it is more consistent with the structural observations to assume that the proportions of the reinforcing fibre phase (the intercrystalline bridge sequences) are increased with increasing draw.

It is most encouraging that the results of these electron microscope studies are qualitatively consistent with previous structural studies of these materials undertaken at Leeds University, and moreover that the histograms support the model approach which has been adopted to explain the high stiffnesses. However, it is appreciated that there will be merit in more comprehensive studies. These are at present being undertaken, primarily with the intention of carrying out both electron microscopy, and more conventional wide-angle X-ray diffraction measurements on identical samples, with a view to advancing the quantitative relationships between structure and properties.

References

1 Capaccio, G. and Ward, I. M. *Nature (Phys. Sci.)* 1973, **243**, (130) 143; *Polymer* 1974, **15**, 233
2 Capaccio, G., Crompton, T. A. and Ward, I. M. *J. Polym. Sci. (Polym. Phys. Edn)* 1976, **14**, 1641
3 Gibson, A. G., Ward, I. M., Cole, B. N. and Parsons, B. *J. Mater. Sci.* 1974, **9**, 1193
4 Barham, P. J. and Keller, A. *J. Mater. Sci.* 1976, **11**, 27
5 Smith, J. B., Manuel, A. J. and Ward, I. M. *Polymer* 1975, **16**, 57
6 Capaccio, G., Ward, I. M. and Wilding, M. A. Faraday Discussion 68, 1979
7 Capaccio, G., Gibson, A. G. and Ward, I. M. 'Ultra-high Modulus Polymers', (Ed. A. Ciferri and I. M. Ward) Applied Science Publishers, London, 1979, Ch 1
8 Clements, J., Jakeways, R. and Ward, I. M. *Polymer* 1978, **19**, 639
9 Gibson, A. G., Davies, G. R. and Ward, I. M. *Polymer* 1978, **19**, 683
10 Keller, A. 'Ultra High Modulus Polymers' (Ed. A. Ciferri and I. M. Ward) Applied Science Publishers, London, 1979, Ch. 11
11 Wilding, M. A. and Ward, I. M. *Polymer* 1978, **19**, 969
12 Clements, J., Capaccio, G. and Ward, I. M. *J. Polym. Sci. (Polym. Phys. Edn)* in press
13 Arridge, R. G. C., Barham, P. J. and Keller, A. *J. Polym. Sci. (Polym. Phys. Edn)* 1977, **15**, 389
14 Barham, P. J. and Arridge, R. G. C. *J. Polym. Sci. (Polym. Phys. Edn)* 1977, **15**, 1177

Direct optical and *STEM* observations of the drawing of pressure-crystallized polyethylene

G. E. Attenburrow* and D. C. Bassett

J. J. Thomson Laboratory, University of Reading, Whiteknights Park, Reading, UK

(Received 9 July 1979)

Studies of structure–property relationships for synthetic polymers are rendered particularly difficult, in comparison with other technological materials, by problems of adequate textural characterization and, especially for mechanical behaviour, the inability to examine the morphology of the same specimen before and after deformation. Whereas recent advances in electron microscopic techniques have at last made it possible to reveal representative lamellar textures in polyethylene and other polyolefins, these techniques, and, indeed, electron microscopy, with its attendant radiation damage, are not suited to the study of progressive deformation. The purpose of this Communication is to report how, in one system, that of pressure-crystallized (or anabaric) polyethylene, it has been possible to follow the progress of individual lamellae during drawing by direct optical observations allied to *STEM* (Scanning Transmission Electron Microscopy) of the same samples.

Materials and Techniques

The polyethylene used was Hifax 1900 (Hercules Powder Corporation) with a reported molecular mass (mass-average) above 2×10^6. It was crystallized using established methods[1] from the melt at 4.9_5 kbar and cooling through the crystallization region at ~0.5 K min^{-1}. This results, firstly in the formation of thick, so-called chain-extended, but actually fold-containing lamellae of the high pressure disordered hexagonal phase, which subsequently transform, at essentially constant lamellar thickness into the familiar orthorhombic modification[2]. The mass-average lamellar thickness of the samples used, determined by gel permeation chromatography following 3 days digestion in nitric acid at 60°C[3] was ~600 nm with a good proportion of lamellae being thick enough to be resolvable in the optical microscope. The specimen itself was crystallized in the form of a dumb-bell 3 mm long and 1 mm wide. From this 2.5 μm thick sections were microtomed at ~–40°C for deformation in a microstrain gauge mounted on a Zeiss Universal optical microscope. It has previously been reported[1] that Hifax 1900, and other very high molecular mass polyethylenes, are not prone to the brittleness usually associated with anabaric polyethylenes and can be extended to draw ratios of about 6 under tensile deformation at 80°C. In the present circumstances, however, it was desirable to avoid, at least initially, the provision of heating the microstrain gauge and its environment above ambient temperature so that room-temperature ductility was induced in the specimens by immersion in xylene for 24 h at 23°C.

Prior to immersion in the xylene, the section had a

Present address: Raychem Ltd, Dorcan, Swindon, Wilts, UK

0032–3861/79/111312–04$02.00

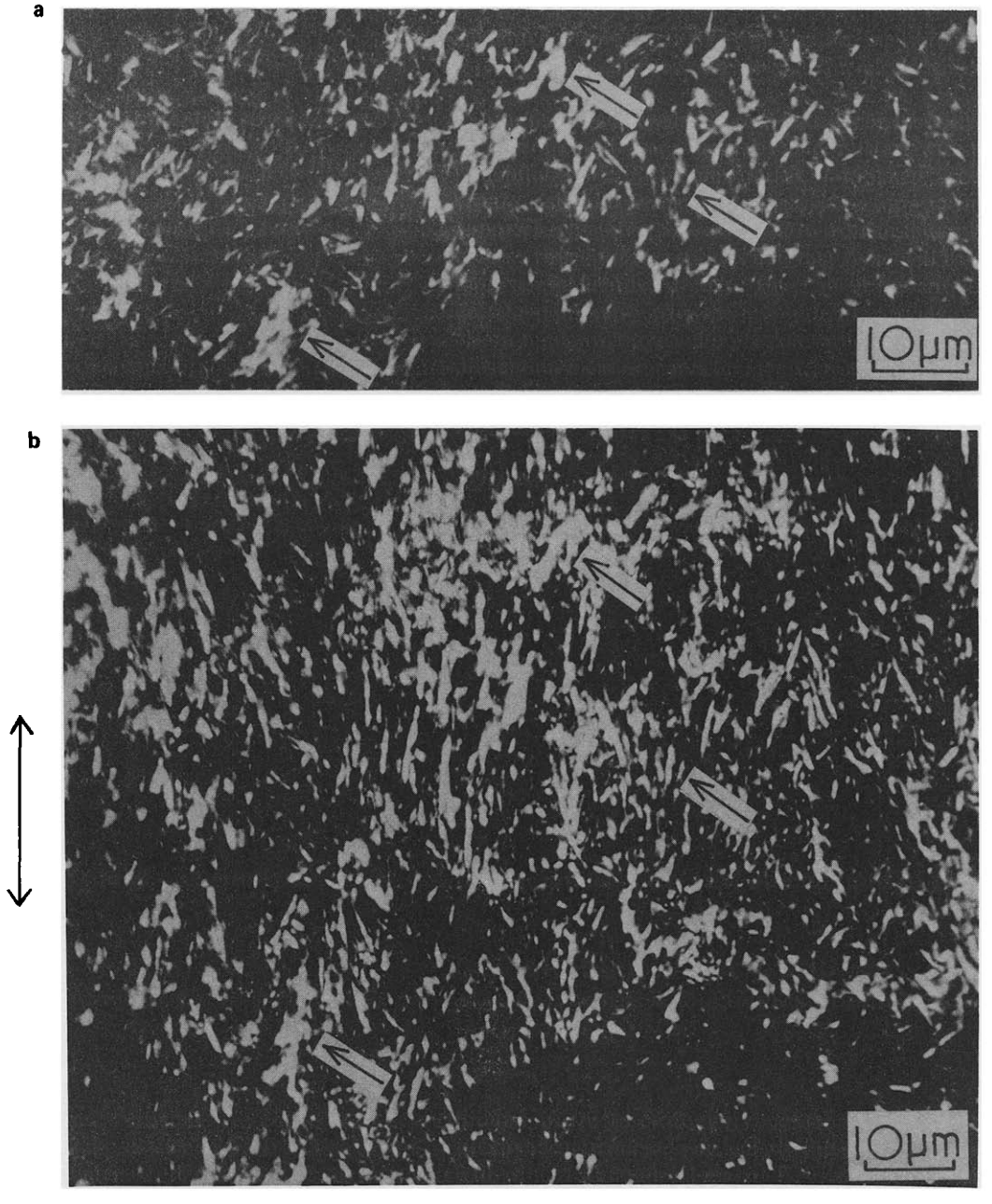

Figure 1 Same area of anabaric polyethylene viewed between crossed polars (whose traces lie at 45° to the vertical on the page) before (a) and after (b) extension by 100% in the vertical direction. Three pairs of features occurring in both photographs are arrowed

lettered electron microscope grid placed on it and both were coated with a thin aluminium film; this gave a recognizable pattern over the specimen to assist in the identification of particular crystals throughout deformation. It also allowed the measurement of the tensile strain which was 100% in the examples to be shown.

Results and Discussion

The same area of the sample, before and after 100% deformation, is shown in *Figure 1*, with the specimen photographed between crossed polars whose traces lie at 45° to the vertical on the page; the tensile axis is vertical. Three pairs of corresponding details in the two micrographs are arrowed. Many more lamellae are visible after deformation. This is a consequence of the increased alignment and the bright contrast which only results for lamellae whose *c*-axes lie close to the specimen plane and at substantial angles to the directions of the polars.

Despite the limitations of optical microscopy, various features of the deformation can be established unequivocally.

(1) The centres of mass of separate lamellae tend to move apart along the tensile axis, although extension is inhomogenous with some clusters preserving their relative positions more or less intact and others not.

(2) There is increased alignment of lamellae toward the draw direction, with examples of the lamellar outline rotating appropriately.

(3) The aspect ratio of lamellae increases on deformation, a feature recorded previously when this polymer was drawn at 80°C and shown there to be associated with high shear parallel to the chain axis[1]; the direction of extinction for a

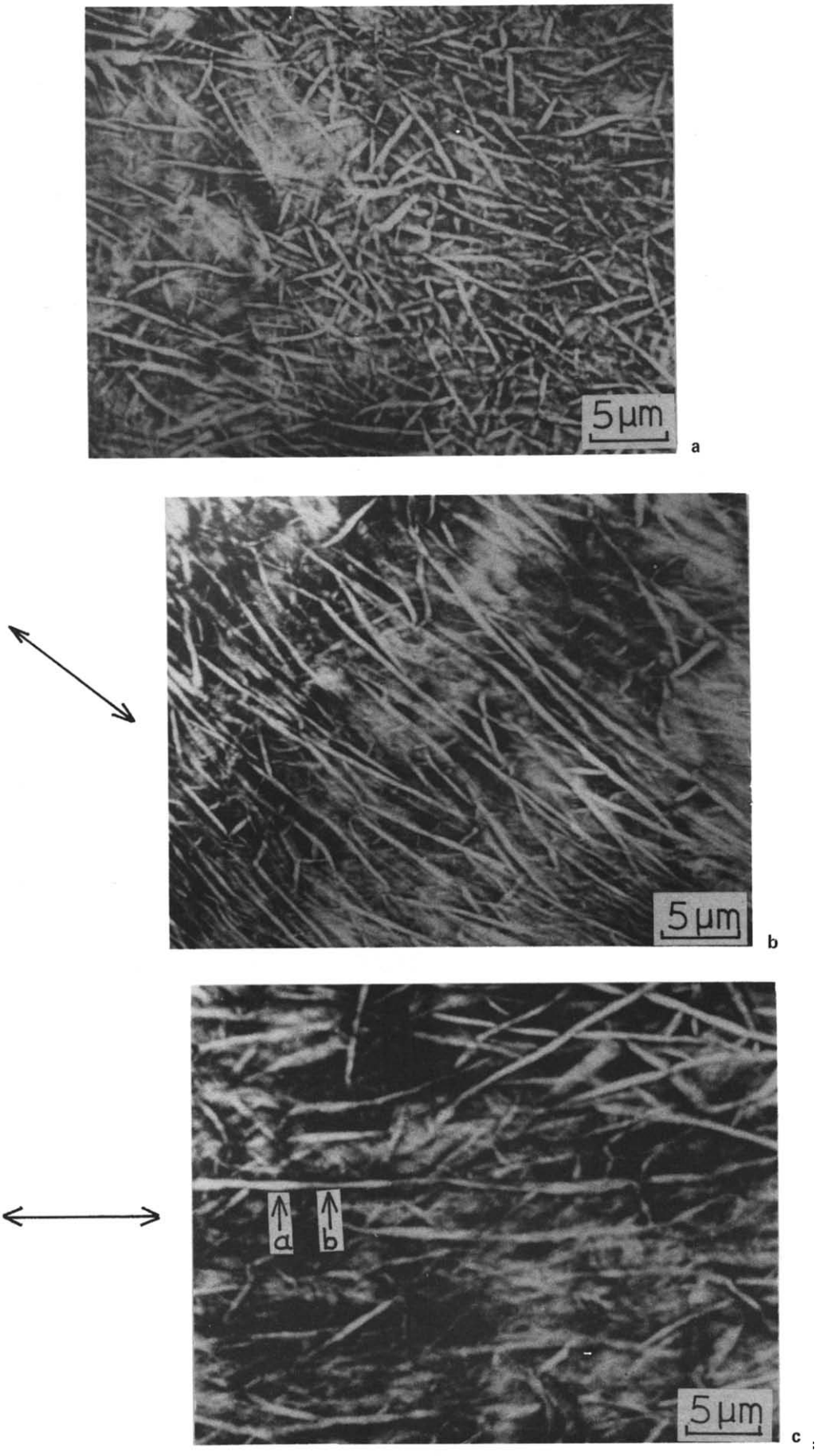

Figure 2 *STEM* images, taken at 80 kV, of the same specimen as in *Figure 1* but after chlorosulphonation. The original undeformed sample is seen in 2a whereas 2b and 2c show the deformed condition. The draw direction is horizontal in *Figure 2c* but in the 45° position (top left to bottom right) in *Figure 2b*

particular lamella shows that this is also occurring in these specimens.

Higher resolution than that allowed by the optical microscope can be provided at any stage, at the cost of irreversible alteration of the sample, by preparing it for electron microscopy. Particularly suitable has been the examination of the whole 2.5 μm thick sample in transmission using the *STEM* attachment to a Philips EM301 electron microscope. For this the entire specimen was soaked in chlorosulphonic acid at room temperature for 3 days (higher temperatures allow the specimen to relax and contract) followed by uranyl acetate according to the technique introduced by Kanig[4] and used previously in this laboratory to study anabaric polyethylenes[5]. This stabilizes a polyethylene specimen in the electron microscope and, by adding electron dense atoms to lamellar surfaces, outlines layers in black in the micrographs. Comparatively low resolution microscopy still adds valuable detail to the optical story, as illustrated in *Figure 2*†. (There is also the possibility of using diffraction techniques though this has still to be exploited.)

Particularly evident is the greater extension of lamellae in the draw direction, the mean aspect ratio has increased from ~15 to ~25*. In areas such as that of *Figure 2c*, lamellar profiles can show significant modulation, as at the points marked a and b, reflecting some inhomogeneity of texture, possibly micronecking related to inhomogeneous shear. An important new feature shows up well in *Figure 2b*. It is the more diffuse contrast between the lengthened lamellae. Coupled with an apparent decrease in the amount of thick lamellae per unit area and the knowledge that drawing at 80°C disrupts 20% or more of the sample into a lower-melting form[1], it is probable that this diffuseness is associated with once-thick lamellae now broken up by the deformation. Drawing would thus produce a double texture of highly sheared, lengthened lamellae on one hand dispersed within a matrix formed from broken-up lamellae on the other. Such a morphology has, indeed, subsequently and very recently, been established in substantial detail for anabarically crystallized Hifax drawn at 80°C using the permanganic etching technique[6]; this will be published later.

† For reasons which have yet to be fully resolved the thickness of lamellae appear to be substantially reduced after chlorosulphonation (see ref 5)

Conclusions

A combination of direct optical and *STEM* observations on pressure-crystallized (anabaric) high molecular mass polyethylene has allowed individual crystals within a melt-crystallized specimen to be observed before, during and after tensile deformation. It has been shown that some lamellae become highly sheared and survive the draw but appear to be surrounded by a matrix produced from other crystals which have been disrupted.

References

1 Attenburrow, G. E. and Bassett, D. C. *J. Mater. Sci.* 1977, **12**, 192
2 Bassett, D. C. *Polymer* 1976, **17**, 460
3 Bassett, D. C., Khalifa, B. A. and Olley, R. H. *J. Polym. Sci. (Polym. Phys. Edn)* 1977, **15**, 995
4 Kanig, G. *Kolloid Z.* 1973, **251**, 782
5 Hodge, A. M. and Bassett, D. C. *J. Mater. Sci.* 1977, **12**, 2065
6 Hodge, A. M. and Bassett, D. C. to be published