Crystallization and morphology of nylon-6,6 crystals: 1. Solution crystallization and solution annealing behaviour

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(*Received* 2 *November* 1979; *revised* 16 *May* 1980)

In the course of crystallizing nylon-6,6 from solution, previous studies on the relation between lamellar thickness (l) as assessed by low-angle X-ray scattering and crystallization temperature (T_c) were extended further. This includes the extension of the T_c range and the use of solvents also other than butane-1,4-diol employed hitherto. Upwards extension of the temperature range was achieved by the annealing of crystals, formed at a lower T_c, in their own concentrated mother liquor at higher temperatures (T_A). Most surprisingly, the l *versus* T_c curve joined up smoothly and with considerable overlap with the l *versus* T_A curve, a behaviour which if to be proved general may have weighty implications for existing ideas on the origin of chain-folding. The use of different solvents confirmed that l is determined by the supercooling (and not by T_c or T_A alone) also in the present polymer. The l *versus* T_c/T_A relation consists of a long horizontal plateau followed by an upswing at higher T_c/T_A values. As in previous works, along the horizontal plateau and at the beginning of the upswing the X-ray diffraction pattern displayed two subsidiary (non-Bragg) maxima. However, at the newly achieved higher end of the upswing three such maxima could be obtained, this being the first instance of a variation in the number of such maxima in a given polymer. The number of subsidiary maxima provides a direct measure of the length of the fold stems, and their intensities gives information on the nature of the fold. The newly achieved 3-maxima case reaffirms and strengthens previous evidence that there is a strong preference for acid units within the fold portions and that along certain positions of the l *versus* T_c/T_A curve the fold is tight (one acid unit). Heating in a non-solvent provided new examples of distinct doubling of the initial fold length in the course of conventional annealing treatment. Calorimetric (d.s.c.) studies were also carried out on many of the nylon-6,6 preparations. D.s.c. melting curves indicate that changes in the internal morphology of nylon-6,6 crystal occur if scanning speeds less than 80 K min^{-1} are used. Measurements on single crystals prepared at different solution and/or annealing temperatures yield a heat of fusion value of 61 cal g^{-1} for the ideal nylon-6,6 crystal. The value of 69 erg cm^{-2} is obtained for the fold surface energy of the single crystals. The thermodynamic melting temperature, T_m^0, for this polymer is found to be the surprisingly high value of 301°C.

INTRODUCTION

Since its discovery[1], nylon-6,6 has commanded considerable interest, not only because of its technological importance[2,3] as a useful commercial polymer, but also because of the complexity of morphological changes associated with its crystallization behaviour, not only in the solid state[4-6] but also from solution[7-12] and melt[12-17]. Studies of nylon-6,6 crystallization have involved many techniques.

The morphology of single crystals[7-11] and spherulites[12-19] have been studied widely. The basic crystal morphology is typically lath-like[6-11] (sometines aggregated) and of limited thickness (50–60 Å) when crystallized from solution. A survey of the X-ray long spacing results of numerous polyamides[8,10,11] has shown that few crystallographic repeat units are involved in forming these crystals. The hydrogen-bonding[20] of the CONH dipolar arrays in polyamides strongly influence the internal stability of the crystals formed (specifically contributing about 40% to the heat of fusion[21] of nylon-6,6). Furthermore, such stabilizing effects have led others[8] to suggest that the fold period in polyamides is related to the length of the crystallographic repeat unit and number of hydrogen bonds within the crystal lamellae.

More details of the intricate morphology[7] of nylon-6,6 single crystals have come to light from a combined analysis of both wide-angle and small-angle X-ray diffraction data on single crystal mats. Arising from the small number of monomeric repeat units within the crystal stem, subsidiary X-ray diffraction maxima have been observed. These reflections lie between the first-order small-angle region and the 002 and 001 meridionals, respectively. It follows from the theory of one dimensional scattering that the number of weak subsidiary reflections should be n-2, where n is the number of repeating units in the structure. Accordingly these features, unprecendented in polymer crystallography, provide a direct measure of the number of crystallogrpahic, hence monomer, repeats along the straight chain segments traversing the lamellae, and thus provide uniquely definitive information about the long-standing problem of how the lamella is sudivided into crystal core and fold surface contributions, at least in those cases where such subsidiary maxima are discernible.

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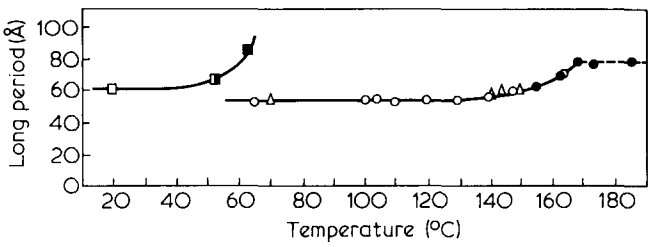

Figure 1 Dependence of the long periods, *l* (Å) of nylon-6,6 crystals on the isothermal crystallization and solution annealing temperatures in butane-1,4-diol and formic acid solutions. —○—, Isothermal crystallization; —●—, annealed 120°C and/or 140°C preparations, overlap region 148° to 164°C from butane-1,4-diol (there are many more measurement points along this overlap region than displayed in the Figure). —□—, Isothermal crystallization; —■—, annealed, overlap region is 53° to 63°C; from formic acid —△—, Hinrichsen[11]. Data from Dreyfuss and Keller (not shown) closely follow this curve in the range 70° to 155°C (ref 22)

It therefore follows that: (1) the visibility of these maxima in itself implies a significant uniformity of the crystal core; (2) merely by counting the number of maxima we can assess how thick this core is, and when compared with the total layer thickness (determined by low-angle X-ray diffraction), the maximum thickness which can possibly be comprised by the fold surface layer; (3) as a further refinement, the related intensities of the subsidiary maxima themselves provide potential information on the nature of the chain portion constituting the fold. In previous reports on nylon-6,6 crystallized under these experimental conditions the number of subsidiary maxima was always 2, thus corresponding to 4 repeats (for exact definition of the repeating units — pairs of oxygen atoms along the chain, see ref 7). Ideally this leaves only a few angstroms along each surface to be accommodated in the fold (for details see ref 7) which accordingly comprises no more than half a monomer unit, at least in those preparations in which the subsidiary maxima were best defined and hence used for analysis. In an attempt to define which half of the nylon-6,6 monomer unit is involved, in case there is any preference at all (along route 3 above), the somewhat surprising conclusions is that it is the acid portion which is more likely to form the fold. In the present work, further reliance will be placed on these subsidiary maxima. Attempts were made particularly to alter the crystal thickness over wider limits than achieved previously, by extending the investigation to higher crystallization temperatures where hopefully variation in the number of subsidiary maxima could be accomplished.

Unfortunately, the amount by which the crystal thickness could be increased in excess of that achieved elsewhere[22] by direct crystallization was rather limited, since the temperature of crystallization in the same solvent could not be extended sufficiently towards higher temperature while maintaining specimen integrity. However, it was found in the course of the present work that where the crystals, once formed, were heated above their crystallization temperatures while still in contact with their own solvent, the layer thickness could be increased beyond that achievable by direct crystallization. This *solvent annealing* procedure features prominently in the present paper. Not only did this facilitate the growing of thicker crystals beyond what was otherwise possible, or convenient, by direct crystallization, but rather unexpectedly revealed a relation between annealing and supercooling which, if proven to be of wider valdity, could significantly influence our ideas on polymer crystallization.

The thermal properties of nylon-6,6 crystals are also to receive special attention, in which respect due regard was taken of recent studies of Hinrichsen[11].

EXPERIMENTAL

Materials

Commercial grade nylon-6,6 used in most of this work was kindly supplied by Mr C. G. Cannon of ICI Fibres Ltd, as polymer chips, free of additives.

Single crystal preparations

The solution was made up by dissolving nylon-6,6 chip primarily in butane-1, 4-diol. Polymer concentrations used were in the range 0.04 and 0.2% (w/v) except for the higher crystallization or annealing temperatures where even more concentrated solutions were required. Crystals were grown isothermally by the self-seeding technique[23] and filtered *in situ* in the crystallization bath at the crystallization temperature. The crystal mats produced from alcoholic solutions were freed of residual solvent through washing with methanol or acetone followed by vacuum drying to constant weight. Since it proved to be difficult to induce nylon-6,6 to crystallize isothermally in useful amounts above 165°C from butane-1, 4-diol solvent, higher temperature preparations were made by isothermal annealing of crystal mats prepared at lower temperatures (mostly at 120 and 140°C, but also below this range). This procedure also provided some overlap between direct solution crystallization and annealing regimes.

A limited number of isothermal crystallization and annealing experiments were conducted in benzyl alcohol and formic acid to establish the morphology and crystallization behaviour in other solvents.

Crystallizations from benzyl alcohol were carried out in the temperature interval 150°–160°C and annealing experiments up to temperatures as high as 185°C for prolonged periods. Crystallization from formic acid, being a highly polar and more volatile solvent, were carried out at the lower temperatures of 20°–60°C.

A fes mats prepared from butane-1, 4-diol at 120°C were suspended in n-paraffin wax solutions and then heated stepwise in tubes to temperatures as high as 240°C. This hydrocarbon medium (solid at room temperature) offered some oxidative protection to the nylon-6,6 samples although specimen discoloration did occur. Enthalpy of fusion measurements from DSC-2 melting curves were used as criteria for assessing degradation.

X-ray diffraction

Single crystal mats were examined using both wide- and small-angle X-ray diffraction techniques. Fine collimation and an evacuated camera were found advantageous, and, in some instances, an Elliott Focussing Toroid camera was particularly useful for investigating reflections in both the wide-angle and subsidiary maxima regions. Small-angle X-ray patterns were recorded with a Franks camera using a point-collimated CuKα X-ray source and/or with a Rigaku–Denki small-angle camera using a rotating anode generator. Ni-filtered CuKα was employed throughout the X-ray work.

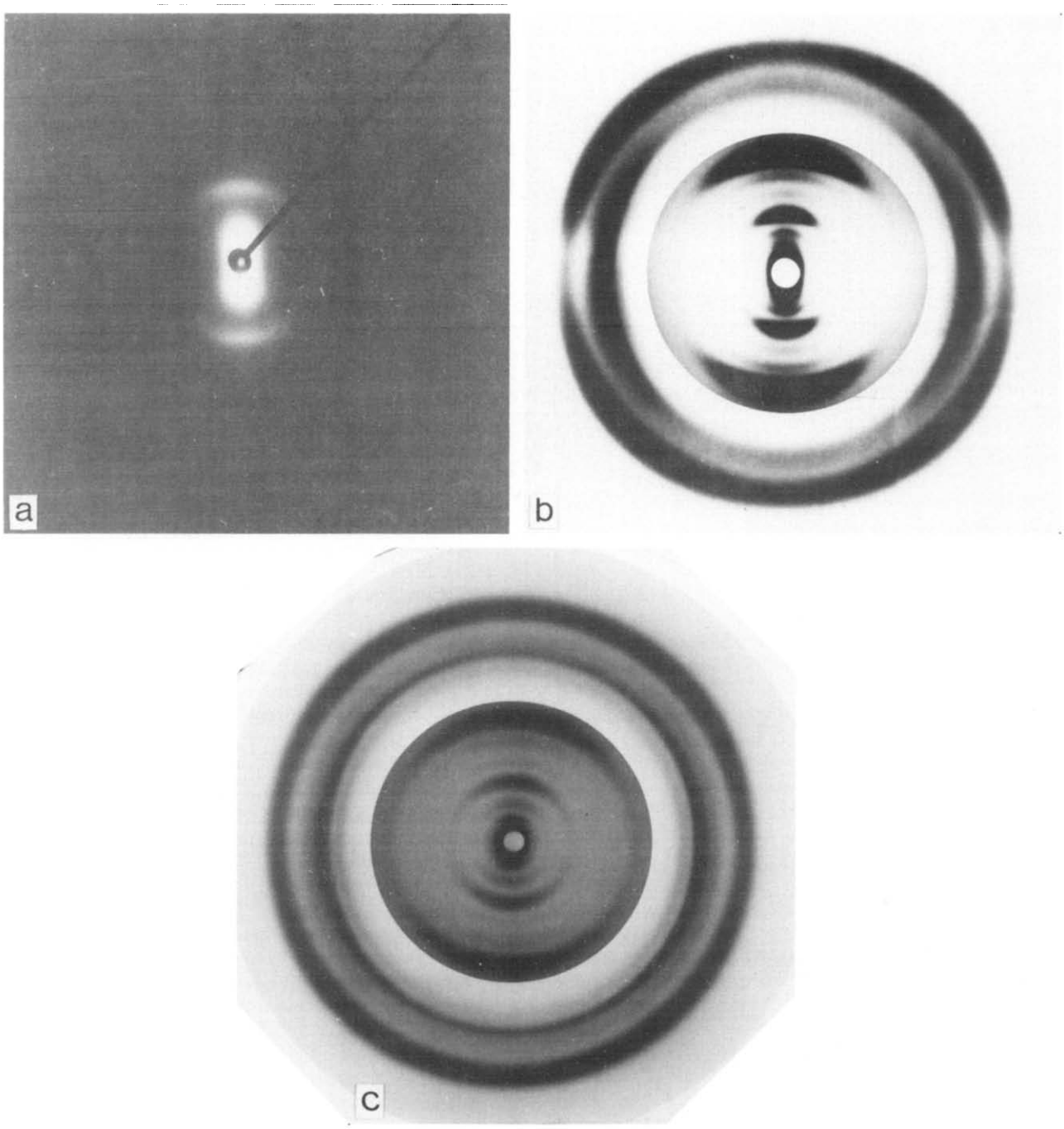

Figure 2 (a) Typical small-angle X-ray diffraction pattern from nylon-6,6 single mats prepared by isothermal crystallization at 120°C from butane-1,4-diol solvent. (b) Corresponding wide-angle X-ray diffraction pattern of sample *Figure 2a.* Note the weak but distinct meridional reflections that lie between the small-angle region (not shown) and the 001 (001 and 002) reflections. The inner portion of the diffraction pattern is printed more strongly to emphasize these subsidiary maxima. (c) Typical wide-angle pattern obtained for nylon-6,6 single crystal mat prepared at 25°C from formic acid solution. Low-angle pattern is similar to 2a. Inner portion printed more strongly

Thermal measurements

Melting points and heats of fusion of the crystal mats were assessed using Perkin–Elmer differential scanning claorimeters, models DSC-1B and/or DSC-2. The instruments were calibrated at different scan speeds using standards such as indium, benzoic acid, lead, tin and zinc, following the recommended procedure. Highly pure indium was used as a calorimetric standard for heat of fusion calibration.

RESULTS

X-ray diffraction

Small-angle spacing — temperature dependence. The dependence of the small-angle diffraction spacing of nylon-6,6 on crystallization temperature from butane-1, 4-diol (*Figure 1*) shows a horizontal plateau followed by a monotonic increase with crystallization temperature (T_c) at high T_c, in good agreement with literature results[11,22],

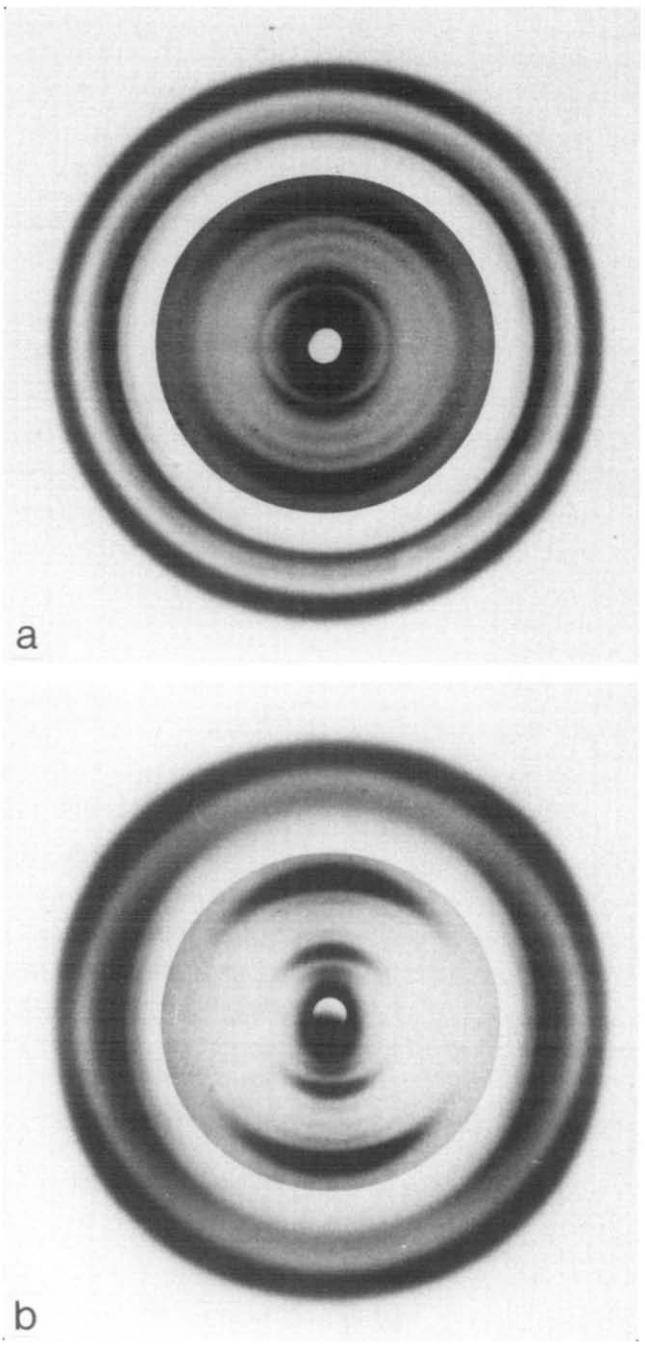

Figure 3 (a) Illustration of subsidiary maxima in nylon-6,6 crystallized at 148°C from butane-1,4-diol solution. A weak third reflection is noticeable just outside the 001. (b) X-ray diffraction pattern obtained from single crystal mats prepared by isothermal crystallization from butane-1,4-diol solution at 160°C showing three subsidiary maxima. (Again the inner reflections are printed more strongly to enhance the subsidiary maxima)

which extend up to ~150°C. Beyond this, our results now extend this trend until about 170°C where an unexpected levelling-off is noted. Below 170°C, the results on the solution-annealed crystal preparations and those on samples crystallized directly from solution overlap smoothly. Beyond 170°C, an increase in crystal thickness would be anticipated but has not been observed for reasons unknown at present. The annealing in the presence of paraffin — a non-solvent for nylon — transformed a crystal of 54 Å to 105 Å, a result to be referred to later.

The few points obtained using benzyl alcohol (not entered in *Figure 1*) fall on a line parallel to that for butane-1, 4-diol but displaced by 7°–10°C towards lower temperatures, undoubtedly because of the lower thermodynamic dissolution temperature. This shift is much larger for the better solvent formic acid, amounting to about 100°C. The latter points are displayed in *Figure 1*.

Subsidiary maxima. It is appropriate now to examine the wide-angle X-ray scattering patterns for subsidiary maxima, which are expected to appear between the 001 and 002 reflections (the two strongest reflections along the meridian, see ref 7) of the diffraction patterns given by oriented mats of single crystals. Verifying as well as extending previous work[7], the existence of two subsidiary maxima is revealed in crystals fomed between $T_c = 80°$ and 142°C from butane-1, 4-diol and between 20° and 53°C from formic acid* (*Figure 2*). In these T_c ranges the crystal thickness is constant or just starts to increase at the higher T_c end of the respective scales. When examining crystals formed above these respective temperatures, changes in the subsidiary maxima were noted. At first, at $T_c = 148°C$ (*Figure 3a*), a further reflection is visible just outside the (001) while the position of the two subsidiary maxima, as previously identified, is shifted as compared with *Figure 2*. At $T_c = 155°C$ there are now three reflections between 001 and 002, equally spaced, exhibiting a pattern of subsidiary maxima commensurate with 5-monomer repeating units. *Figure 3b* shows such an example for direct crystallization at 160°C from butane-1, 4-diol. Further increases in crystal thickness up to the limits indicated by *Figure 1* (which could only be achieved by solvent annealing) unexpectedly did not lead to further changes in the subsidiary maxima. At the higher temperatures, *Figure 4* shows three examples from the upper plateau of *Figure 1*. Three similar subsidiary maxima patterns were obtained also on nylon crystallized from benzyl alcohol (*Figure 5a*) and from formic acid at 53° and 63°C, corresponding to the highest temperature point along the formic acid curve in *Figure 1* (*Figure 5b*); in this example the sample was heat-treated subsequently at 205°C, which, however, did not lead to any further increase in the long period, which was 76 Å. We illustrated it here as it represents the most clearly defined example of 3 maxima so far, and it will be discussed below.

The relative intensities of the three subsidiary maxima can be roughly assessed from *Figures 4* and *5*, where it is seen that the one closest to the (002) meridional is somewhat more intense than the inner two which are about of equal intensity. More quantitative information on this point is provided by photometer traces. *Figure 6* reproduced here was of the pattern in *Figure 5b*.

Thermal behaviour

Melting behaviour. *Figure 7* shows d.s.c. thermograms as a function of heating rate. Two melting peaks are apparent at slow heating rates where the one at the lower temperature is becoming increasingly more prominent on faster heating, until at a rate of 80°C min^{-1} approximately only one peak is observed. This behaviour is the familiar pattern associated with 'reorganization' during heating, the higher temperature peak corresponding to the more stable 'reorganized' state which is comprised of thicker crystals. Above a heating rate of 80°C min^{-1} this reorganization is entirely suppressed. *Table 1* provides a

* Such maxima are seen also in *Figure 3* of ref 11, even if not commented on by the author

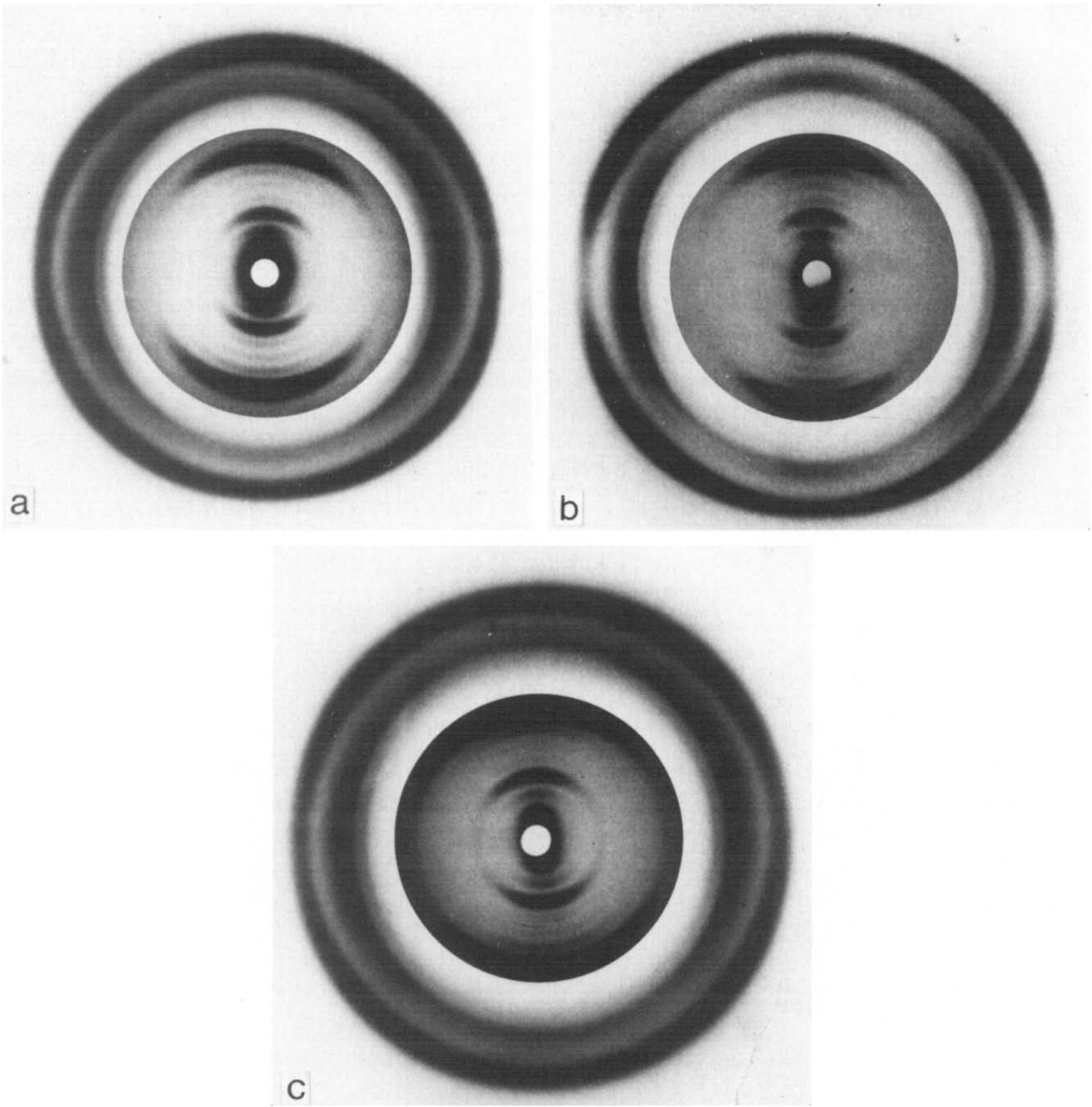

Figure 4 X-ray diffraction patterns of nylon-6,6 single crystal mats prepared from butane-1,4-diol solution initially by isothermal crystallization at 120°C followed by annealing at (a) 169°C; (b) 173°C and (c) 185°C, respectively. (Inner reflection printed separately so as to enhance the subsidiary maxima)

summary of the relevant melting experiments in this work as regards the number of peaks observed for all but the highest crystallization temperatures. For the highest T_c values, where the three subsidiary maxima are found, only one peak is observed for all heating rates. *Table 2* contains a series of fusion experiments carried out at a rate of 10°C min^{-1} on crystals which were annealed in solvent after formation at a specified lower temperature. Preparations from three solvents are involved with the appropriate crystallization and annealing temperatures as indicated. Only one peak is found in all but one of these cases. Some of the melting curves underlying *Table 2* are displayed in *Figure 8*. Accordingly, this kind of behaviour, namely a single melting peak for high temperature preparations (i.e. for the thicker crystals) seems to be general. Conversely, double melting peaks are observed only for the thinner crystals, including those along the 54 Å plateau of *Figure 1*.

Heat of fusion. Enthalpy results were determined from d.s.c. melting curves obtained on nylon-6,6 mats prepared by (1) isothermal solution crystallization or (2) from isothermal annealing of specimens obtained in (1). Heat of fusion results, ΔH_m, obtained by integration of the melting curves (based upon a pure indium standard) are plotted in *Figure 9*. The heat of fusion is independent of heating rate (see *Figure 10*). Our results are in reasonable agreement with those of Hinrichsen[11] (also plotted in *Figure 9*) which do not go above 150°C. At lower crystallization temperatures ΔH_m is invariant with temperature, but above about 120°C, the enthalpy increases appreciably up to ~145°C, before levelling-off and finally

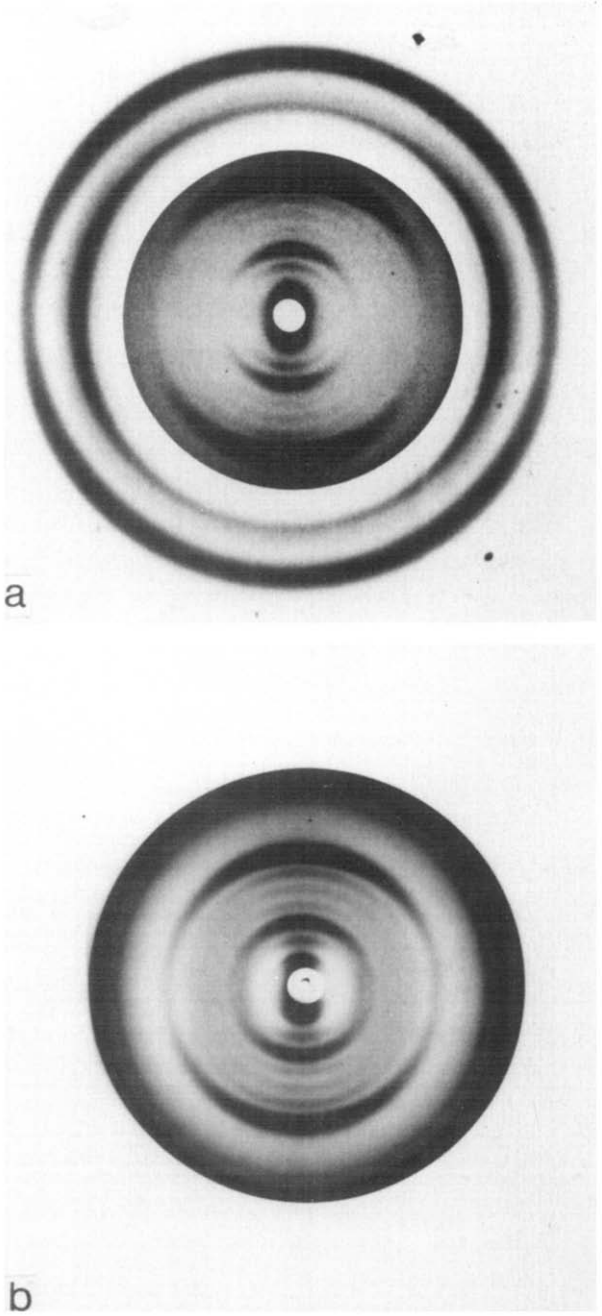

Figure 5 X-ray diffraction pattern with three subsidiary maxima obtained from nylon-6,6 single crystal mats prepared by isothermal crystallization from: (a) benzyl alcohol solution at 150°C followed by the annealing in the same solvent at 160°C. (Inner reflections printed as indicated in *Figures 2* and *3*); (b) formic acid solution at 63°C and heat treated at 205°C subsequently. Direct, single exposure print made possible by the exceptional definition of subsidiary maxima

decreasing. This unexpected decrease in the enthalpy of fusion presumably arises as a result of thermal degradation associated with the higher temperatures to which these crystals have been exposed. (There was no decrease in ΔH_m in the corresponding series from formic acid, not illustrated.)

DISCUSSION

X-ray results

l vs. T_c *curves.* These curves represent the dependence of the crystal thickenss, and hence fold length, on the crystallization temperature, a relation which is of fundamental importance in polymer crystallization studies. The curves in *Figure 1* consists of three regions:

(i) at lower T_c values, l is constant;

(ii) at a certain T_c value l starts to increase at a gradually accelerating rate;

(iii) at the highest T_c values for the butane-1,4-diol curve, l again becomes constant.

Region (iii) is accompanied by discoloration, presumed to be degradation. In view of this, and because it has no precedent, we choose to leave region (iii) out of consideration of the present paper and quote it merely for the record in case the effect re-emerges again in the future.

Historically it is region (ii) which has become the recognized feature of polymer crystallization. This corresponds to the behaviour displayed by materials such as polyethylene, polyoxymethylene, etc., over a much wider temperature and fold length range. Existing crystalli-

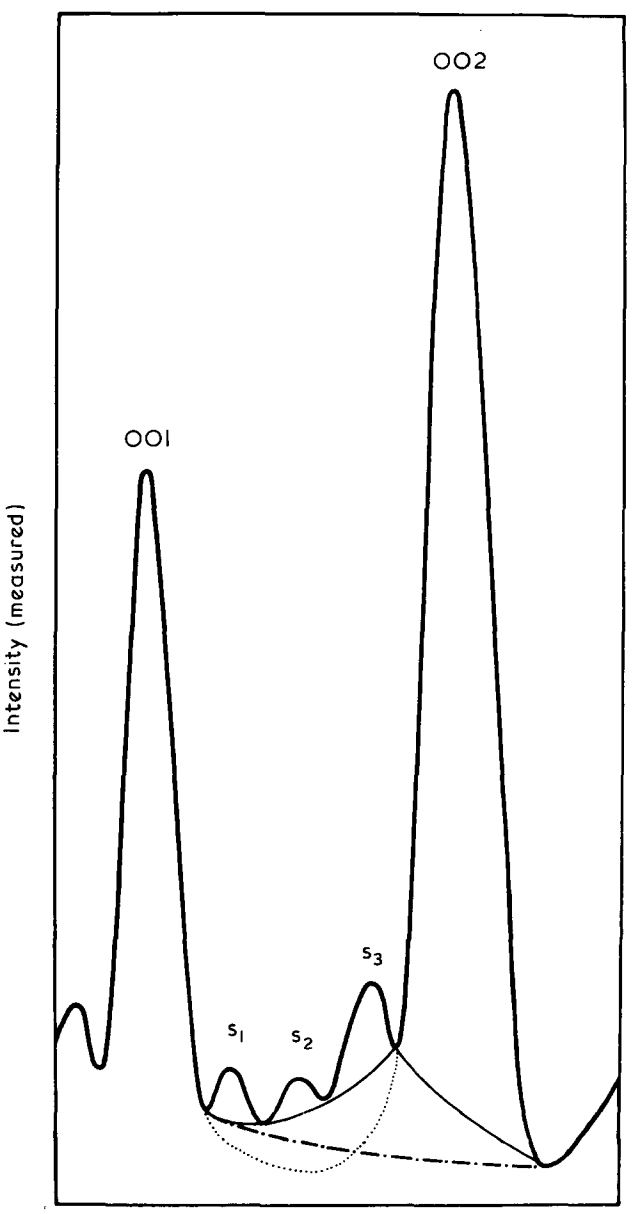

Figure 6 Observed intensity vs. $h = 2\sin\theta/\lambda$ (θ = scattering angle; λ = wavelength) plots by densitometry of pattern in *Figure 5b*. The three maxima between 001 and 002 reflections are denoted by s_1, s_2 and s_3. We see that $s_3 > s_2 \sim s_1$. The broken and thin solid lines represent attempts to define background

zation theories were designed to account for these observations. All the earlier experimental work was carried out on polymers which crystallized readily, preventing high supercoolings from being reached and hence the low T_c region from being attained. Extension of the relevant l *versus* T_c studies to high supercoolings occurred rather gradually in the case of some specific polymers where a low temperature region was accessible. In all these latter cases, which included crystallization both from solutions[25-27] and melts [28] an invariance of l with T_c became apparent. Nylons were amongst the first polymers where such behaviour was recognized [22]. The present work represents an extension of these earlier studies explicitly aimed at increasing the experimentally accessible range of crystallization temperatures in the upward direction so as to extend region (ii).

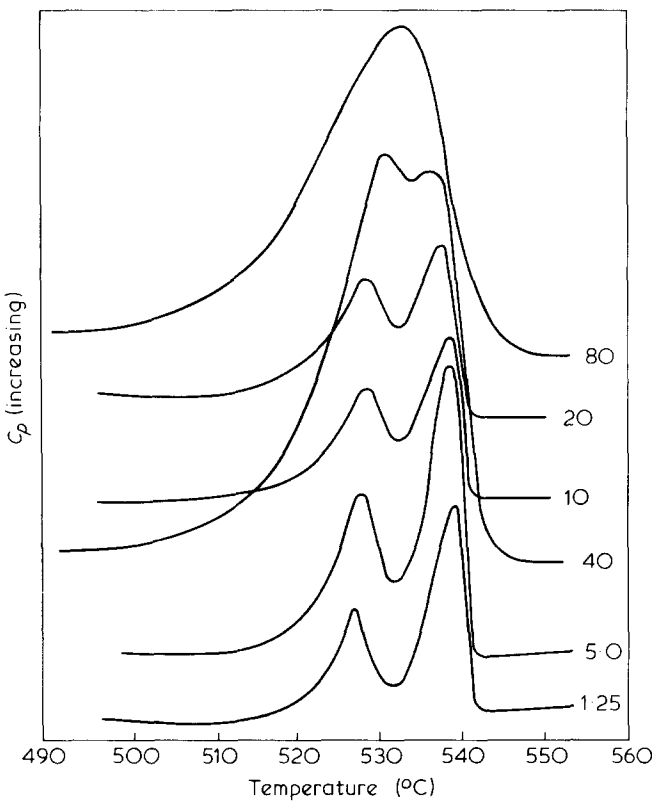

Figure 7 Effect of heating rate upon the melting behaviour of nylon-6,6 single crystal mats prepared at 120°C from butane-1,4-diol. Thermograms obtained with scanning rates ranging from 1.25°C to 80°C min^{-1}. Note that only one peak is present at the fastest scan rate

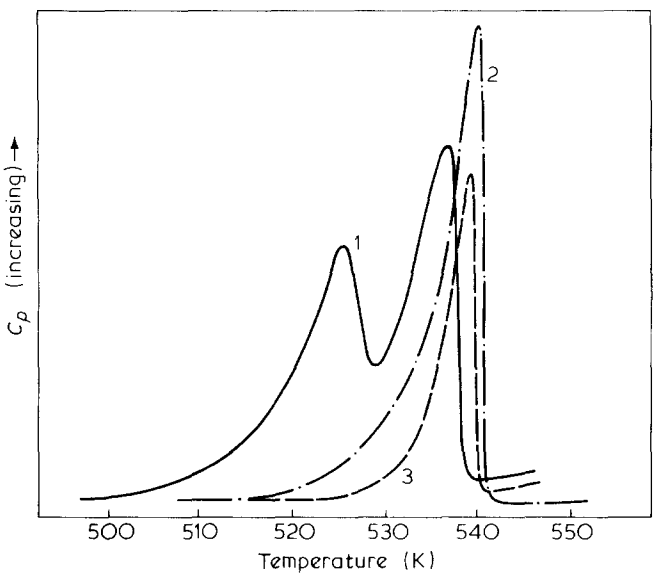

Figure 8 D.s.c. melting curves for nylon-6,6 single crystal mats crystallized from butane-1,4-diol solution at different crystallization temperatures. All heating rates were 10°C min^{-1}. Sample details are (1) T_c, 100°C, (2) T_c, 160°C and (3) T_c/T_a, 120°/164.4°C. In (3) the first temperature is the isothermal crystallization temperature, and the second the annealing temperature for the 120°C crystals

Table 1 Number of melting peaks for solution crystallized nylon-6,6 crystal mats obtained from butane-1,4-diol, benzyl alcohol and formic acid solvent

Heating rate (°C min^{-1})	Crystallization temperature (°C)							
	25(++)	53(++)	100	104	140	142	155(+)	160
1.25					2			
2.5				2	2	2	2	1 (s)
5.0					2			
10			2	2	2	2	2	1
20	2	1		2	2	2	2	1
40			2	1 (sh)	2	1 (sh)	2	1 (s)
80			1 (s)		1			1
160								1

(sh) denotes peak with shoulder
(s) indicates skew melting peak
Most crystallizations were made from butane-1,4-diol; some from benzyl alcohol (+) and from formic acid (++)

Table 2 Number of melting peaks for some typical solution annealed nylon-6,6 single crystal mats prepared in butane-1,4-diol, benzyl alcohol and formic acid solvents.

Heating rate (°C min^{-1})	Crystallization conditions (°C)							
	25/63*	53/63*	120/163.4	120/169	150/160	150/170+	150/173+	150/185
10			2	1	1	1	1	1
20	1	1						

The first temperature denotes the solution crystallization; the second denotes the solution annealing temperature; * denotes formic acid, + signifies benzyl alcohol and the remainder from butane-1,4-diol

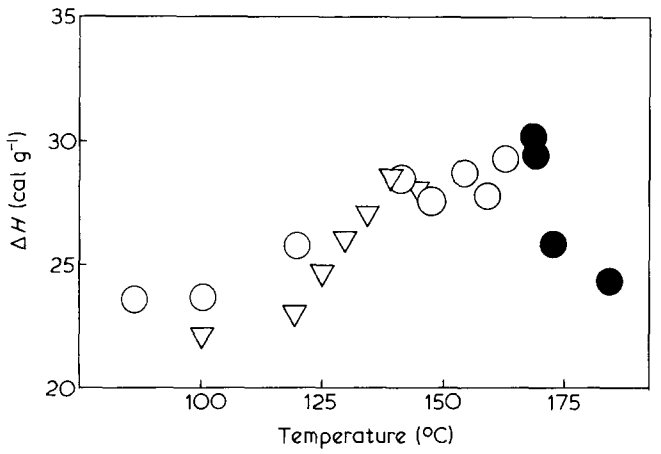

Figure 9 Heat of fusion values derived from integrated d.s.c. melting curves of nylon-6,6 mats as a function of crystallization (including solution annealing) temperature (open and filled circles, this work; filled circles refer to solvent annealing; inverted triangles from work by Hinrichsen[22])

In summary, the general trend which is now becoming consolidated is therefore a strong fold length–crystallization temperature dependence in the traditional sense (as observed for instance with polyethylene) at high crystallization temperature, and an invariance of fold length at low crystallization temperature, respectively. Further, as the two curves in *Figure 1* show, it is the supercooling and not the absolute temperature which is the relevant variable within this temperature range. Depending upon whether the chosen polymer is highly or poorly crystallizable, either regime (ii) or (i) will be prominent, as the only régime in evidence, which could give the mistaken impression that the fold length is necessarily variable with temperature, or alternately that it is completely constant over the full crystallization range. Theoretical developments[29,30] have been shaped by the former view with revisions and adaptations necessitated by the subsequent recognition of the existence of regime (i). It is by no means clear as yet whether adaptation of existing theories such as in ref 29 will suffice for a fully satisfactory description of crystallization over the full range, or whether quite new considerations[31] which nevertheless still rely on the basic framework of the kinetic theories will need to be invoked for region (i), or even if the entire framework of the kinetic theories should be abandoned[32]. The fact that points along the curve of *Figure 1* were obtained both by primary crystallization at T_c and by subsequent solvent annealing of crystals already formed, and further that the respective curves smoothly overlap is of particular significance in this latter respect, and will be commented upon in a separate chapter at the end of this discussion. First, however, some of the properties of the crystals as displayed as a function of l (i.e. when going along the curve of *Figure 1*) will be scrutinized.

A comment is required about the observed continuity of the l *versus* T_c curves. In each polymer, we would expect the crystal thickness to vary in discontinuous jumps which are integral multiples of the crystallographic repeat along the chain direction. In the case of polyethylene such repeat lengths are small, hence the discreteness of the fold length variations would not be detectable experimentally. However, this is not so with a polymer like nylon-6,6 where the repeat is 17.2 Å. Even allowing for the fact that increases by half repeats would suffice and for chain inclinations (see ref 7) the discreteness of the jumps should still be in evidence. There is no sign of this in the curve of *Figure 1*. This phenomenon is quite general amongst polymers with long repeat units and has been more exhaustively discussed in the case of polyesters where wider variations in l could be achieved[33]. Here it will only be stated that the present observations fall in line with this general trend.

Subsidiary maxima

It was stated in the Introduction that the number of subsidiary maxima between the 001 and 002 reflections provide a direct measure of the coherently diffracting stem length in the crystal layer. By having extended the range of crystal thicknesses beyond those achieved previously we may look for corresponding variations in the subsidiary maxima.

It is evident that the situation as regards what is to be expected in the thickness region corresponding between say 4 and 5 monomer units will be complex, and in particular will depend on how the continuous increase in thickness is to be visualized in molecular terms. Nevertheless the situation should greatly simplify for crystal thicknesses which are integral multiples of repeat units such as are necessarily comprised by the l *versus* T_c curves.

As seen from *Figure 3b* the stage of three subsidiary maxima has been reached, which by the rule[7]:

Number of subsidiary maxima =

Number of monomer repeats -2

should correspond to 5 repeats along the stems. The effect appears wherever l attains or exceeds the value of 67 Å. Remembering that the two maxima were found for $l = 54$ Å and that the thickness increment of 13 Å is close to one monomer repeat projected on the lamellar normal (which is along the 001 reciprocal vector), we see that the increase in crystal thickness is in accord with the increase in the number of subsidiary maxima. Conversely, this correspondence implies that the full increase in layer thickness is constituted by the lengthening of straight stems. We note further from *Figures 4* and *5* that the change from 2 to 3 subsidiary maxima takes place irrespective of solvent and irrespective of whether the crystal thickness in question was reached by primary crystallization or by subsequent annealing in contact with solvent.

As already pointed out, this is the first instance where the number of subsidiary maxima in a given polymer

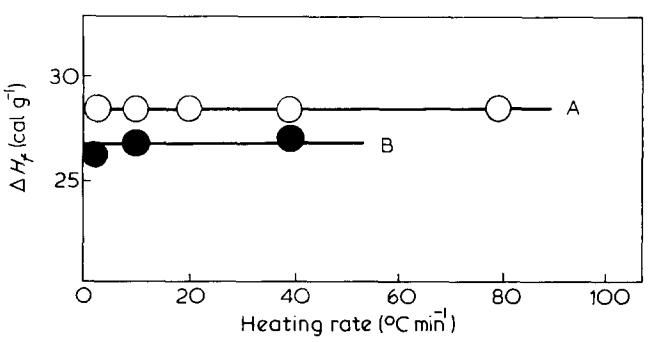

Figure 10 Heat of fusion, ΔH_m, (cal g^{-1} vs. heating rate (°C min^{-1}) for two different nylon-6,6 single crystals prepared at (A) 142°C, (B) 104°C from butane-1,4-diol solution using the self seeding technique

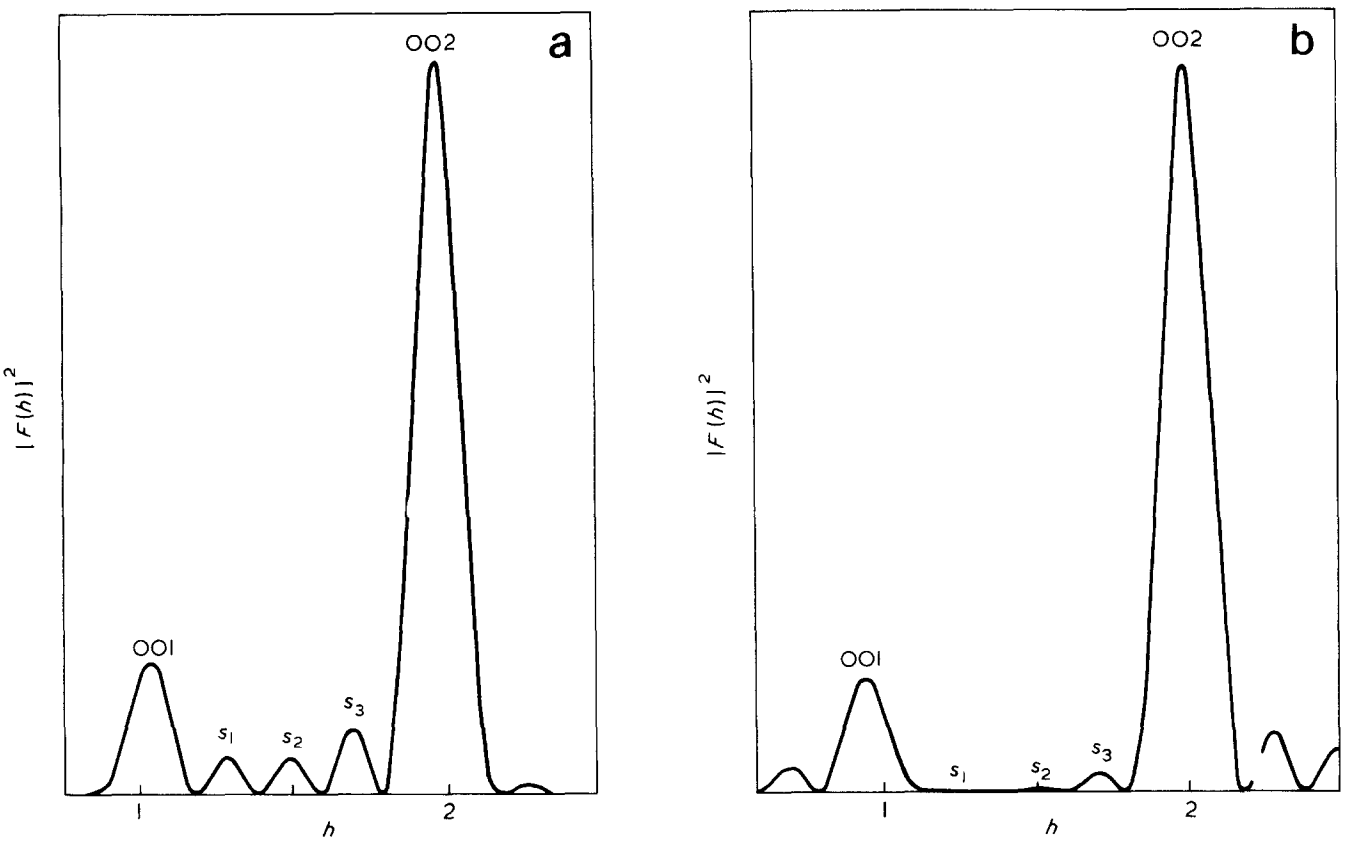

Figure 11 Calculated squared structure amplitudes as a function of the reciprocal lattice vector, h, for nylon-6,6 with five monomer repeats (i.e. three subsidiary maxima); (a) corresponds to acid folds, and (b) amine folds (courtesy of Atkins, Meader and Abdullah, unpublished)

could be altered by varying the crystallization conditions. We regard this as a satisfactory and significant result as it demonstrates beyond any doubt that the wide-angle diffraction effects in question are not the consequence of the crystal structure as such, but are associated with the size of the crystals. In the first place, this confirms that the reflections in question are subsidiary maxima, and secondly it demonstrates that they can be used to determine the size of the crystal core. In the upper plateau region (*Figure 1*) with l just below 80 Å, (irrespective of the origin of the plateau) a fouth subsidiary maximum would be expected. In *Figure 4* this is not observed. As we could not raise l higher, we cannot tell whether we were just at the threshold for it to appear or whether the structure of the lamella, i.e. the fold–core ratio, was changing. In any event, detection of a higher number of subsidiary maxima is expected to be increasingly difficult for two reasons. Firstly, because the intensity of the subsidiary reflections is to decrease in inverse proportion to the square of the number of repeat units, and secondly because the requirement for relative stem length uniformity is becoming increasingly stringent for these reflections to remain distinct. (i.e. fluctuations by the same fraction of the stem length will have a larger effect).

Finally, we revert to the question of what happens for l values that lie between the 2 and 3 subsidiary maxima case as well as beyond 3, an issue closely linked to the problem of how to visualize the continuous increase in l (*Figure 1*). Possibly a mixture between 4 and 5 repeat units (or even 5 and 6, in the latter case) could account for this. The observations imply that in such a mixed case the number of reflections correspond to the smaller number of repeat units, the additional reflection only appearing when the system becomes practically uniform, chiefly consisting of the larger repeating species.

The intermediate case in *Figure 3* is difficult to explain without invoking additional factors. The position of the subsidiary maxima is not expected to vary in any other way than what corresponds to either the two or three maxima case on its own. Previously, it was noted that such changes in angular position could occur through the intervention of an interference effect ascribed to the regularity in lamellar stacking*. In fact, split 001 reflections of the kind shown in *Figure 3* are known to arise from this cause. We therefore tentatively attribute the effects in *Figure 3* to interlamellar interferences.

Where three subsidiary maxima are present, we may attempt to utilize their relative intensities to obtain information about the fold in the same was as was for the two maxima cases in ref 7.

Figure 11 shows the intensities calculated in the way described in ref 7. *Figure 11a* represents the case where the stems all terminate, at both of their ends, with the amine portion of the monomer, which means in the case of a fold consisting of half a monomer that the fold portion must be an acid. *Figure 11b* represents the other extreme case of exclusive acid stem termination implying by the above argument that the fold itself consists of an amine portion. The two cases, *Figures 11a* and *11b* will be referred to below as acid and amine folds, respectively. (It is to be noted that the calculations strictly refer to the stem structure only; their use for identifying the fold itself was explained in ref 7 and will be commented on again further below). Visual comparison with the experimental trace in *Figure 6* immediately reveals that the acid fold is preferred by our system in accord with the previous conclusion

* It is to be recalled here that for straightforward interpretation of the subsidiary maximum effect the lamellar stacking regularity is being kept deliberately poor so that the interference function arising therefrom fades out in the angular range under consideration (see ref 7)

Table 3 Peak intensity ratios of the subsidiary maxima s_1, s_2, s_3 and 002 reflections. The first three rows are from the photodensitometer trace *Figure 6* for three different backgrounds. The fourth and fifth rows are as calculated for acid and amine folds (*Figures 11a* and *11b*), respectively

Background in Fig. 6	$\frac{s_3}{s_2}$	$\frac{s_3}{s_1}$	$\frac{s_2}{s_1}$	$\frac{002^*}{s_3}$	$\frac{002^*}{s_2}$	$\frac{002^*}{s_1}$
——	2.5	1.9	0.8	12	27	23
– – –	2.8	2.9	1.1	7.8	21	23
·····	1.4	2.1	1.5	12	11	16
Calculated† acid fold	1.5	1.2	0.8	9.5	14	11
Calculated† amine fold	3.9	27	7	30	118	820

* The 002 peak value as displayed in *Figure 6* was reduced by 0.8 for the calculation of these ratios to allow for the non-linear blackening characteristics of the photographic film at these higher intensities

† The calculated peak values as displayed in *Figure 11* were multiplied by the correction factor $1 + \cos^2 2\theta/\sin 2\theta$ for this tabulation so as to provide a fairer comparison with the observed values

reached for the two maxima case[7]. As this issue is of some consequence we shall give it further scrutiny.

The original finding that an acid fold is preferred to an amine one, or to random mixing of the two, was unexpected, partly because the acid portion is the shorter one, and partly because preference for an amine fold has been claimed previously on spectroscopic grounds[3,4]. Since the original publication of ref 7 the authors of that work have given further attention to the latitude permitted by different methods of background subtraction in photometer traces such as in *Figure 2* of ref 7. While preference for an acid fold was always retained, its strength was found to be greatly dependent on the choice of background (unpublished). In view of all this, new experimental evidence about the point in question, such as the presently achieved 3 maxima, becomes highly pertinent. In what follows we shall therefore subject the first visual impression to closer quantitative scrunity.

In *Figure 6* three backgrounds are drawn beneath the peaks s_1, s_2, s_3 and 002. We reckon that between them they at least bracket all the possibilities. [The method of connecting minima — solid line — was used in the corresponding trace of *Figure 2* in ref 7. The adherence to this method in the present case leads to the reversal in slope beneath the 002, which, however, will be of no consequence for our purposes (see *Table 3* and below)].

The peak height ratios for each of the three background subtractions, together with those arising from the calculations (*Figure 11*) are displayed in *Table 3*. We see that without exception by all criteria listed the acid fold is strongly, and in a number of instances overwhelmingly, favoured in agreement with the conclusions in ref 7 from the 2 maxima case.

A feature to which we have given more attention presently is the inclusion of the 002 amongst the various ratios. The ratios involving 002 provide possibly the strongest evidence in the acid vs. amine fold issue. Beyond this, the normalization of the subsidiary maxima with respect to the 002 peak is of even greater significance than the numbers in themselves convey. Namely, *all* crystalline nylon-6,6 contributes to the 002, however, not all crystals need to contribute to the peak value of the subsidiary maxima. Thus, if the stem lengths are not the same in all crystals, or are non-uniform in a given crystal, or if the crystals are stacked so that they produce their own interlamellar interference effects (see ref 7), the subsidiary maxima will be modified and different modifications will be superimposed which will always result in lowered peak values. In other words, any departure from the ideal situation will lower the s values but will not affect the 002. As we cannot create more intensity for the subsidiary maxima than that calculated, it follows that the calculated $002/s$ values will be lower limits for each fold case.

It will be apparent therefore from the $002/s$ ratios in *Table 3* that no conceivable modification could bring an amine fold in line with experiment. Conversely, the good agreement of the observed $002/s$ ratios with the expectations from an acid fold (they agree all within a factor of 2 and in several cases much more closely than that) tells us not only that acid fold is preferred, but also that a significant majority of the crystals contributes to the diffraction phenomenon which is being analysed.

This last point throws some new light on sample-to-sample variations as far as the distinctness of the subsidiary maxima in the diffraction patterns are concerned. As already stated they are only exceptionally as well-defined as in *Figure 6*; normally they are weaker, i.e. the $002/s$ ratios are larger, even if the ratios of the different subsidiary maxima themselves are hardly affected as far as this can be assessed within the more limited accuracy permitted by such weaker patterns [e.g. the s_3 peak will become less readily separable from the tail of the comparatively more intense 002 (see *Figure 2* of ref 7)]. Clearly in the light of the foregoing discussion, this means that in such samples not all the crystals contribute to the subsidiary maxima in a reinforcing manner. Or conversely, correspondence to the calculated $002/s$ ratio (for whichever fold type pertains) represents the most favourable situation for the study of the subsidiary maxima, and hence forms an objective criterion to aim for in the preparation of samples. This situation has also quite recently been attained for the 2 maxima case in the course of a different study in this laboratory (Spells, Sadler and Keller, to be published) reinforcing the present conclusion of a strong prefernce for an acid fold, in addition to what has been provided by the earlier works[7].

Finally a comment on the justification of identifying fold type from the mode of stem termination, the information directly provided by experiment. Strictly speaking for a given mode of stem termination the fold must contain an odd number of half monomers. Thus, for amine termination, the fold portion can only be acid, or

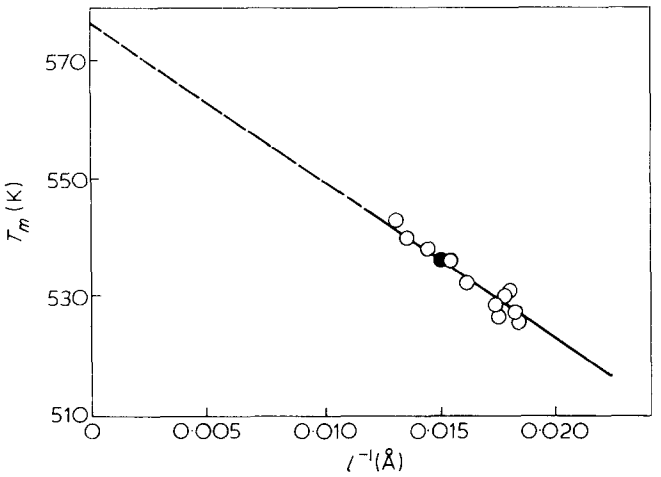

Figure 12 Plot of original crystal melting temperature T_m vs. reciprocal crystal thickness, l^{-1}, ($Å^{-1}$). Intercept corresponds to T_m^0, the thermodynamic melting temperature

acid–amine–acid, or acid–amine–acid–amine–acid, etc. In the case discussed in ref 7 the layer thickness (as measured by low-angle X-ray diffraction) exceeded the stem length (as assessed from the number of subsidiary maxima) by no more than 5 Å on each layer side which also includes the interlamellar gap, if present, in the appropriately sedimented mats. This does not permit the accommodation of a chain portion of 24 Å corresponding to 3 half monomers, the next up on the one half monomer unit, which by the above argument can constitute a fold: consequently the single half monomer unit pertains, in particular the acid-only fold. The situation just discussed pertains to the case where the difference between fold stem length, as derived from the number of subsidiary maxima, and the lamellar thickness, as assessed by low-angle X-ray diffraction in well-stacked layer mats (see ref 7) is 5 Å per layer surface or less. This is satisfied along the horizontal plateau (two subsidiary maxima) and along one specific point (where 3 subsidiary maxima first appear) along the upward curving part of *Figure 1*. In view of the fact that along the upward curving part the long period changes continuously over regions where the number of subsidiary maxima is constant, the difference between stem length and layer thickness can be larger than the ~5 Å quoted. (It can be much larger in dry annealed systems, part 2, to be published.) This would leave much more scope to accommodate the substantial amount of amorphous material required by the heat of fusion data (see below) and, more pertinently to the subject being discussed here, would allow for larger folds. However, in view of the fact that the relative intensities of the subsidiary maxima remain unchanged, the fold portion must still terminate mainly by acid portions, so as to join up with the amine terminated stems.

Thermal properties

The purpose of this section will be to obtain extrapolated values for the thermodynamic melting points and the heats of fusion of nylon-6,6 crystals. In all extrapolations involving l, only that portion of the curve in *Figure 1* can be used where l shows substantial variations. As the range of l values involved is small, the extrapolation will be necessarily of limited accuracy. In analogous work on isotactic polystyrene[35], significant variations in thermal properties were also found along the horizontal portion of the appropriate l *versus* T_c curves. Such effects, i.e. changes in T_m and ΔH_m in the constant l region, do occur but are much smaller in the present case of nylon-6,6. While taking note of the fact that the crystal perfection does change without corresponding changes in crystal thickness, we do not pursue this important issue further at this point. We merely note that we satisfied ourselves that in our case it has little influence on the extrapolation performed.

Melting points. Typical melting temperatures, T_m, and small-angle X-ray periodicities (corresponding to lamellar thickness, l) obtained for similar samples are plotted in *Figure 12*. Use is made of the familiar relationship:

$$T_m = T_m^0[1 - 2\sigma_e/\Delta H_m l] \quad (1)$$

where ΔH_m is the heat of fusion, σ_e the fold surface energy and T_m^0 the melting point of the infinitely-extended crystal. From this plot of observed T_m *versus* l^{-1}, a T_m^0 value 301°C is obtained. This thermodynamic melting point is much higher than previously reported literature values[1,3,11,15] but corresponds closely with the figure of 300°C in a most recent report[36], which appeared while the present publication was being prepared. A confirmatory high value for nylon-6,6 is also found from dry annealing experiments conducted by us on similar crystal mats (Part 2 to be published). Equation (1) allows an assignment of l values to the high melting peaks in two peak thermograms, such as in *Figure 8*, through the relation:

$$\Delta T_{m1}/\Delta T_{m2} \sim l_2/l_1 \quad (2)$$

where $\Delta T = T_m^0 - T$ and the subscripts 1 and 2 refer to the virgin and stabilized crystals, respectively. For a crystal of initial thickness of 54 Å, this procedure yields a thickness of 108 Å based upon an experimentally observable T_{m2} value. The result is consistent with the previously reported[22,10] doubling of layer thickness on dry annealing of nylon-6,6 crystals and also with the present annealing experiments in paraffin, which is a non-solvent for nylon-6,6 (the increase from 54 to 105 Å reported in the Experimental section). Much larger spacings have been found recently for bulk material[24] but no melting points were recorded.

Heat of fusion. Having established that the heating rate-dependent crystal transformation does not influence the heat of fusion values (*Figure 10*) we can proceed with some confidence to obtain ΔH_0, the heat of fusion of the infinite crystal. Plots of ΔH_m *vs.* l^{-1} yield $\Delta H_0 = 61$ cal g^{-1} in essential agreement with Hinrichsen[11] (*Figure 13*).

In possession of this value, we can now apply equation (1) to *Figure 12* to obtain σ_e. We obtain 69 erg cm^{-2} for the fold surface energy, a value much higher than that reported by Hinrichsen but in accord with values calculated by us from most recent literature data[36].

Degree of crystallinity

In possession of ΔH_0, the degree of crystallinity can be assessed. Irrespective of whether one uses the measured ΔH_m values as such or one corrects the values for fold energy first (the method adopted by Hinrichsen which essentially redefines the meaning of crystallinity in the presence of chain folds), the crystallinity of single crystals falls in the range of 50 to 65%. This is lower than inferred

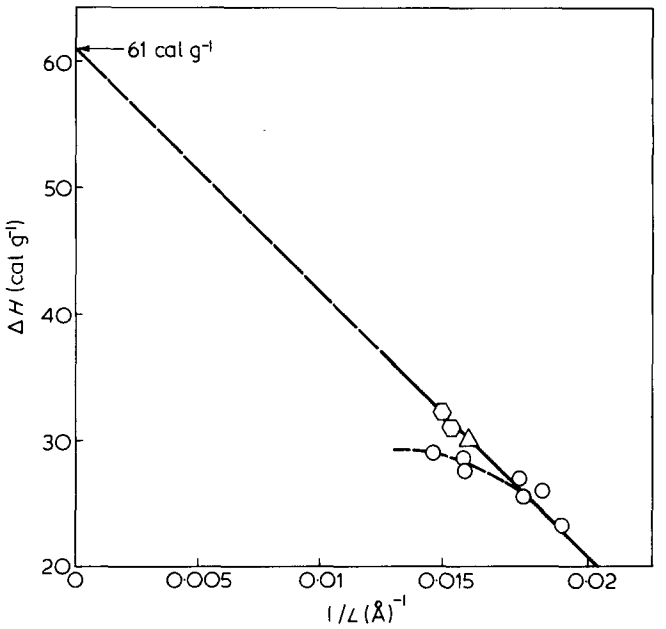

Figure 13 Heat of fusion, ΔH_m (cal g^{-1}), vs. reciprocal crystal thickness l^{-1} ($Å^{-1}$). Hexagons crystallized from formic acid; triangles from benzyl alcohol; circles from butane-1,4-diol. The fall-off in enthalpy for butane-1,4-diol crystallizations/annealings at the larger *l*s (i.e. higher crystallization temperatures) are tentatively attributed to degradation

in refs 7 and 8 and makes the problem raised there even more acute.

Thanks to the existence of subsidiary maxima we have now a uniquely decisive and simple measure for the thickness of the crystal core. As stated above this allows us to make an estimate of the thickness of the fold surface layer which in the present case, depending on the position along the l vs. T_c curve in *Figure 1*, can be rather small. For example, along the constant lower plateau in *Figure 1*, somewhat dependent on how much space one allows for interlamellar contact, it amounts to about 5 Å per fold surface. The degree of amorphicity this would allow, if attributed to the fold surface alone, would be within 20%.

The question arises: where is the rest of the crystallinity deficiency? Because of subsidiary maxima the crystal interior is now better known than in any other polymer. This question is particularly pertinent, especially as this is now raised in possession of crystallinity values arrived at from our own assessment of the heat of fusion. Beyond raising the question, we have no answer at this point. Nevertheless, attention is drawn to a possible solution based on a few folds terminating in the crystal interior, an inference arising from the conspicuous weakness of the second order low-angle X-ray reflection as observed and evaluated in ref 7, to which we have to refer for details.

Possible implications of solvent annealing results

The upswing in the butane-1,4-diol curve in *Figure 1* is constructed from measurement points obtained on crystals as directly grown at T_c and on crystals, which formed at a lower T_c, and were heat-treated in the presence of solvent subsequently. While higher l values were obtained along the latter route (the purpose of this mode of preparation) the curves join up smoothly and overlap. Neither was there any difference in discontinuity between the two kinds of crystal in any other respect (subsidiary maxima, thermal properties). We feel this is a noteworthy observation and even in its present limited state raises some pertinent questions.

In past reports, primary crystallization and subsequent crystal thickening have been considered as two distinct processes. Primary crystallization, and the fold length that this gives rise to, is universally believed to be controlled by the supercooling. Accordingly, a given l value will arise at a lower temperature of crystallization from a solvent than from the melt, and in the case of the former at lower temperature for the better solvent. In contrast, thickening subsequent to primary crystallization is generally held to be controlled more by the absolute temperature. Nor is there a unique value for the latter case. Irrespective of whether the thickening occurs continuously or in jumps, the l value obtained is time dependent: higher values are obtained for longer times of residence at the annealing temperature‡. The present observations of smooth continuity between as formed and thickened crystal is therefore suprising on two counts. First, because it implies that crystal thickening is also supercooling-dependent which in turn implies that the thickening crystal 'senses' its environment. Accordingly, at a given temperature, crystals will thicken more in the presence of a solvent and more readily the better the solvent if dissolution does not occur. Second, it implies that there is a limiting degree of thickening which places all the l values firmly along the same curve, or otherwise there could be no unique relation between l and T_c (or T_a).

In all the above respects we have to bear in mind certain reservations. Thus nearly all past studies on crystal thickening (annealing) are referred to the dried state and information about thickening in solution is scarce so that theories or models for describing such behaviour hardly exist. (Such as there are refer to polyethylene in much higher dilutions than in the present case and suggests complete dissolution and subsequent recrystallization[38,39].) Further, the l range in nylon-6,6 is undoubtedly narrow as compared with some other crystal thickening experiments. Finally, nylon may well be special in some respects owing to the hydrogen bonding, and in particular owing to the ability of the nylon lattice to incorporate or interact with solvents.

In spite of the above reservations the new results raise some intriguing if not disturbing thoughts. If a given l value along the l vs. T_c curve can be realized in two ways, namely by direct crystallization and by reorganization (possible refolding) of crystals already present, how can we be sure that any l vs. T_c curve results through primary crystallization and not through thickening from some lowest basic l value? The implications of this possibility could be profound, as our entire thinking in the area of chain folding is governed by the idea of there being a unique l vs. T_c relationship in existence. The idea just proposed, i.e. that there is one basic fold length only, and that all other values correspond to crystal thickening may gain support from the following well-established facts. First we know that there exists a constant lowest limiting l value as found in the present work (region i) in curves such as *Figure 1*). Except for a most recent departure[31], this has not been a central issue in the shaping of our thinking in this field. Secondly, we know that there does

‡ The time dependence itself is sensitive to a number of factors. Thus generally it occurs faster at higher heating rates, on upper layers of multilayer crystals, when in contact with an inert liquid[37] (e.g. Woods metal) as opposed to a solid surface, etc.

exist a phenomenon termed isothermal thickening[40]. In the past, this was observed to occur concurrently with primary crystallization increasing the fold length values in the course of time even during isothermal crystal growth. However, such observations have been confined to the melt and are believed to be associated with the higher absolute temperatures (for the same undercooling) pertaining to such crystallization. Even if such fold length modifying effects due to isothermal thickening, which as recently emerged, can become quite striking[41], the familiar underlying l vs. T_c relation has never been questioned even for melt crystallization processes, while the possible presence of such isothermal thickening in solution crystallization has never been suspected. When making these latter statements we have to refer to one exception. Quite recently, Rault[42] has in fact stated that the invariant l value for low T_cs is the only primary product of crystallization, all other l values being the result of subsequent thickening. While we do not subscribe to Rault's theory in many other respects, at least not at present, we see that the possibility suggested by our results is in accord with the model, which serves as his starting point.

Having enumerated these possibilities we do not imply that the evidence as it now stands can justify such far reaching generalization at present: it is on a too specialized a system and it encompasses only a limited range of l values in addition to the other reservations already quoted. Nevertheless, the effects are genuine and are at the juncture of many other puzzling unexplained features; its implications will have to be faced with an open mind.

ACKNOWLEDGEMENT

J.H.M. thanks the Science Research Council for support during the tenure of a Senior Research Fellowship in 1975–76. We wish to thank Dr E. D. T. Atkins, M. I. Abdullah and D. Meader for calculations underlying *Figure 11* and Dr Atkins in particular for constructive discussions.

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