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The problem of thermal expansion in polyethylene spherulites

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It is shown from simple considerations of the arrangement of crystal axes and from the known thermal expansion coefficients along these axes that a polyethylene spherulite would, on cooling from its crystallization temperature to room temperature, form radial voids (amounting to up to 4% of the volume) unless some reversible internal transformation prevents this. To clarify this 'composite' problem a co-ordinated investigation was carried out on changes in the macroscopic sample volume, in the lengths of the crystallographic axes and in the diameters of the individual spherulites with temperature. The results show that the changes in spherulite dimensions conform to those of the sample as a whole thus eliminating the necessity of void formation (which nevertheless appears to arise in thin film spherulites) leaving an inconsistency with the crystallographic data. It was noticed further that the thermally induced reversible changes in the spacing of the extinction bands did not conform to the changes in the spherulite diameter and in addition depended on the radius of the band. It is suggested that the reversible transformation needed to prevent voiding and to eliminate the above inconsistencies is also responsible for the changes in band spacing (possibly in the form of twisting and untwisting of the structure underlying the banding) and represents a novel, as yet unexplored, feature of spherulites.

1. Introduction

Our knowledge of polymer spherulites can be summed up as follows: [1] they are spherically symmetrical aggregates arising from fibrous growth of crystals emanating from a central sheaf. On the optical level, the spherical symmetry (except for the central region of the sheaf nucleus) is revealed by the Maltese-extinction-cross between crossed polaroids. In addition we can often see a system of concentric extinction rings which are known to arise from a periodic rotation of the optical index ellipsoid along a given radius, these variations being in phase around a given circumference. The underlying morphology corresponds to a periodic twisting of crystal lamellae, the schematic representation of Fig. 1 having been drawn accordingly. The details of the mode of twisting and stacking of the lamellae, however, are unknown, and the principles of space filling are not even qualitatively understood. The origin of the twisting itself has so

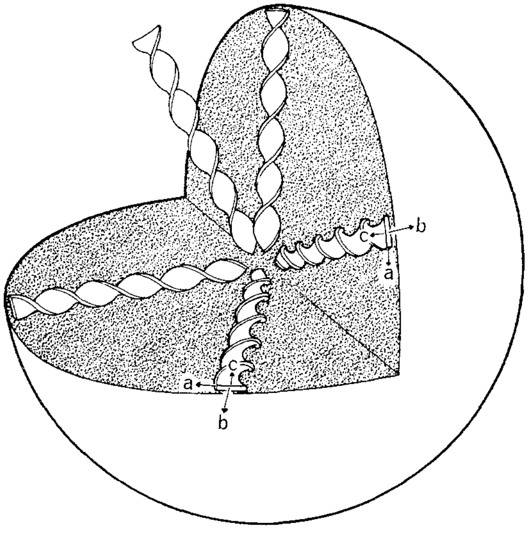

Figure 1 Schematic drawing of a polyethylene spherulite showing the orientation of the crystallographic axes.

far defied all explanation. It needs to be added that none of these phenomena are confined to polymers, hence any future explanations would have to be sufficiently general so as not to rely solely on some specific property of long chain molecules.

In the work to be reported here we have made some observations which may perhaps open up a new approach to these long standing unsolved problems. In any event they should be of some interest in their own right for the study of thermal behaviour of polymers, polyethylene in particular. In the case of polyethylene the arrangement of the crystallographic axes in the spherulites is known, and is indicated in Fig. 1. Thus the *b* axis is radial, while *a* and *c* are tangential and are rotating around the radius *b* [2]. (On the lamellar level, *b* lies in the plane of the lamella, while *c* is either exactly perpendicular, or at a specific large angle to it, depending on the details of the chain obliquity in the corresponding lamellar crystals; correspondingly *a* will be exactly or approximately parallel [3].

Our particular concern here will be the thermal expansion of the polyethylene spherulite, which has arisen from our studies of spherulitic growth and fine structure. In the course of this, we attempted to anticipate what would happen as a spherulite was cooled from its formation temperature to room temperature from the known expansion coefficients of the crystallographic axes. It became apparent that the compounding of the individual crystal expansion coefficients to obtain that of the composite object led to certain significant and unexpected consequences. The thermal expansion coefficient along the *a* axis is known to be greater than that along the *b* axis, while that along *c* is negligible (in fact slightly negative) [4–6]. Calculation shows that the net radial expansion coefficient of a polyethylene spherulite is less than the net circumferential coefficient in the temperature range 20 to 130°C (see the appendix for a detailed calculation based on the values given by Swan [4]). This means that a spherulite formed at the 130°C should, on cooling to room temperature, be expected to contract by a greater amount around its circumference than along its radius. It would therefore be expected to crack (or form voids) along radial lines.

In all volume measurements in the past, such as for example those carried out for determination of crystallinity, it has been implicitly assumed that polyethylene spherulites behave as isotropic spheroids with respect to thermal expansion. If they were to behave anisotropically, and form voids which open up on cooling and close on heating, then such measurements would be of doubtful value unless due correction for this effect were made. It is therefore apparent that the issue, whether or not polyethylene spherulites behave isotropically with respect to thermal expansion, is of notable importance. One might think of reasons why and how spherulites could expand and contract as isotropic bodies, in spite of the anisotropic behaviour of their constituent crystals. Thus there might be some internal disorientation which could compensate for differences between the radial and circumferential thermal strains of the crystals, however, even with an average disorientation of lamellae of 15°, a volume of voids $\sim 2\%$ is still predicted to form on cooling a spherulite to room temperature, as shown in the appendix. Of course the spherulites are not fully crystalline, nevertheless, the possibility that the amorphous component, by having a large thermal expansion coefficient, could produce the additional radial strain required for overall isotropy does not stand up to closer analysis. On quite general grounds, the amorphous content varies according to the type of polyethylene and the crystallization conditions, which in itself seems to exclude the possibility that it would always exactly balance the anisotropic changes in the crystallites. Further it will be apparent that in order for the expansion and contraction of the amorphous component to act predominantly in a radial direction it would have to lie between crystallites (i.e. coupled in series) along the radius. However, according to existing knowledge the opposite is true: by forming the lamellar interfaces, it is in a series arrangement around the circumferential direction and in addition is molecularly coupled to the crystal layers. It is apparent without further consideration, that this arrangement cannot provide the effect in question.

Thus we have to face up to the following situation. When spherulitic polyethylene is cooled from the crystallization temperature to, say, room temperature, which much happen at least once in the lifetime of every melt-fabricated object, voids amounting to up to 4% of the volume must appear unless some internal transformation ensures uniformity of the thermal volume change through-out the spherulites. The important consequences on all previous specific volume studies (not to speak of the consequences for mechanical, permeability, etc. properties) have been referred to above. On the other hand, the nature of the internal transformation required to prevent this situation is not apparent from *a priori* considerations. The examination of this issue is the subject of the present paper. In order to resolve the problem a co-ordinated study of the thermal expansion of individual spherulites, of bulk material and of the individual crystallographic axes is clearly called for and has been undertaken here.

There are no reports in the literature of such co-ordinated studies specifically intended to investigate the thermal expansion of spherulites. Buckley and McCrum [7] have investigated the thermal expansion of single crystal texture specimens of polyethylene in the temperature range 0 to −190° C. The model they propose is based on the generally accepted picture that the spherulites consist of twisting stacks of lamellae with amorphous interlayers between the lamellae, the layer planes being parallel to the spherulite radius which also coincides with the *b* crystallographic direction. They then consider the crystal and amorphous regions coupled in parallel along the *b* direction.

Using this model, they deduced that, due to the twisting of the lamellae, the radial and circum ferential expansion coefficients were approximately equal in this temperature range. However, the work of Buckley and McCrum was carried out at comparatively low temperatures (below 0° C) where the difference between the expansion coefficients of the crystallographic *b* axis and that of the isotropically averaged crystal is very small. Consequently the local anistropy of the crystal does not create such a special issue as at higher temperatures (above ~50° C) where the expansion coefficients diverge. It is the expansion coefficients at the high temperatures which really matter when the sample is cooled following crystallization.

It deserves recalling that very high-dose electron irradiation, such as takes place in the electron microscope, leads to an analogous situation to that of thermal expansion. Thus when polyethylene crystals are subjected to electron irradiation, expansion occurs perpendicular while contraction occurs along the chain direction [8] which leads to the conclusion that in a spherulite which is subjected to irradiation the radius should expand while the circumference should contract. Indeed it was observed [9] that in thin spherulitic films the irradiated, initially flat, spherulites transformed into cones, in qualitative and quantitative agreement with expectation from their constituent crystallites. However, it is obvious that such a mechanism of cone formation, to compensate for differential strains in the radial and circumferential directions, could not occur in bulk spherulites.

2. Experimental

The co-ordinated study of spherulitic expansion indicated in the Introduction was carried out over the temperature range 20 to 130° C. It involved accurate X-ray spacing determinations, dilatometry and optical polarizing microscopy. The first served to determine the *a, b* and *c*-axis expansion coefficients, the second the bulk volume changes, and the third the changes in individual spherulite dimensions; all three determinations being carried out on the same, or equivalent, specimens. In addition some optical microscopic observations of solution cast and subsequently melt-crystallized thin-film specimens were carried out.

2.1. Preparation of specimens

The polymer used to make the bulk specimens was Shell–Carlona 60050 HDPE, which was chosen because it gives unusually large (~ 150 μm) spherulites when slowly (~ 15° C min^{-1}) cooled from the melt. The bulk specimens were all taken from the same sheet, which had been prepared by melting the polymer in a press and allowing it to cool at ~ 15° C min^{-1}, in the press, to about 90° C when it was quenched in cold water. The specimen for X-ray diffractometry was cut out of the sheet which had good flat, surfaces, and mounted in an appropriate sample holder. A series of specimens for optical microscopy were cut using a microtome set to give sections 10 to 20 μm thick, and successive sections were mounted in silicon oil between slide and cover slip (to avoid the constraints imposed on it by the rigid mounting). Thin film spherulitic specimens of the same polymer were made by dropping a small amount of a dilute solution of the polymer in xylene on to a glass microscope slide at a temperature of 150° C. The xylene was allowed to evaporate and the slide transferred to a hotplate at 80° C. The polymer then crystallized on cooling to produce a thin spherulitic film.

In addition a bulk specimen of Rigidex 50 was prepared for optical microscopy to check that the observed behaviour was not unique to the particular polyethylene used. As the results obtained with this polymer correlated with the findings on the Shell–Carlona they will not be itemized, beyond stating that they reassured us that observations on the unusually large Shell–Carlona spherulites were characteristic of polyethylene.

2.2. X-ray measurements

Measurements of the positions of the 110, 200, 210, 020, 220, 011, 310, 111, 201 and 211 reflections were made at a variety of temperatures using a Philips X-ray diffractometer. The lattice parameters were calculated at each temperature using a least squares procedure which minimized the sum of the squares of the differences between the observed and calculated lattice spacings corresponding to the different reflections. Some difficulty was experienced with the 011 and 310 reflections which tended to merge as the temperature rose and these were omitted from calculations above 70° C.

The results of these measurements are tabulated in Table I and plotted on Fig. 2 as relative lattice parameters against temperature.

TABLE I Temperature dependence of unit cell dimensions

Temperature (° C)	a (Å)	b (Å)	c (Å)	V (cm^3 g^{-1})	Standard errors × 10^3		
					x_a	x_b	x_c
24	7.427	4.961	2.544	1.0061	4	3	2
52	7.488	4.964	2.544	1.0150	4	2	2
66	7.517	4.966	2.545	1.0197	5	3	2
75	7.550	4.967	2.545	1.0244	5	3	2
84	7.568	4.971	2.542	1.0265	5	4	3
110	7.652	4.977	2.540	1.0296	5	4	4
128	7.699	4.982	2.538	1.0383	6	4	3

2.3. Dilatometry

Dilatometry was carried out following the method of Bekhedal [10]. The samples were strips cut from the specimen sheet and tightly packed into the dilatometer bulb. Readings were taken both as the temperature was increased and decreased. The density of the polymer was measured at 20° C, using a specific gravity bottle, the density being taken as the mean of five independent measurements. The results of all these measurements are combined in Fig. 3 where the specific volume of the bulk sample is plotted against temperature.

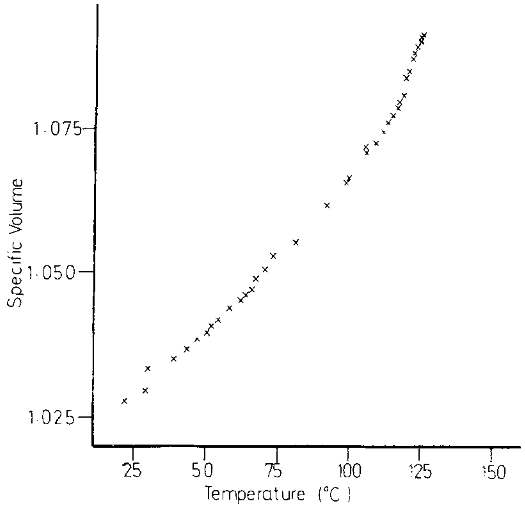

Figure 3 Graph showing variation of bulk specific volume (as measured by dilatometry) with temperature.

2.4. Optical microscopy

Sections, cut and mounted as previously described were examined in the optical microscope. The section which contained the central portion of a

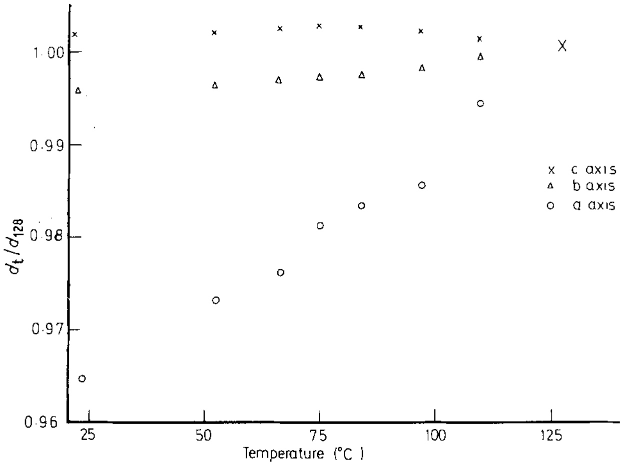

Figure 2 Graph showing the variation of lattice parameters (normalized to unity at 128° C) with temperature. The actual values of the lattice parameters are given in Table I.

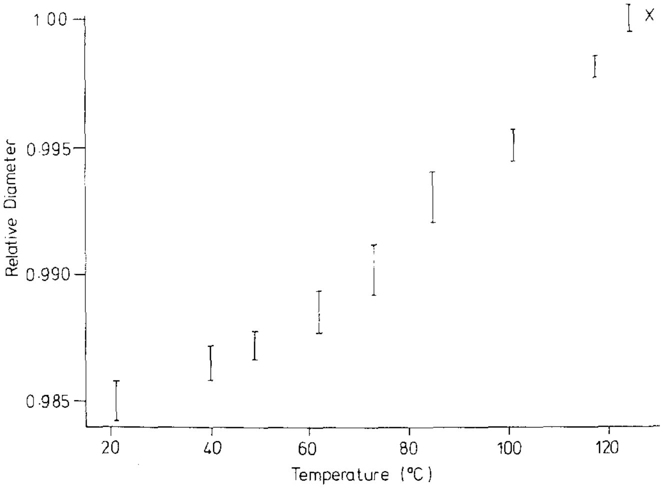

Figure 4 Graph showing variation of spherulite diameter (normalized to be unity at 128° C) with temperature. The error bars correspond to the standard error in a number of measurements as described in the text.

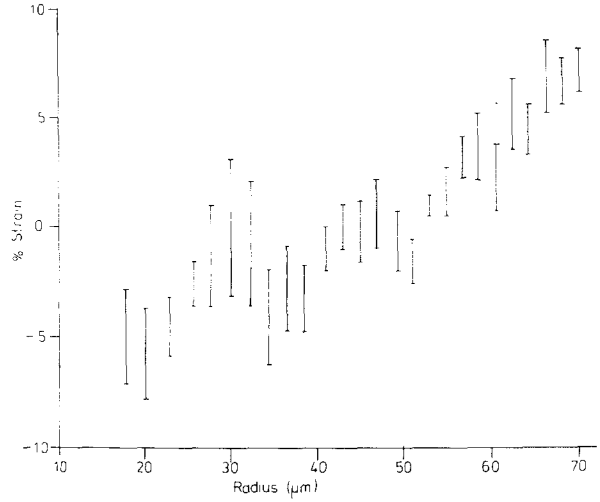

Figure 5 Graph showing the variation strain in band spacing d on cooling, defined as $(d_{120} - d_{20})/d_{120}$ along a spherulite radius (a negative strain means the band spacing has become greater on cooling).

particular spherulite was found by measuring the diameter and band spacing of that spherulite in successive sections and choosing the one in which the diameter was greatest and the band spacing smallest. The central section could thus be located within an accuracy of ± 10 μm i.e. within ± 8% of an average spherulite diameter. Several such central sections of spherulites were found and the behaviour of each was observed as the temperature was varied. Measurements of the spherulite diameter were made from photographic plates. The spherulite "diameters" were measured between easily recognisable points at the edges of the spherulites (the line between such points passing through or near to the centre of the spherulite) using a travelling microscope. Some difficulty was experienced in determining the precise position of the spherulite boundary and a subjective judgement had to be made in some cases, nonetheless an accuracy of measurement to within ~0.5 mm on the plate (~1%) was obtained in each individual measurement (repeated at least five times in order to reduce the statistical error). The data were then normalized against the corresponding measurements made at 128°C so that all the different measurements could be combined. When this was done the standard error was < 0.1% (a total of 82 measurements of different "diameters" were taken from 10 different spherulites at each temperature). The results of these measurements are plotted on Fig. 4. The positions of the bands were also noted and it could be seen that towards the outside of the spherulites the band spacing decreased ion cooling by a much greater amount than the spherulite radius. However, some difficulties with focussing meant that these results were not definitive so the experiments were repeated using spherulites grown from the melt

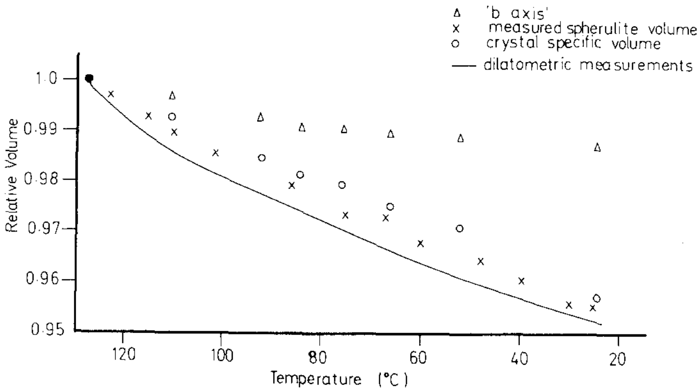

Figure 6 Comparison of data in Figs. 2 and 3 and in the form of the volume of a sphere of material as a function of temperature on cooling.

between cover glass and microscopic slide. The spherulites in these films (which were about $5\,\mu$m thick) showed the same radial expansion behaviour as those from the bulk sections and confirmed that towards the outside of the spherulites the band spacings decreased on cooling. However, we could also see that towards the centre of the spherulites the band spacings increased, by a similar large amount, on cooling. A typical set of results for one spherulite is shown in Fig. 5.

3. Interpretation of results

3.1. Bulk expansion

The dilatometric measurements show how the specific volume of the bulk specimen varies with temperature. The specific volume measured in this way is that of the combined amorphous and crystalline parts of the specimen. The X-ray measurements record the variations of the crystalline specific volume, and also individual lattice parameters with temperature. The question to be answered is "how do individual spherulites behave?" The simplest alternatives are as follows. They have the same expansion coefficient as the macroscopic sample; their radius changes with temperature as the crystallographic *b* axis; or they follow the behaviour of the crystalline specific volumes. In order to distinguish between these possibilities all the measurements must be presented in the same form. The representation chosen here is the volume of a "sphere" of material as a function of temperature; the volume at 128°C being defined to be unity. Thus for the dilatometric results all measurements of specific volume must be divided by the specific volume at 128°C; for the crystalline specific volume the required quantity is the product of the three lattice parameters at the particular temperature divided by their product at 128°C (i.e. $a_t b_t c_t / a_{128} b_{128} c_{128}$), for the *b*-axis expansion the quantity is b_t^3/b_{128}^3, and the actual measured spherulite radius is r_t^3/r_{128}^3. These quantities are all plotted together on Fig. 6. (It should be stressed that the "relative-volume" axis on Fig. 6 does not in any way represent an actual specific volume, it merely compares variations in volume with temperature). It is clear from Fig. 6 that the spherulites do not behave as would be expected from the thermal expansion coefficients of the lattice parameters in the arrangement appropriate to the texture of the spherulite (i.e. their volume does not vary, as would follow from variations in the *b*-axis). Instead their behaviour appears to fall somewhere between that of the crystalline specific volume and that of the whole material. This shows firstly that the thermal volume change of spherulites closely simulates that of the isotropic average of crystals, and secondly that these volume changes are somewhat smaller than those displayed by the whole sample. The latter implies that the spherulites contain less amorphous material than the sample as a whole, which could be due to some accumulation of amorphous material around the spherulite boundaries.

3.2. Expansion of thin-film spherulites

The thermal expansion of "thin-film" spherulites corresponds quite closely to the crystallographic *b*-axis expansion measurements, as can be seen from Fig. 7 on which both are plotted, along with the expansion which would be expected from an isotropic crystal (in this case the radius of a disc of material, defined to be unity at 128°C, is plotted against temperature). No information is available about changes in band spacing in these specimens since in these very thin "spherulites" the banding does not show up in the optical

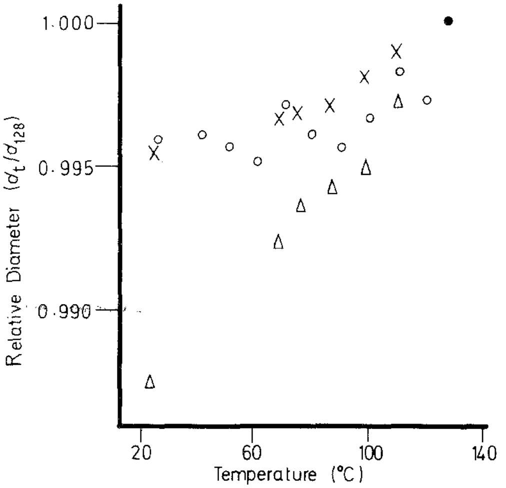

Figure 7 Graph of relative diameter as a function of temperature for thin film spherulites; ○ measured values, △ values expected for isotropic behaviour, X values for *b*-axis orientation.

microscope. The conclusion to be drawn from Fig. 7 is that these specially prepared thin "spherulites" have an anisotropic thermal expansion behaviour i.e. they would be expected to form radial cracks on cooling.

Indeed such cracking can be seen in many published electron micrographs of thin film spherulites (e.g. see [11]). While this cannot be directly attributed to differential thermal contraction, since it may have been introduced either through the effects of electron irradiation described in the Introduction or by mechanical damage during preparation, we believe that such cracking does occur. It is noteworthy that this cracking produces fibrils bridging the gaps (e.g. Fig. 13 of [11]) such have been observed in different contexts relating to interlamellar links [12].

4. Discussion and conclusions

The principal issues of this paper are, in their appropriate sequence, as follows: First, the recognition of the problem that the thermal expansion of polyethylene spherulites, if calculated by a simple summation of their constituents, would, (a) not correspond to that of a macroscopic sample and, (b) would necessitate a disruption of their internal continuity. Second, the establishment of the fact that the measured spherulitic expansion *does* agree very closely with of the macroscopic sample, and with that of the isotropic average of its constituent parts. This, while eliminating the serious problems which would be otherwise created by (a) and (b), itself creates a new problem, namely to visualize a continuous and *reversible* structural transformation within the spherulites as they are heated and cooled. There are no indications as to what this transformation might be from our existing knowledge of spherulites. The third issue of this paper is the detection of the peculiar behaviour of band spacings as the temperature is altered; these reversible changes definitely indicate some reversible, internal, structural change of the spherulites. While we can offer no quantitative explanation of this effect at present, we can suggest two possible forms of transformation which would affect band spacings. The first is that the individual helicoidal units wind up further, or unwind, by varying degrees in the different parts of the spherulite, and the second that there is no additional winding but that separation of bands occurs which is caused by the differences between the circumferential expansions of dark and bright regions which would correspond to different expansions along the *a* and *c* axes, and the consequent stresses and strains which might be expected to occur.

To sum up we have shown that polyethylene spherulites behave as isotropic spheroids with respect to thermal expansion and have shown that some internal reversible structural change is required to account for this behaviour. We have also found indications of a reversible structural change in the band spacing behaviour. We have been unable as yet to find any suitable mechanism which provides for both the equalization of circumferential and radial thermal strains, and for the band spacing behaviour; however, it would be most surprising if the two effects were not linked.

Further study of these effects in this and other spherulitic systems (not necessarily polymeric) may then lead to the discovery of such a mechanism which could be expected to throw new light on some aspects of the spherulitic morphology. In this context it should be noted that since the arrival at the present descriptive knowledge of spherulites, dating from the turn of the century [13], and the recognition of its applicability to polymers in the 1950's, there has been virtually no advance in our understanding of why crystals twist within spherulites, of how that twisting is to be envisaged, or how space-filling may be achieved. We hope that further studies of the thermal behaviour of spherulites may answer some of these questions.

Appendix

Calculations of the expected behaviour of spherulites on cooling from the crystallization temperature

(1) For a spherulite with the b axis radial the linear thermal strain on cooling from 130 to 30° C along the radius will be $(b_{30} - b_{130})/b_{130}$, and the volume strain will be $(b_{30}^3 - b_{130}^3)/b_{130}^3$. The volume strain for "isotropic polycrystal" will be

$$\frac{a_{30}b_{30}c_{30} - a_{130}b_{130}c_{130}}{a_{130}b_{130}c_{130}} = \frac{V_{30} - V_{130}}{V_{130}}$$

where V is the specific volume. So the volume difference between a b-axis oriented spherulite and an isotropic sphere of the same radius would be

$$\frac{b_{30}^3}{b_{130}^3} - \frac{V_{30}}{V_{130}} \text{ per unit volume.}$$

Swan (1964) gives $b_{30} = 4.936$ Å; $b_{130} = 4.942$ Å; $V_{30} = 1.002\,\text{cm}^3\,\text{g}^{-1}$ and $V_{130} = 1.041\,\text{cm}^3\,\text{g}^{-1}$ giving a volume difference of 3.4%. That is a b-axis oriented spherulite will have a volume 3.4% greater than a sphere of an "isotropic crystal", i.e. voids should be formed on cooling such a b-axis oriented spherulite, the volume of such voids being 3.4% of the volume of the spherulite.

(2) For a spherulite with the b-axis only approximately radial we define an average disorientation of the b-axis, θ, the angle between b and the spherulite radius. Then normalizing the radius to unity at 130° C we get

$$\left(\frac{R_{30}}{R_{130}}\right)^2 = \frac{b_{30}^2 \cos^2\theta + a_{30}c_{30}\sin^2\theta}{b_{130}^2 \cos^2\theta + a_{130}c_{130}\sin^2\theta}$$

and the difference in volume is given by

$$\frac{R_{30}^3}{R_{130}^3} - \frac{V_{30}}{V_{130}}.$$

So for $\theta = 15°$ and using the values for a, b and c given by Swan (1962) we get $V = 2.25\%$, i.e. in this case the volume of radius is reduced to 2.25%.

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