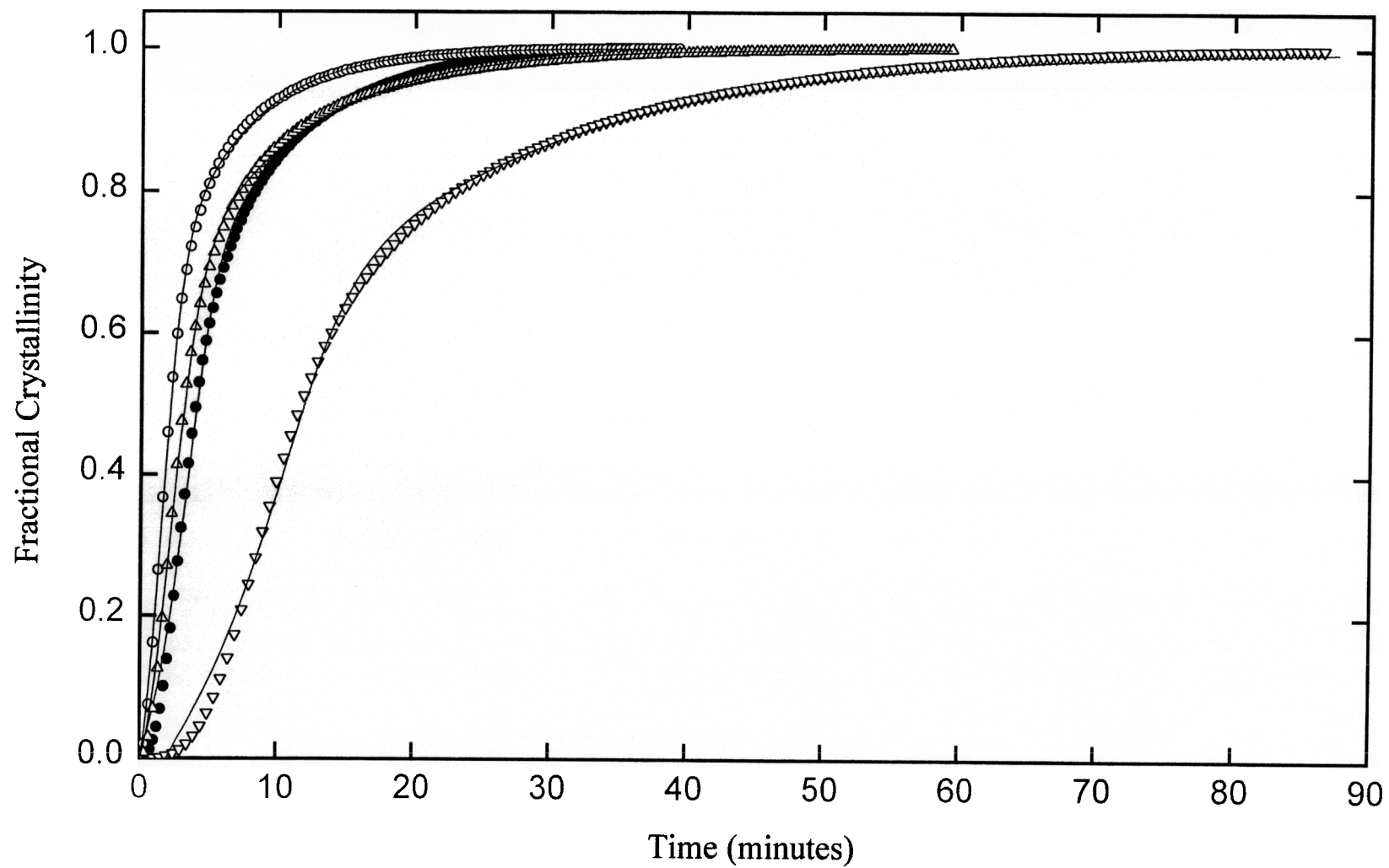


Fig. 11. A comparison of the fit obtained using equation 6 with measured data for samples containing 0.13% wt/wt phthalocyanine blue at the following temperatures; $\circ$ = 398.6 K, $\triangle$ = 399.1 K, $\bullet$ = 399.6 K and ∇ = 400.6 K.

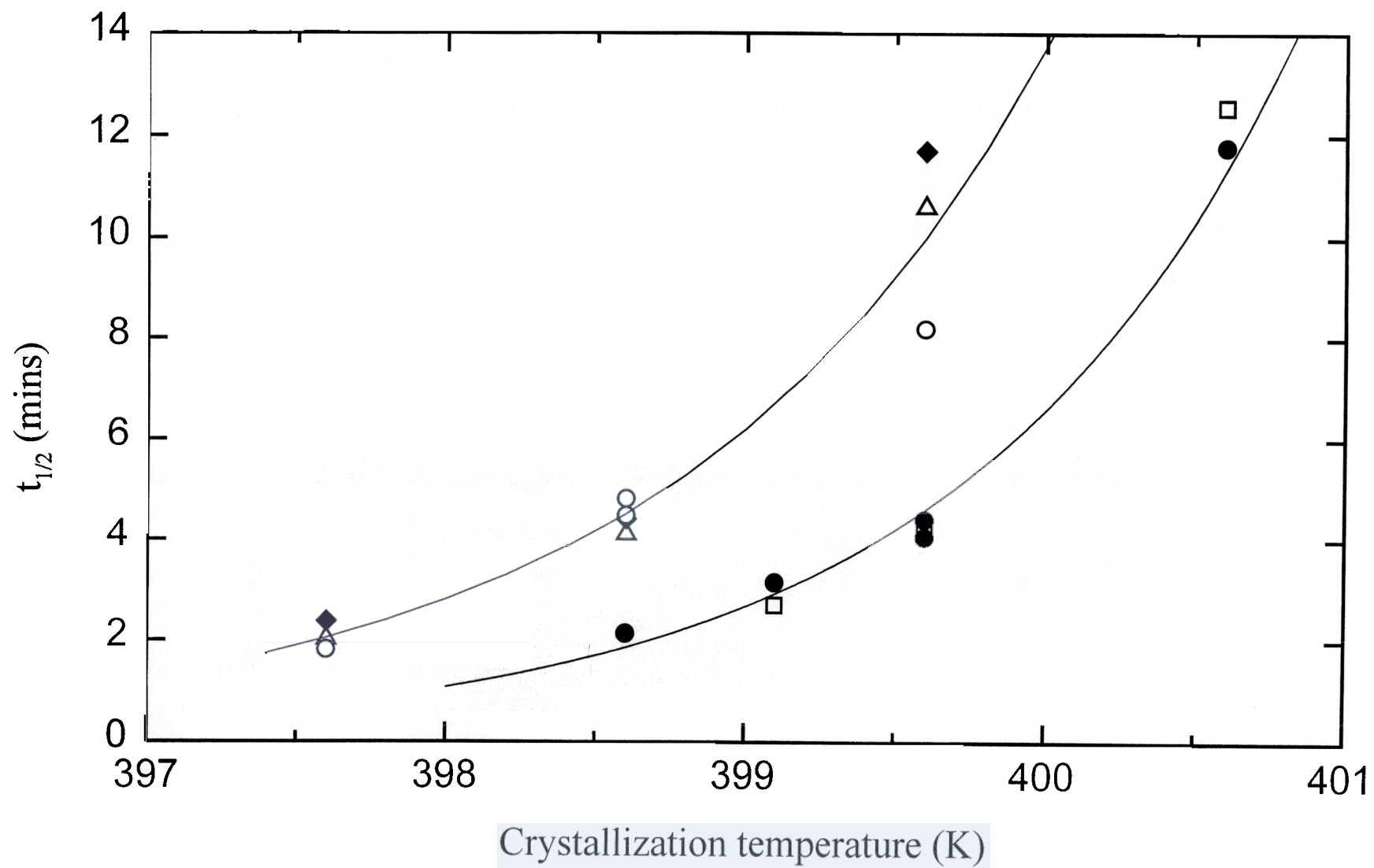


Fig. 12. The dependence of $t_{1/2}$ on crystallization temperature for HDPE containing the following pigments: $\circ$ = no pigment, $\triangle$ = yellow 93, $\blacklozenge$ = yellow 62, $\bullet$ = phth. blue, and $\square$ = mod. phth. blue. The solid lines are exponential fits to the data.

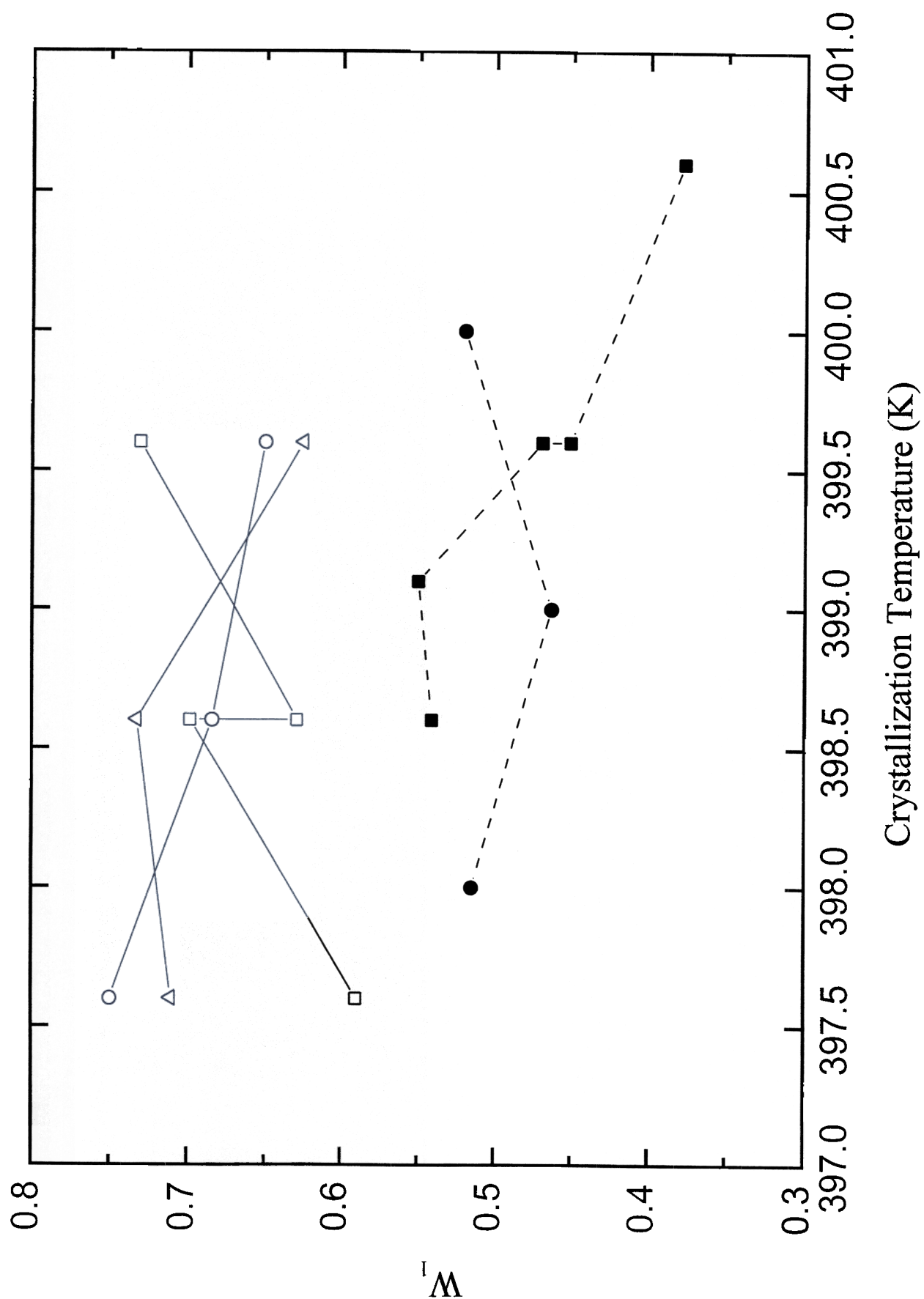


Fig. 13. The proportion of primary crystallization depends on pigmentation. o = yellow 62, Δ = yellow 93, □ = un-pigmented HDPE, ● = mod. phth. blue, ■ = phth. Blue.

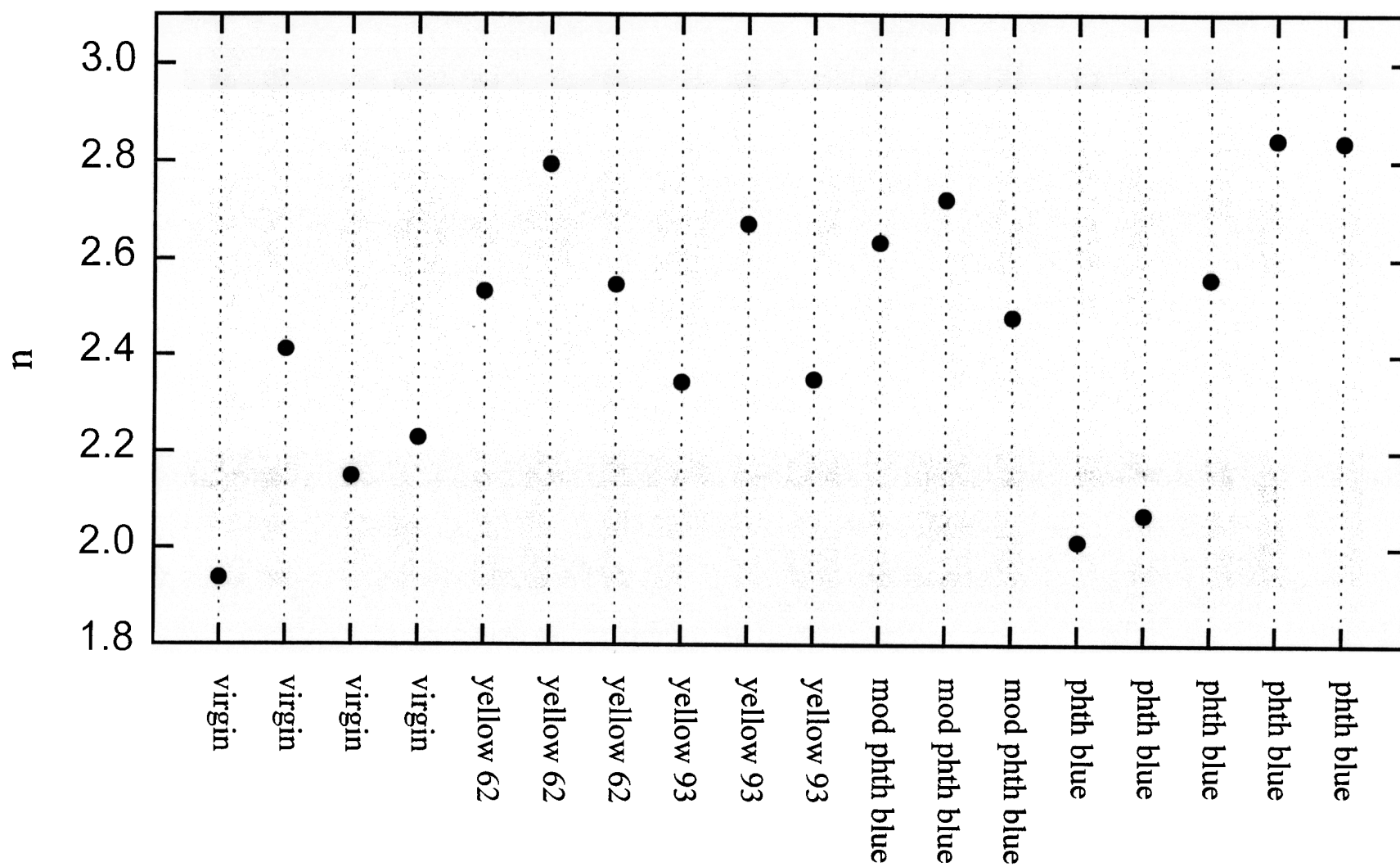


Fig. 4. The shape factor n does not show any systematic dependence on either pigmentation or temperature. (To aid visual clarity the isothermal crystallization temperatures have been omitted from the figure).

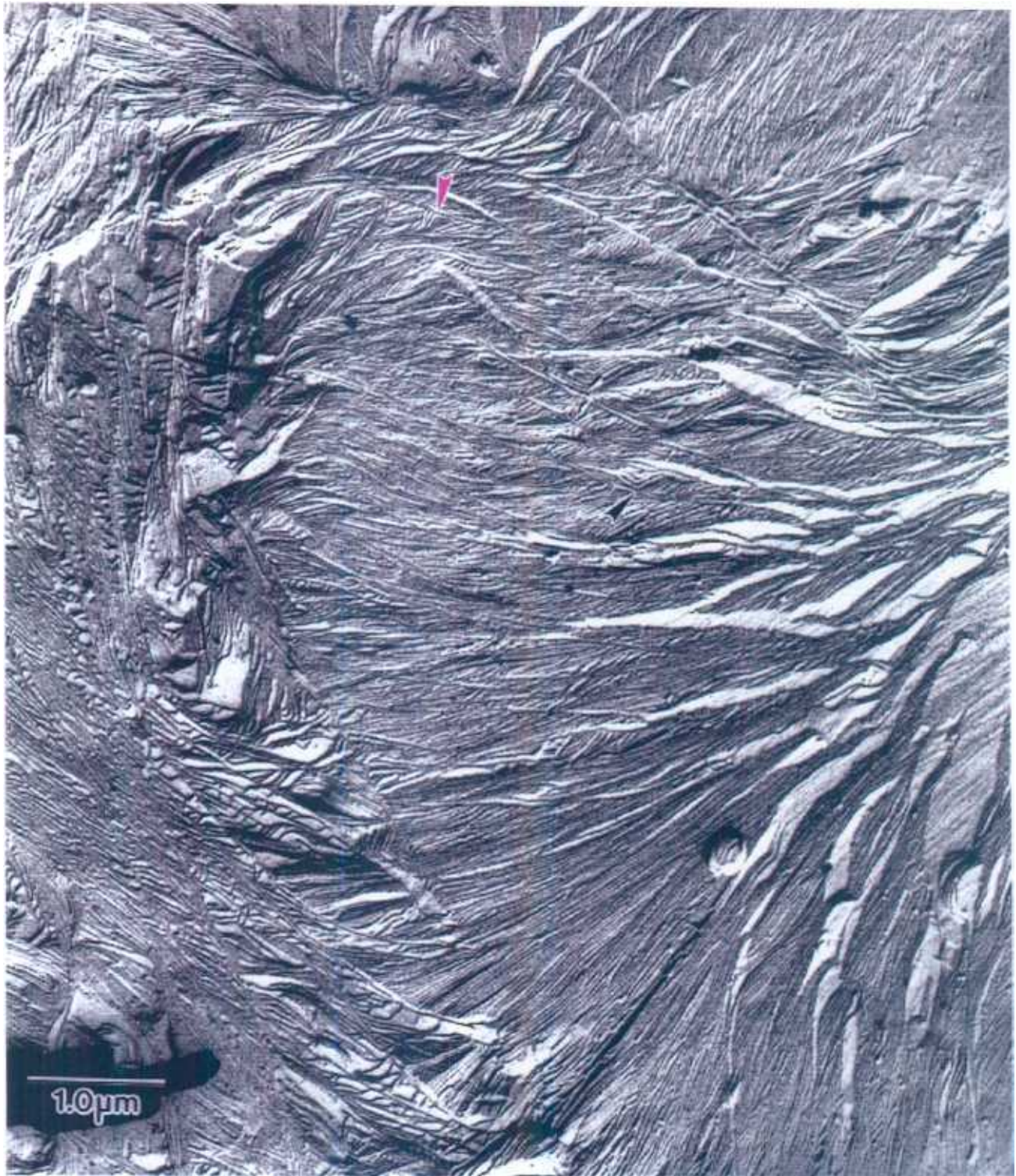


Fig. 15. TEM carbon replica of dry permanganically etched virgin HDPE crystallized under controlled cooling conditions of 10K/min from 430K. Region highlighted is of a spherulite and inter-spherulitic region to the left of dominant and in filling structures.

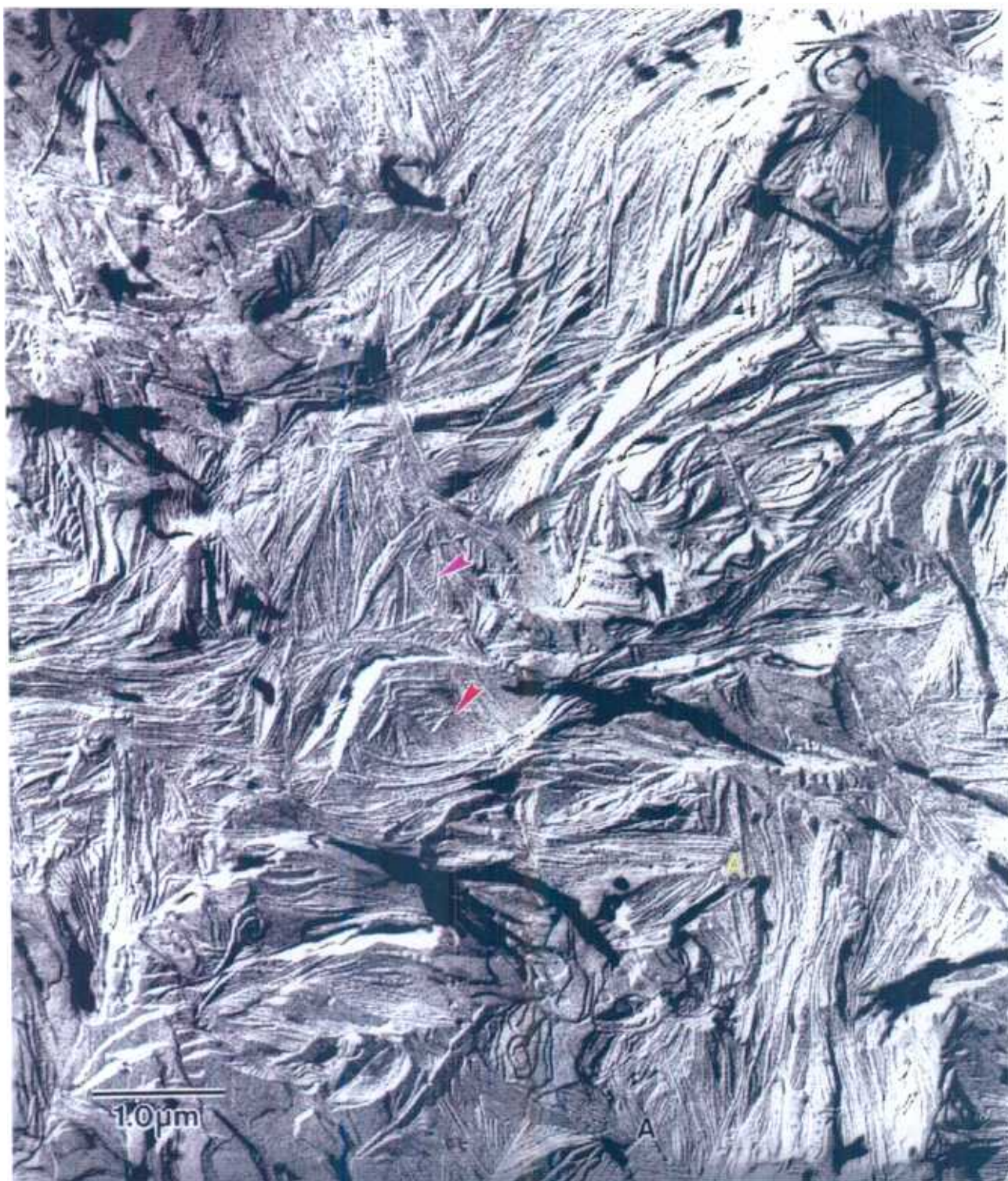


Fig. 16 TEM carbon replica of dry permanganically etched phthalocyanine blue crystallized under controlled cooling conditions of 10K/min from 430K. Anisotropic lamellar domaining consisting predominantly of in-filling lamellae is the dominant crystalline texture.



Fig. 17 TEM carbon replica of dry permanganically etched yellow 93 crystallized under controlled cooling conditions of 10K/min from 430K. Region highlighted is of a spherulitic sheaf (centre) with characteristic dominant-subsidary structures and areas of spherulitic impingement on either side.

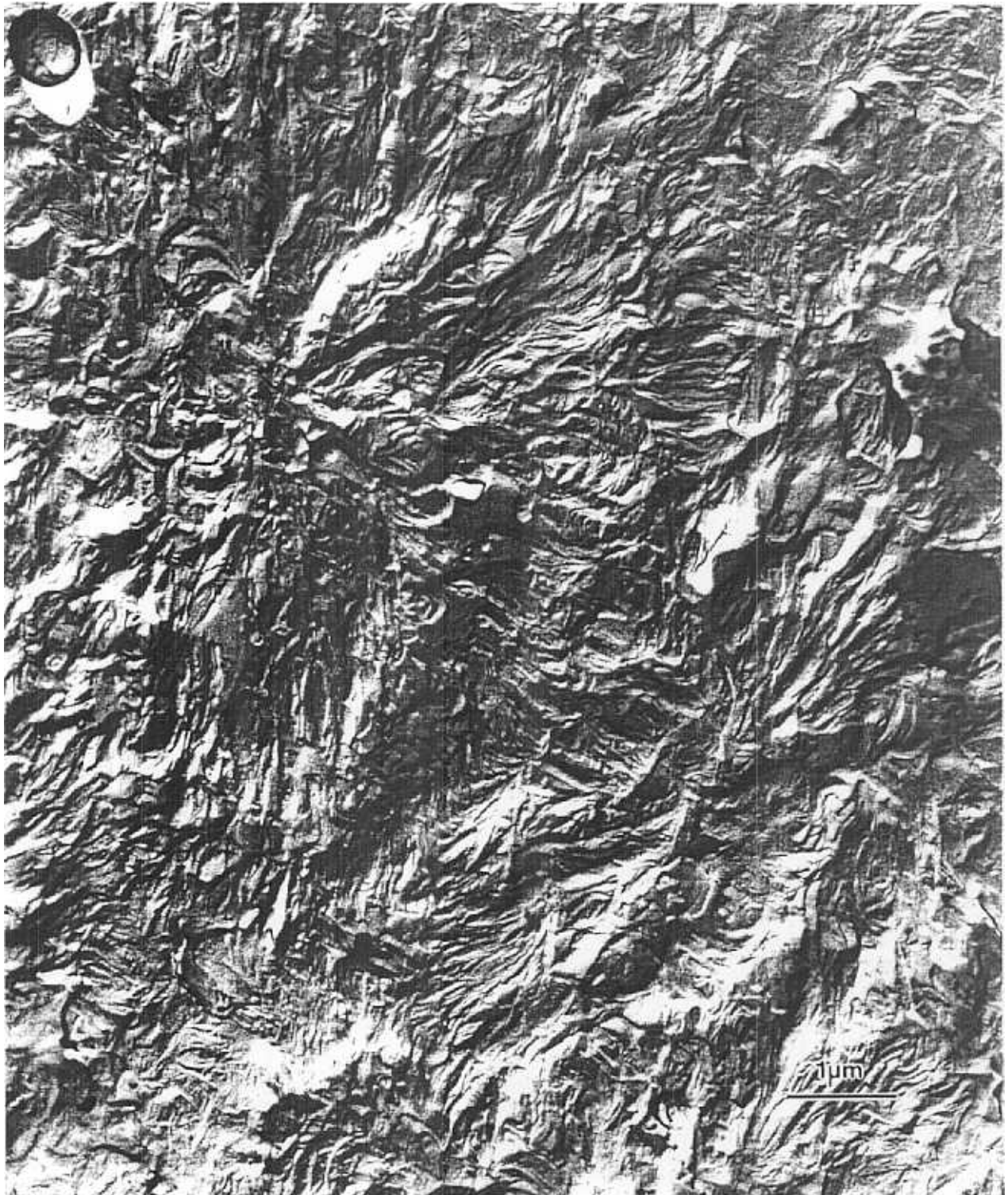


Fig. 18 TEM carbon replica of dry permanganically etched section of moulded virgin HDPE. Remnants of spherulitic structure exist (centre) among surroundings that no longer show clearly dominant-subidiary structures once present in Fig. 15.

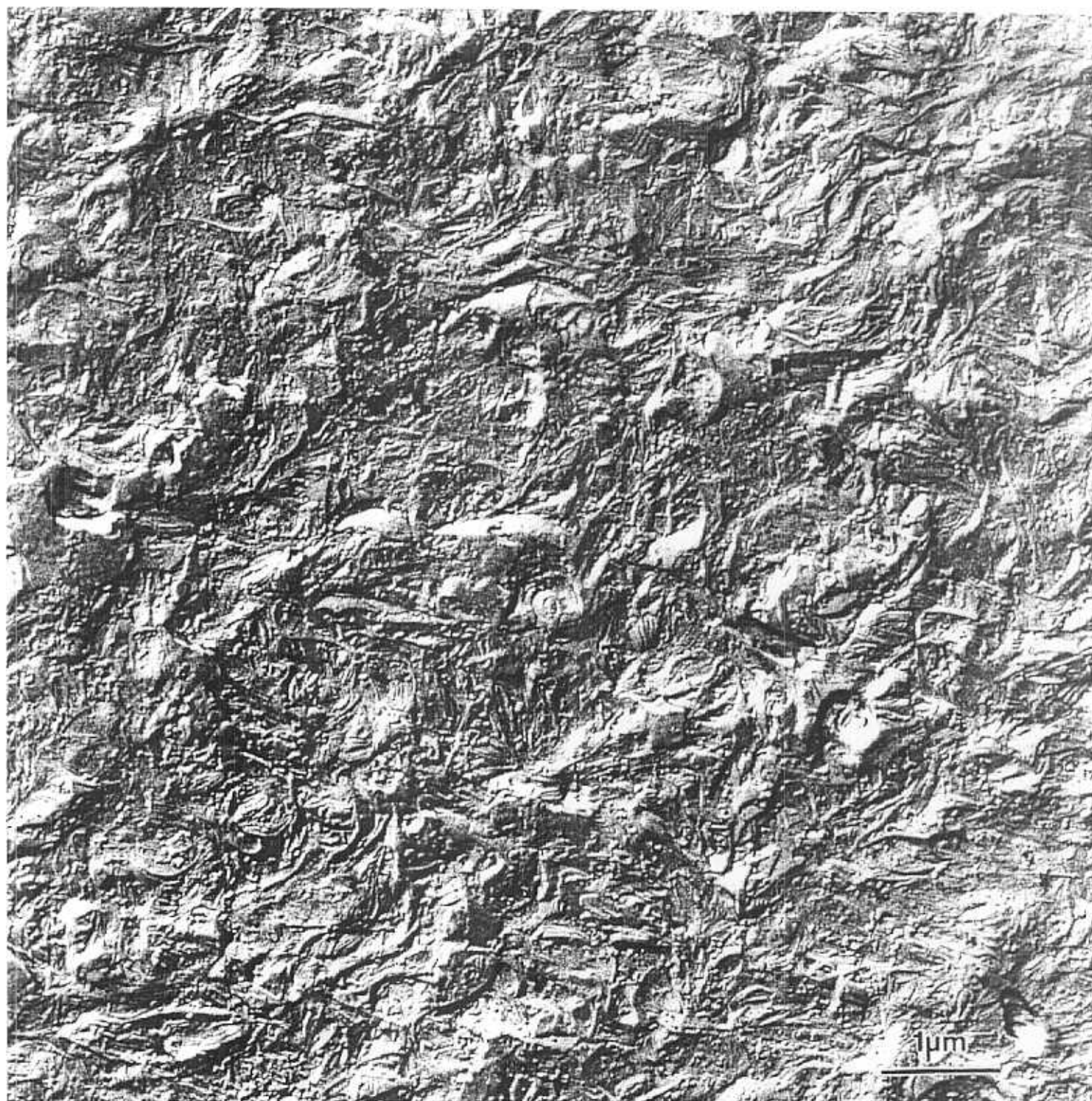


Fig.19 TEM carbon replica of dry permanganically etched section of moulded phthalocyanine blue. Lamellar domains and the clear presence of partially ordered in-filling lamellar crystals dominate the observed melt-crystallized morphology.

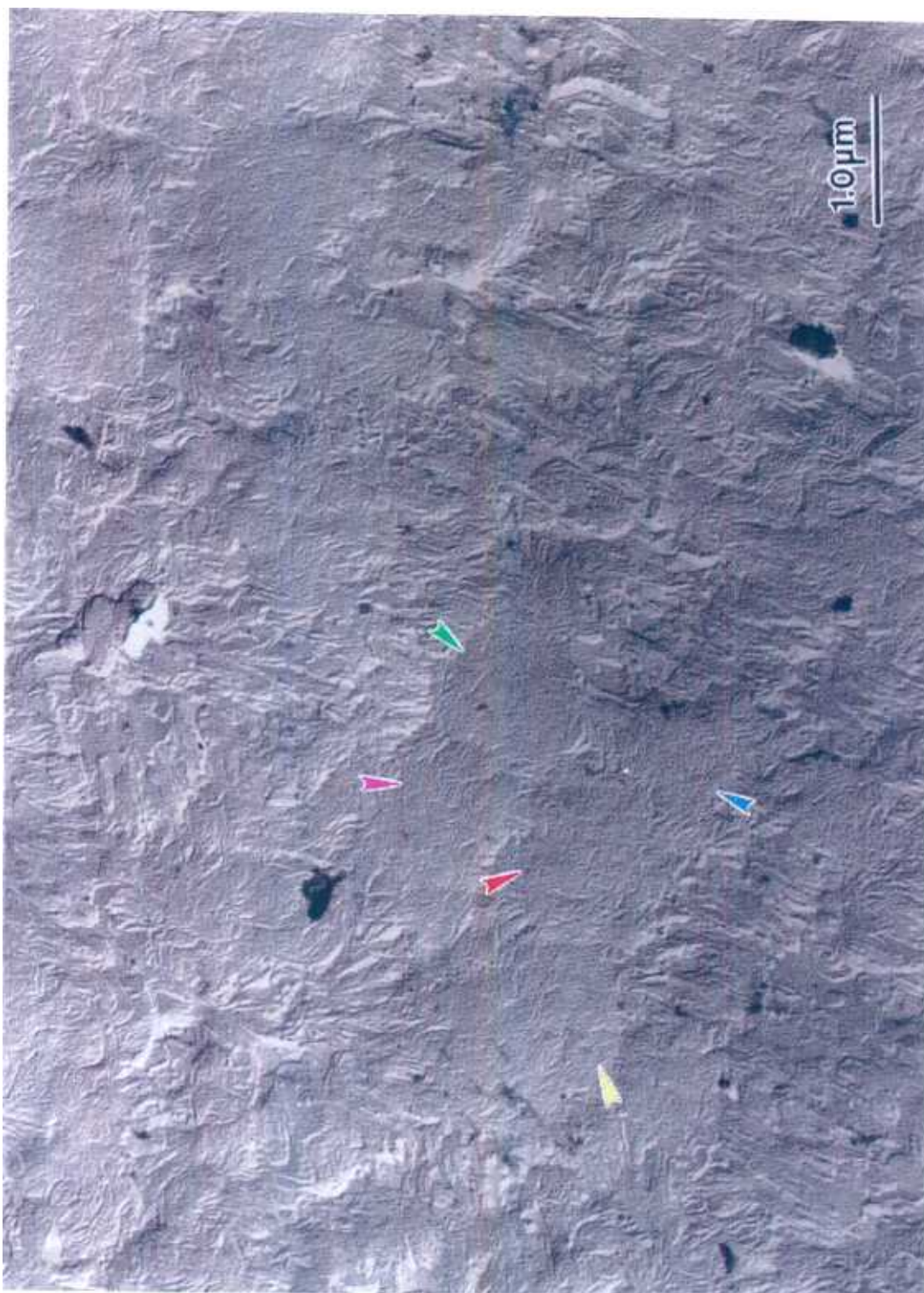


Fig.20 TEM carbon replica of dry permanganically etched section of moulded yellow 93. Remnants of dominant-subsidary lamellar crystals exist on a reduced scale where these are now organised into lamellar domains rather than with a spherulitic architecture.