Direct observations of differential lamellar deformation on drawing isolated polyethylene spherulites

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The deformation of isolated linear polyethylene spherulites, to at least 7 times extension, has been observed with lamellar resolution in a dilute blend with branched polyethylene as matrix. Drawing occurs in two temperature ranges. In the low temperature range, from 25 to 100 °C, spherulites deform as a whole within a solid matrix with longitudinal dimensions increasing by the draw ratio. From 120 °C to 130 °C, when the matrix is fully molten, the principal effect is to detach lamellar fragments along the line of greatest extensional stress while leaving the majority of the spherulite little affected. In the low temperature range, deformation differs according to the inclination of lamellae to the tensile axis. Under tension or shear, lamellae rotate, disrupt and/or fragment; under compression they buckle then kink co-operatively where the stress is highest. After deformation, spherulites tend to have become cylindrical within well demarcated lateral boundaries parallel to the draw direction. It is suggested that this reflects differences in the extensibility of the molecular networks on either side of the boundary.

1. Introduction

The importance of basing interpretations of texture in deformed crystalline polymers on microscopic observation, albeit complemented by diffraction data, was well understood by Andrew Keller and was a continuing theme of his research. Interpretation in terms of lamellae [1] became possible following his identification of chainfolding, although for long their observation was neither easy nor controlled. Even with the advent of chlorosulphonation and permanganic etching, techniques which introduced systematic electron microscopic study to crystalline polymers, the inherent textural complications of deformed systems made unambiguous interpretation difficult. In practice, idealized morphological models of long-standing have continued in use [2] for the interpretation of ever more refined diffraction data [3] notwithstanding their more or less tenuous links to real-space information. At the same time knowledge of actual textures, before and after deformation, has developed to the extent that the inadequacies of older models, not least in their neglect of lateral organization, have been identified [4–6]. A proper understanding of the subject requires the combination of the new inputs from both real and reciprocal space.

The problems encountered in microscopic studies include the difficulty of identifying local crystallography, which is needed for the phase and shear strain to be characterized, and whether the lamellae observed are deformed originals or ones created subsequently e.g. after adiabatic local melting and recrystallization. The present paper gives an overview of experiments in which the deformation of individual lamellae can be traced within individual spherulites. This has been accomplished using linear polyethylene as the minority component in blends with the branched polymer. In this way it is possible to prepare morphologies of isolated spherulites of linear polyethylene within a matrix of the copolymer. Their deformation has been followed as functions of draw ratio, strain rate, and drawing temperature following preliminary experiments in this laboratory by Drs Y. Zhao and I. L. Hosier. It is intended to publish this and continuing work elsewhere more extensively than is possible here; the present paper identifies principal results in their context.

Drawing is possible over two temperature ranges. From room temperature to 100 °C, the system draws as a whole with drawn spherulites becoming confined within a cylindrical envelope of affine dimensions. Individual lamellae respond according to their inclination to the tensile axis. Those which are extended are liable to rotate, disrupt and/or fragment, more so with higher draw ratios and temperature. Those which are compressed tend to bend, buckle and kink co-operatively in bands parallel to the tensile axis - a distortion incompatible with truly affine deformation – especially in the centres of spherulites where the stress is greatest. From 120 °C to 130 °C, the matrix is fully molten and flows around the spherulites, causing them to extend, by the draw ratio, but only along the singular centre line. No

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sign of local melting contributing to deformation has yet been identified.

2. Experimental

The polyethylenes used in this study were Rigidex 140–60 (BP), a linear polymer for which $M_w = 54,000$; $M_n = 17,000$ and Escorene LD100BW (Exxon), a conventional branched low-density polymer for which $M_w = 87,000$; $M_n = 10,000$. Henceforth these are referred to as HDPE and LDPE respectively.

Blends of 5% by weight of HDPE in LDPE were melt-mixed for 30 min, under nitrogen, in a Winkworth twin z-blade mixer, model IZ, at 160 °C. Melt-pressed sheets, 1.4 mm thick, of this blend were remelted at 160 °C, crystallized for 1 h at 123 °C then quenched in cold water to provide the material for drawing.

Dumb-bell specimens cut from the above, 5 mm wide over the 20 mm gauge length, were drawn in the high temperature oven of a Monsanto Tensometer 2000 after being heated over some 10 min to the chosen temperature then maintained there for 5 min. The nominal temperature values cited in the paper are, except for room temperature, those measured by a thermocouple located to the side of the specimen. These are systematically high by ∼5 K, according to the changes in melting endotherms of samples taken from the undrawn shoulders of specimens. The precise value of drawing temperature does not, however, materially affect the significance of the results of this paper. After drawing all samples were cooled, initially at 30 K·min^{-1}, to room temperature; only then were they removed from their clamps. Unclamping produced a retraction of some 20% for specimens drawn in the low temperature range but dimensions were stable for those drawn in the high temperature range. Local draw ratios were measured after removal from the clamps from the distance apart of carbon bars, applied by coating through a grid before drawing.

Drawn specimens were cut open at −70 °C with a glass knife and microtome to reveal the desired cross-section, then etched prior to examination by scanning electron microscopy (SEM). Etching was for 1 h at room temperature with a 1% w/v solution of potassium permanganate in a 10 : 4 : 1 mixture (by volume) of sulphuric acid, 85% orthophosphoric acid and water respectively. Etched specimens were coated with gold prior to examination by SEM.

3. Results

The initial undeformed objects consist of immature spherulites of linear polyethylene widely separated within a matrix of branched polyethylene (Fig. 1a), frequently appearing, as in Fig. 1b, sheaflike in projection; the three dimensional geometry is expected to be axialitic, lacking full cylindrical symmetry about the axis of the sheaf. Additional individual lamellae which have grown at an arbitrary angle to, and to greater length than, the remainder of the main sheaf may also be present. They are unique to the particular objects but of minimal importance to the present report except in so far as they indicate that each object will have its own distinct identity leading to minor textural variations on drawing.

From room temperature, 25 °C, to 100 °C drawing is possible to ratios, λ, of 5 or 7, at strain rates of both 5 and 1000 mm·min^{-1}, i.e. initial strain rates for a 20 mm gauge length of 4.10^{-3} and 0.84 s^{-1} respectively. A neck may or may not result as shown in Table I, more so for the higher draw rate. Attempted drawing to such extensions at immediately higher temperatures is unsuccessful. For example, at 110 °C when the LDPE is nearly completely molten and shows unusual fracture properties, the maximum extension obtainable was 2.2. Drawing to higher ratios, now to at least thirty times, becomes possible again at 120°C to 130°C. This reflects the change from both blend components being solid in the range to 100 °C to the condition where only the HDPE is so in the higher temperature interval with the LDPE component then completely molten. Henceforth we shall refer to these two temperature ranges as those of low and high temperature respectively.

Differences in outline deformation are seen well at low magnification (Fig. 2). Maximum longitudinal dimensions have increased by the draw ratio. In the low temperature regime the projected envelope of the drawn spherulites tends to have become a cylinder, well-demarcated laterally, lying parallel to the draw direction (Fig. 2a and b). In these circumstances, the spherulites are deformed as a whole, with lamellae responding according to their orientation to the draw direction. This is no longer the case at 120 °C and above. Then the bulk of each object is no more than modestly deformed, even in specimens drawn thirty times, but the extreme ends are extended in lines along the draw axis, either one or two at each end depending on the orientation of the sheaf as identified further below. At both 120°C (Fig. 2c) and 130°C (Fig. 2d) maximum longitudinal dimensions are again increased by the draw ratio.

The details of such behaviour in the low temperature range depend upon the orientation of the initial object to the tensile axis. A comparison in Fig. 3 of two objects, both drawn at the higher rate to $\lambda = 1.5$ at 100 °C, shows that when the axis of the sheaf is along the draw direction, Fig. 3a, the outer lamellae have rotated towards the tensile axis, as expected for appropriate slip and show interrupted linear contrast with disruptions at intervals of ∼1 μm or less. In some places, e.g. along the centre line to the right, where lamellae will be expected to have deformed in tension, etched lamellae are clearly fragmented. On the other hand, when the sheaf axis is transverse, Fig. 3b, lamellar rotation and disruption are still evident – the latter, for example, also in the horizontal lamella to the right – but in addition, the envelope could be inscribed to an ellipse of similar shape to that expected for affine deformation. Kinking has developed in the waist of the sheaf giving way to buckling at greater radial distance, both in response to transverse compression. Fig. 3c, a transverse section for the same extension but drawn at 70 °C, shows both lamellar disruption and central kinking from a different perspective and confirms the essentially circular cross-section. The contrast of transverse sections fades rapidly with draw ratio and is hard to observe beyond $\lambda = 3$.

Fig. 4, a similar comparison of differently oriented sheaves for $\lambda = 3$ at 70 °C, reveals the same features as above but with longitudinal disruption of contrast now

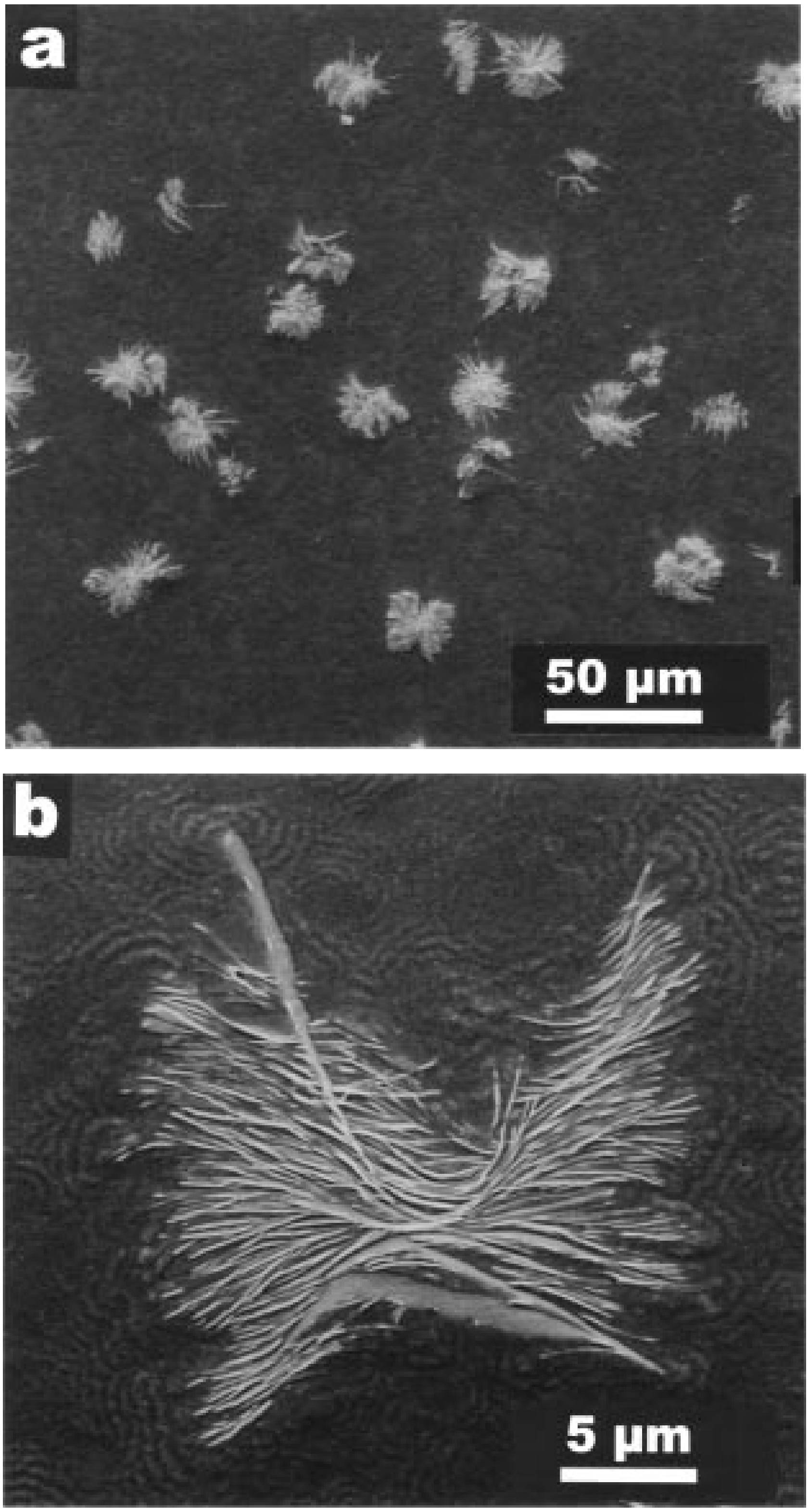


Figure 1 (a) Undeformed immature spherulites of HDPE in a matrix of LDPE; (b) Detail of one such object showing the axialitic or sheaflike geometry in projection.

TABLE I

Temperature/°C	Code/Elongation at break/Necking					
	5 mm/min			1000 mm/min		
25	A	5	Y	B	7	Y
70	C	5	N	D	7	Y
100	E	5	N	F	5	Y
110					2.5	N
120				G	11	N
130				H	27	N

widespread in both sheaf orientations. Moreover, the tendency for well-demarcated parallel lateral boundaries is already present in both Fig. 4a and b, although in the former a dearth of lamellae in the centre is inevitable. This tendency will be found to develop more strongly for still higher draw ratios. In Fig. 4b it is accompanied by curving of individual lamellae along the transverse perimeter.

It is a striking observation that, for moderately high draw at low temperatures, the envelope of a drawn

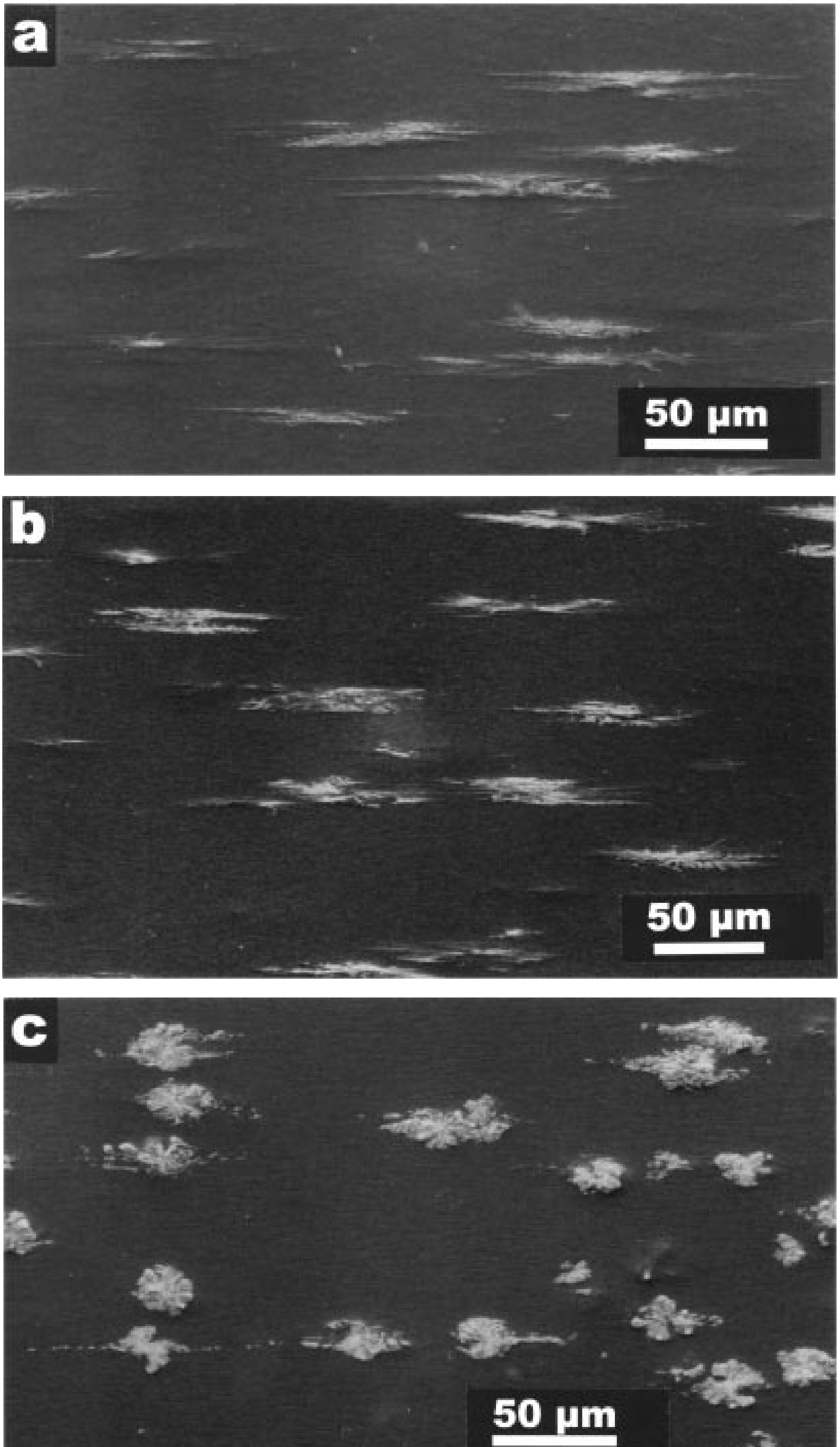


Figure 2 Overviews of spherulites drawn at the higher strain rate as follows: (a) $\lambda = 4.5$; 25 °C; (b) $\lambda = 4.5$; 100 °C; (c) $\lambda = 4.5$; 120 °C; (d) $\lambda = 7.0$; 130 °C. In all cases the tensile axis is horizontal on the page. (*Continued*.)

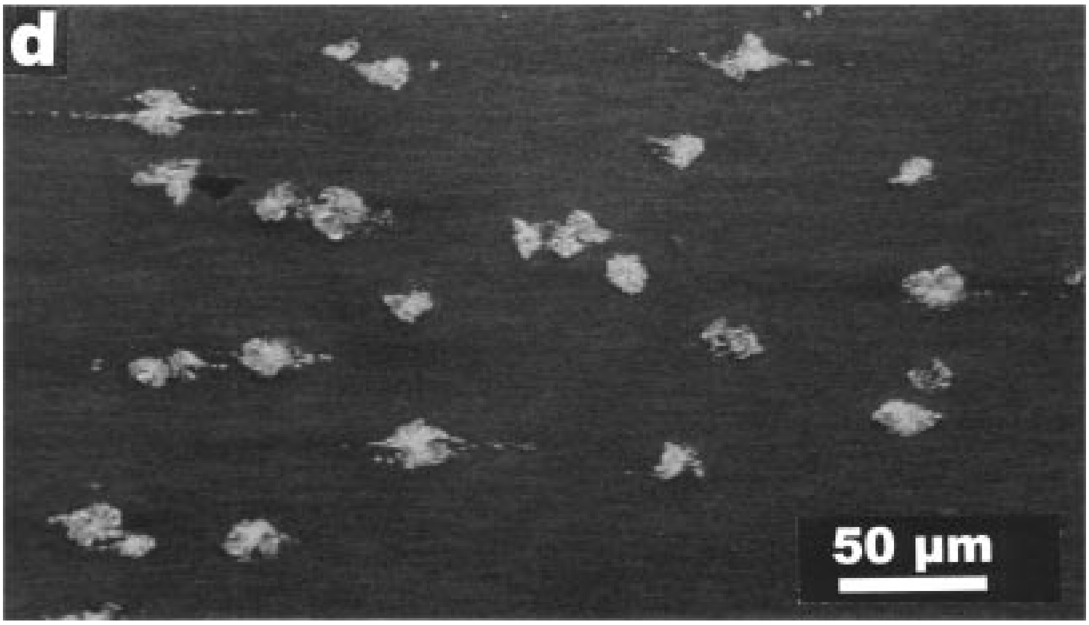


Figure 2 (*Continued*.)

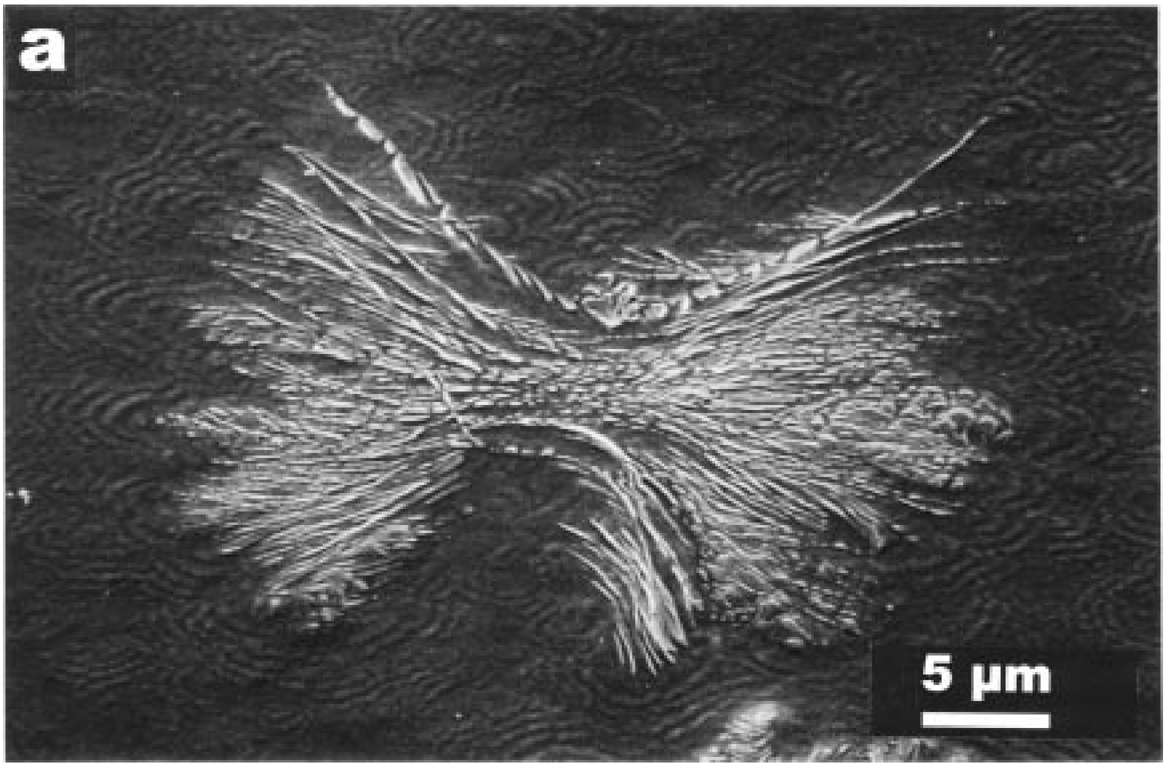


Figure 3 Lamellar detail of spherulites drawn to $\lambda = 1.5$ at the higher strain rate: (a) and (b) at 100 °C, tensile axis horizontal; (c) at 70 °C, section transverse to the draw direction. (*Continued*.)

spherulite tends to have become a cylinder lying parallel to the draw direction, most clearly so when the axis of the original sheaf lay across the draw direction (Figs 2a and b and 5a). Contrast fades differentially for higher draw ratios in the more highly drawn parts of an individual object (Fig. 5a). The centre of objects with a transverse axis (as in Fig. 5b, showing a spherulite drawn to $\lambda = 4.3$ at 70 °C) generally displays kinking, of lamellae which would initially have been perpendicular to the tensile axis, giving way to traces with interrupted contrast for lamellae less inclined to the draw direction.

The aspect ratios of all such cylinders, including their precursors at lower draw ratio, have been calculated from measured maximum lengths and widths. According to Fig. 6a, they scale closely as $\lambda^{3/2}$, i.e. in agreement with expectation for affine deformation at constant volume. This follows because in such circumstances a sphere transforms to an ellipsoid of revolution i.e. in section a circle transforms into an ellipse.

Experiments in the high temperature range were performed at the highest available speed attempting, successfully, to avoid failure by operating within the lifetime of transient entanglements in the matrix. This can

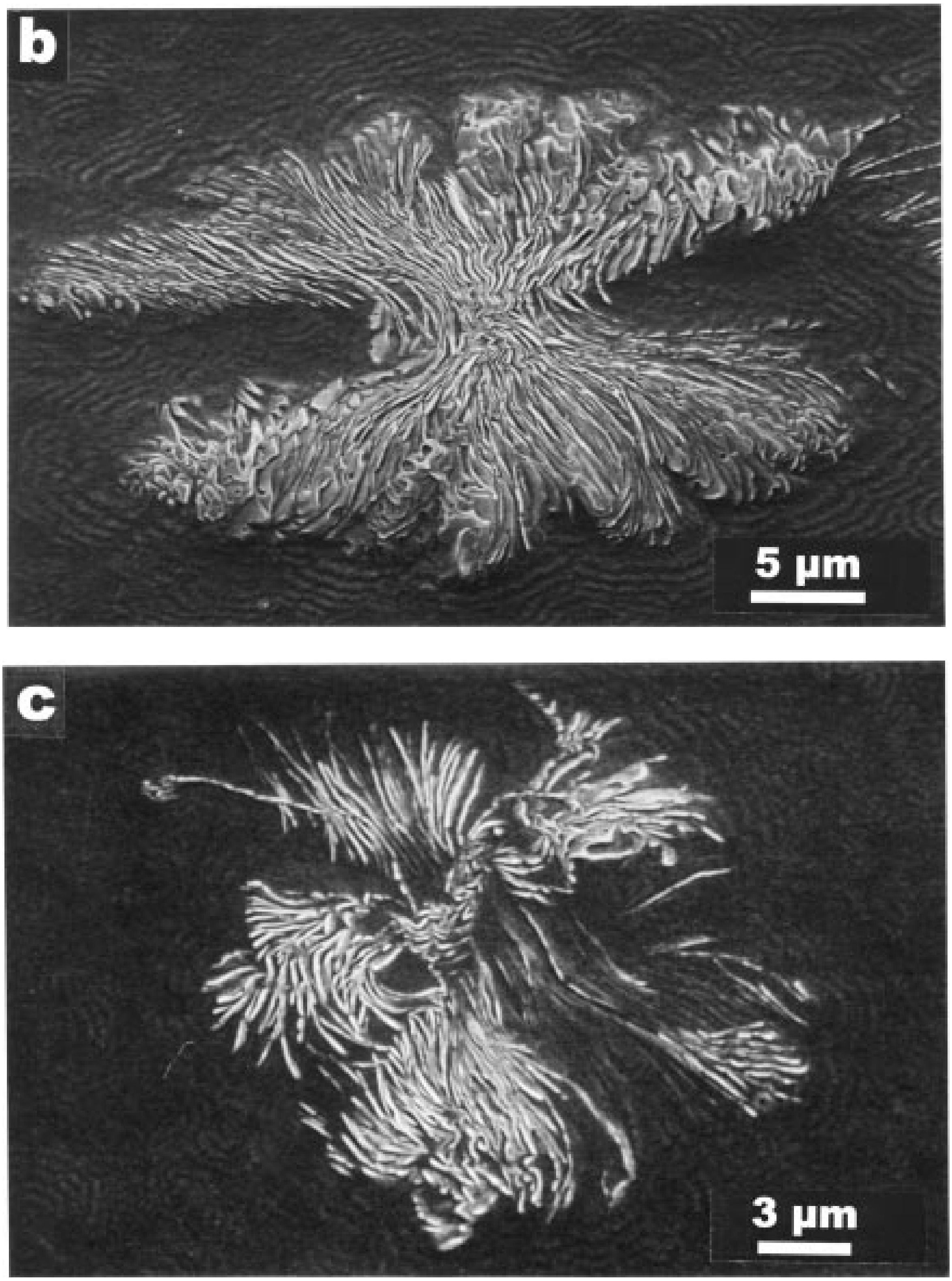


Figure 3 (*Continued.*)

be seen to have flowed around the objects and drawn them out along the singular line(s) of the flow i.e. centrally for a sphere or its perturbed equivalent(s) for sheaflike geometries. The data of Fig. 6b are consistent with the maximum extension being that of the draw ratio and no lateral contraction. The flow pattern in the matrix around the object for drawing at 120 °C shows well in Fig. 7a due to the very fine texture resulting from the small amount of solid HDPE dispersed in the LDPE melt. A comparable pattern is present but not so marked at 130 °C because of the obscuring effect of the isolated self-seeding nuclei of HDPE the melt then contains. However, the HDPE in the main objects is still largely intact. An object such as in Fig. 7b shows, in addition to the drawn-out lamellae in the prongs, that there is no evident sign of a local melting and recrystallization process having occurred.

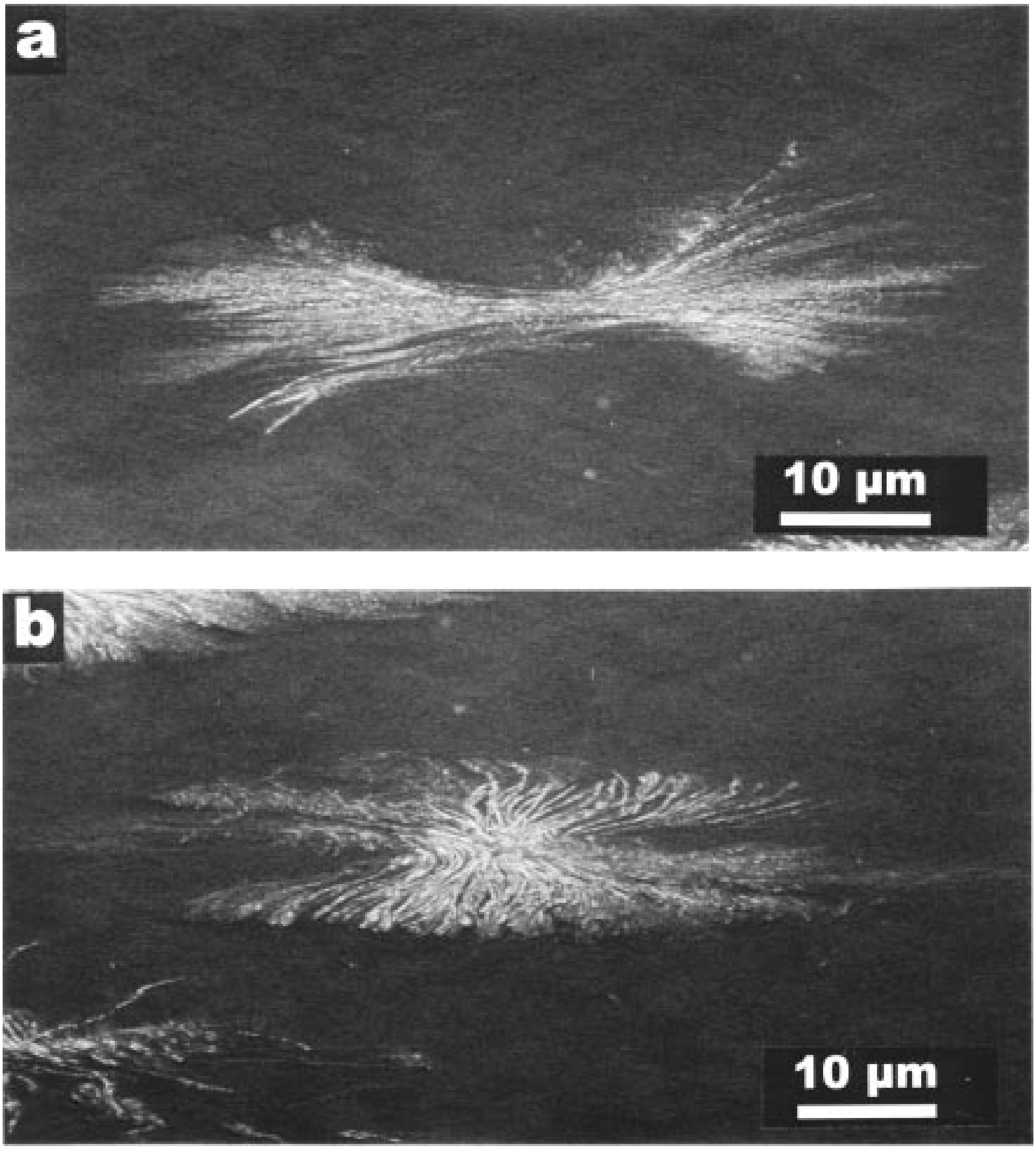


Figure 4 A comparison of differently oriented spherulites drawn to $\lambda = 3.0$ at 70 °C and the higher strain rate: sheaf axis (a) parallel and (b) transverse to the horizontal draw direction. Note the co-operative kinking in the centre of (b).

4. Discussion

This exploration of how individual spherulites respond to drawing in both solid and molten matrices shows certain features which would have been expected coupled with novelties which microscopy has brought to the fore. The former are the differential responses of lamellae according to their orientation to the applied tensile stress. The latter include the unambiguous demonstration that individual objects are extended by the draw ratio together with the specific mechanisms of co-operative kinking, the development of a cylindrical envelope and the high temperature response. Underlying all of these is the application of stress to polymer lamellae organized within spherulites and how this is accomplished on a molecular level.

It is well known that polyethylene lamellae deform by mechanical twinning, martensitic phase transformation and slip. Identified intralamellar modes of the last are chain slip $\langle 001\rangle\{010\}$, i.e. along $\langle 001\rangle$ directions in $\{010\}$ planes, or $\langle 001\rangle\{100\}$ and transverse slip $\langle 100\rangle\{010\}$ and $\langle 010\rangle\{100\}$; all operate under suitable shear stresses [2, 3]. The principal stresses in tensile drawing are elongation in the stretching direction and compression normal to it, making shear stresses maximum at 45° to the tensile axis. Given that **b** is the radial growth direction, this leads to the expectation of maximum slip and elongation by shear in a cone around the draw direction. The H outlines of deformed spherulites in e.g. Fig. 5a support this kind of angular dependence. Although these profiles are, in part, a consequence of the axis of the initial sheaf being transverse to the draw direction with few if any lamellae present initially along the draw direction, the central loss of contrast, as in Fig. 5c, even when there are lamellae along the draw direction is, nevertheless, an indication of more-disrupted, possibly fragmented lamellae

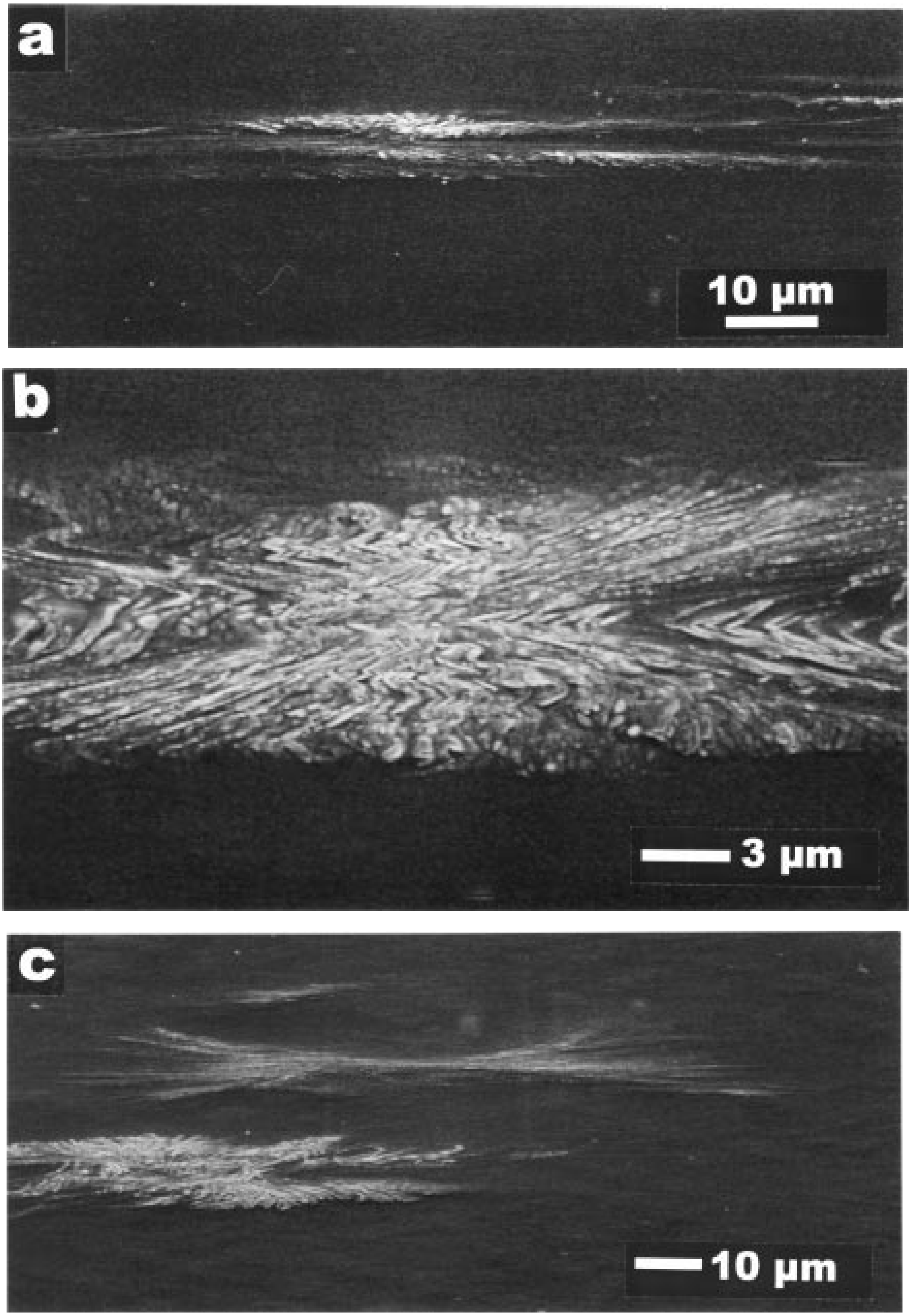
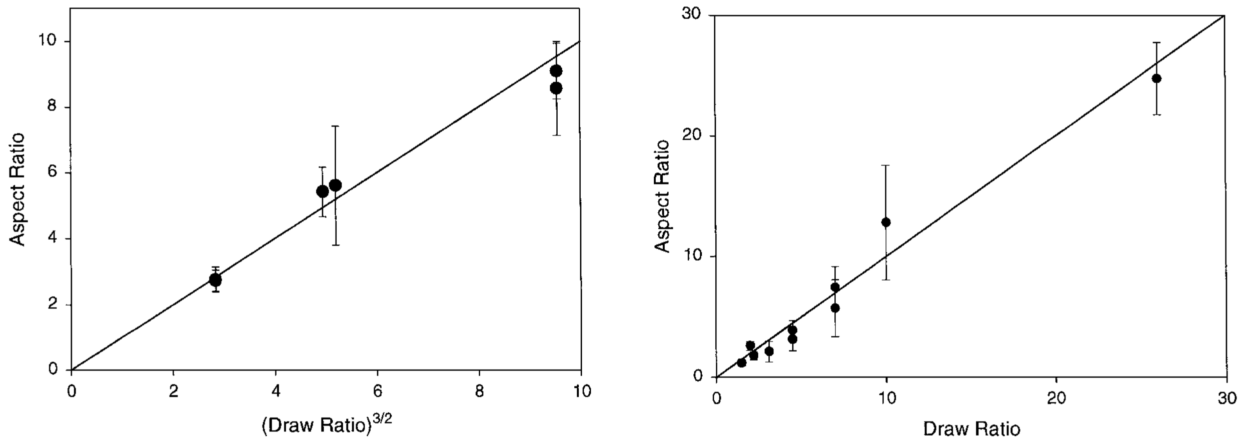


Figure 5 Differential contrast in spherulites drawn at the higher rate with draw direction horizontal: (a) drawn to $\lambda = 7.0$ at 25 °C; (b) and (c) drawn to $\lambda = 4.3$ at 70 °C.

in this direction when they are unable to deform by shear.

Permanganic etching develops weaknesses in lamellae according to the accessibility they give to the etchant, producing surface topography which is the principal source of the contrast in SEM. When this is weak, in etched specimens, the implication is that accessibility of the etchant has been increased along lamellae by the deformation. After etching, separated lamellar fragments are clearly visible in certain



(a) (b)

Figure 6 (a) Aspect ratio plotted against (draw ratio)$^{3/2}$ for samples drawn at 100 °C. The full line is the theoretical one for affine deformation; (b) Aspect ratio plotted against draw ratio for samples drawn at 120 and 130 °C. The line is the theoretical 1 : 1 plot.

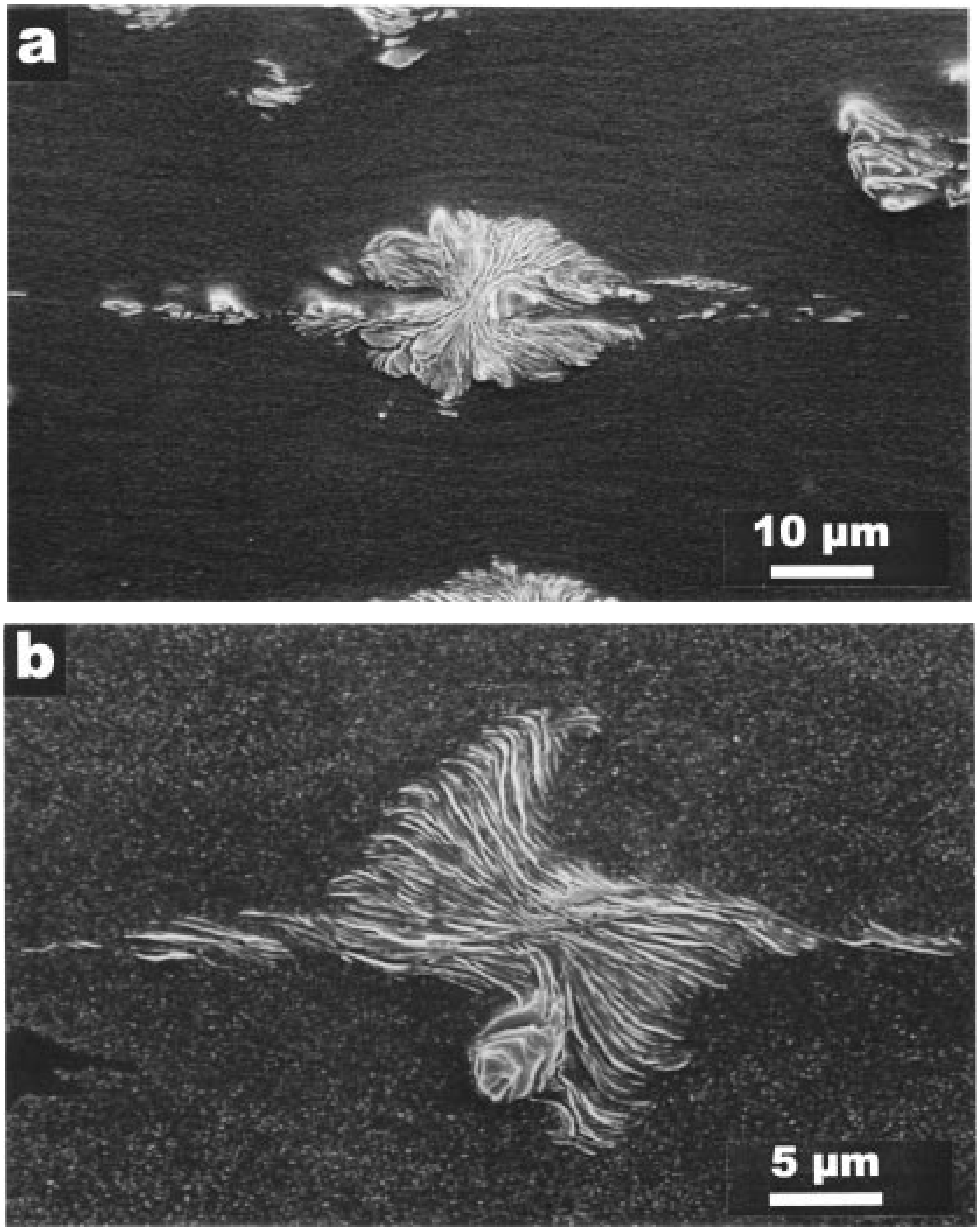


Figure 7 Spherulites deformed at the higher rate to $\lambda = 4.5$. (a) At 120 °C; (b) At 130 °C.

instances, e.g. at the top of Fig. 3a; in others actual or incipient failure, either by shear or cracking, may be inferred from the interrupted contrast along what is clearly one original lamella. Differentiation between failure modes is more possible with the higher resolution of transmission electron microscopy and shows the expected change from cracking to shear deformation as the angle of lamellae to the draw direction increases; this will be discussed in future papers.

The contrasting response to compression is well exemplified by Fig. 3b. Especially directly above the waist, once-planar lamellae have buckled, displaying S and C-shaped profiles. Further into the waist, where the stress will be higher because of the reduced area, the buckling has become co-operative kinking. This is neither mechanical twinning nor martensitic transformation, both of which operate in {001} planes for polyethylene [2], but rotation of lamellae so as to achieve the necessary lateral contraction and longitudinal expansion. The extension of kinking along the draw direction reveals that lamellar response is not solely a function of their inclination, as would be the case for affine deformation. Nevertheless, as e.g. Fig. 5b reveals, inclination to the tensile axis remains the major determinant of lamellar response in the low temperature range.

The operation of the several deformation mechanisms tends to give a drawn spherulite a well-defined lateral boundary and a cylindrical shape especially when the sheaf axis lay transverse to the draw direction. Such cylindrical envelopes are, of course, larger than the drawn objects they contain and could not be filled at constant volume; Fig. 5c, which shows adjacent objects deformed to $\lambda = 4.3$ at 70 °C for both principal orientations of the sheaf, makes the point. The fact that aspect ratio scales as for an affine deformation (Fig. 6a) – which is a constant volume transformation - is probably to be interpreted as an alteration in the shape of the object. A similar change towards a more cylindrical geometry was observed previously for the deformation of spherulites in bulk [7]. The very striking lateral demarcation here is very probably a consequence of the differing character of the entangled molecular network inside and outside the deformed spherulites. As is well understood, it is these networks which transmit the applied stress through samples; if they fail or are discontinuous, samples break. The relevant point here is that a network entirely in the matrix will be more longitudinally extensible than one which incorporates the linear polymer. This follows from considerations of crystallinity and lamellar thickness. The boundary between such regions will, therefore, tend to align along the draw direction.

Once the matrix of branched polyethylene is fully molten a different pattern of behaviour ensues. The solidified pattern in the matrix of Fig. 7a is as expected for flow at low Reynolds number, circumstances in which maximum elongational stress will be exerted along the centre line of a sphere [8]. For less regular geometries the flow pattern will be distorted and the locations of maximum stress displaced. Fig. 7a and b indicate that these are now at the extremities of principal protuberances where they have caused lamellar portions to be detached from the spherulites and displaced downstream to give an overall aspect ratio equal to the draw ratio (Fig. 6b). Some modest deformation of spherical envelopes to elliptical contours occurs at 120 °C (Figs 2c and 7a) - though much less than for a third of the draw ratio at 100 °C (Fig. 3a). At 130 °C, with a less viscous matrix, object centres appear effectively unchanged. For both temperatures, pronounced lamellar distortion is confined to the lateral borders of the spherulite where there is local bending (Fig. 7a and b) consistent with viscous interaction with the matrix.

5. Conclusions

This paper has shown that the deformation in bulk of isolated polyethylene spherulites in a copolymer matrix can be observed with lamellar resolution to at least 7 times extension.

Drawing occurs in two temperature ranges. Spherulites deform as a whole within a solid matrix from 25 to 100 °C with longitudinal dimensions increasing by the draw ratio. From 120 °C to 130 °C, when the matrix is fully molten, the principal effect is to detach lamellar fragments along the line of greatest extensional stress while leaving the majority of the spherulite little affected. Maximum extension is again that of the draw ratio.

In the low temperature range, deformation differs according to the inclination of lamellae to the tensile axis. Under tension or shear, lamellae rotate, disrupt and/or fragment. In compression they buckle then kink co-operatively where the stress is highest.

The lateral boundary of deformed spherulites tends to be well demarcated and parallel to the draw direction. It is suggested that this reflects differences in the extensibility of the molecular networks on either side.

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