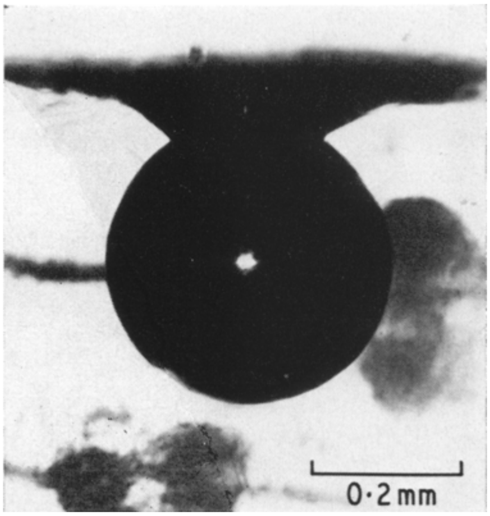

*Figure 6* A transmitted light micrograph showing the way in which planar cracks are deviated in the presence of voids.

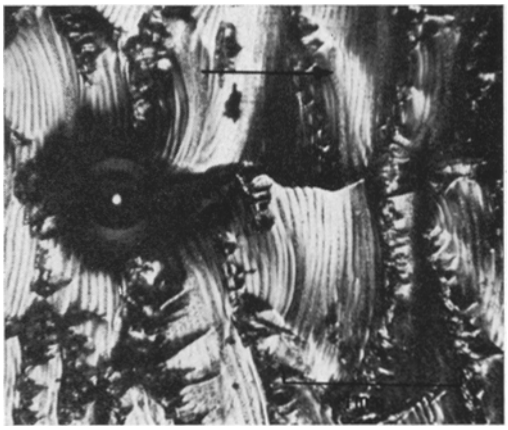

*Figure 7* Fracture surface showing the interaction of a moving crack with a void. The direction of crack propagation is indicated by the arrow.

cantly retard the rapidly moving cracks characteristic of the "hackle" region. The "slip-stick" marks on the surface indicate that the crack may bow slightly at voids as shown in Fig. 7 but there is a great deal of scatter on these observations, and the major feature of crack-void interactions in this region is the long steps in the fracture surface left trailing behind voids after a crack has passed.

Similar effects to those described here may also be expected in thermoplastics containing particles whose elastic modulus is less than that of the matrix. In particular, the low stress region above and below low modulus particles may have an effect on the properties of more technologically important particle modified materials than the one described here.

## References

1. G. B. BUCKNELL, *British Plastics* **40** (1967) 84.
2. L. E. NIELSEN, "Mechanical Properties of Polymers" (Reinhold, New York, 1962).
3. J. W. HANCOCK, University of Glasgow, Internal Report (1974).
4. S. L. MADORSKY and S. STRASS, *J. Res. Nat. Bur. Stand.* **40** (1948) 417.
5. P. BRADT, V. H. DIEBLER and F. MOHLER, *ibid* **50** (1953) 201.
6. P. I. VINCENT, *Polymer* **1** (1960) 425.
7. R. V. SOUTHWELL and H. J. GOUGH, *Phil. Mag.* **1** (1926) 79.
8. J. N. GOODIER, *J. Appl. Mech. Trans. ASME* **55** A-39 (1933).
9. J. MURRAY and D. HULL, *J. Mater. Sci.* **6** (1971) 1277.
10. S. STERNSTEIN, L. ONGCHIN and A. SILVERMAN, Appl. Polymer Symp. Vol. **7** (Interscience, New York, 1969) p. 175.

*Received 22 November 1974*
*and accepted 24 January 1975*

JOHN HANCOCK
*Department of Mechanical Engineering,*
*University of Glasgow, UK*

---

## *The structure of the high pressure phase in* cis*-polyisoprene*

In studies of the crystallization of polymers under high pressure, two new crystalline forms have been reported, one in *cis*-polyisoprene [1, 2] and one in polyethylene [3-5]. The morphological form of both species is similar, being ellipsoidal (oblate or prolate) although the species in polyethylene are up to a thousand times larger than those in *cis*-polyisoprene (Fig. 1). Precise identification of these phases is difficult since in neither case may the phase be maintained at atmospheric pressure and room temperature. With *cis*-polyisoprene we have recently succeeded, by quenching to 0°C before releasing the pressure, in producing a stable specimen. The specimens, which as detailed previously [1, 2] were in the form of thin films supported by electron microscope grids, were stored in liquid nitrogen prior to performing the electron microscopy. Electron diffraction

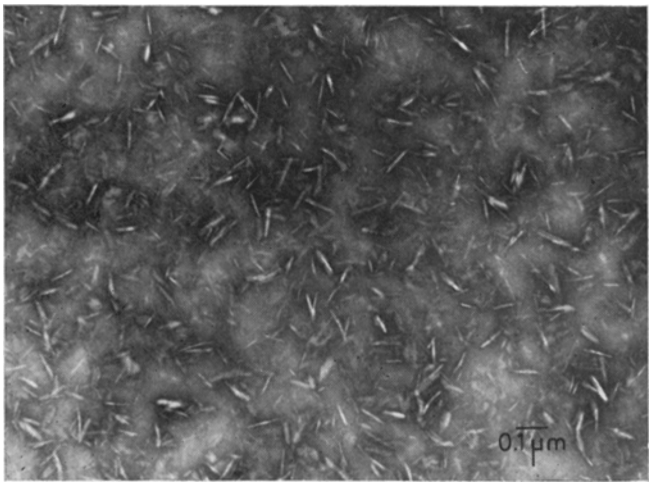

*Figure 1* The high pressure phase in *cis*-polyisoprene (stained film; grown at 28°C and 3 kbar).

patterns were obtained using a JEOLCO JEM-7 transmission electron microscope, with cold stage attachment, operated at 100 kV. The film was scanned under diffraction conditions at sub-visual intensities and the pattern recorded using fast photographic plates (Ilford X-M). A bright-field image of the selected area was then obtained to confirm the nature of the morphological species producing the pattern. Diffraction patterns of the spherulitic structures which grow out of the high pressure phase after long times were also obtained. They were identical to patterns obtained from normal spherulitic growth at atmospheric pressure.

The patterns characteristic of (a) the high pressure phase, (b) normal spherulitic growth and (c) the amorphous phase are given in Fig. 2. Microdensitometer traces of patterns (a) and (b) together with reflection assignments are given in Fig. 3 to facilitate a comparison. Only two crystalline reflections may be resolved from the amorphous background for the high pressure phase. These rings may be identified with the (020) and (002) reflections of normal spherulitic lamellar crystals. Particularly noticeable is the absence of the (200) reflection which is always the most intense of the reflections characteristic of *cis*-polyisoprene crystals. Clearly the two structures bear some resemblance to one another but that of the high pressure phase is much less ordered.

The (002) reflection is characteristic of the *c*-axis spacing in *cis*-polyisoprene and indicative of the ordering along the molecular axis. Molecular conformation typical of the more usual crystal has, therefore, been retained in the new phase. The (020) reflection is the usual manifestation of the *b*-axis spacing, but in this case since it is the only (*hko*) reflection the structure is uniaxial about *c* with axes perpendicular to *c* having lengths equal to the former *b*-spacing. Hexagonal or tetragonal symmetries are possible and a definite assignment cannot be made. A considerable amount of disorder must, however, exist in the (*hko*) plane since the (020) reflection is very broad (the spacings associated with the half-width points are 4.70 and 4.30 Å respectively. This could be due to the protruding methyl groups preventing such close packing from being completely achieved. Conspicuous by their absence are reflections corresponding to other planes in a fully-ordered hexagonal or tetragonal system. Unlike in high pressure X-ray studies [5], there are no experimental reasons for believing that an incomplete pattern has been obtained. Any postulated structure must account for the lack of appropriate reflections. Two alternative structures are (1) a canonic crystal [6] or (2) a semi-ordered smectic liquid crystal [7, 8]. Canonics are known in solutions of polymers and correspond to a packing of rods in a hexagonal array. A set of X-ray reflections is characteristic rather than a single line. There are many variants of smectic liquid crystals, the common feature being a layered structure. In smectic $B_A$ liquid crystals [8] the characteristic wide-angle X-ray spectrum comprises a broad reflection corresponding to the average spacing between the molecules. The molecules are oriented perpendicular to the major dimensions of the "crystal", a situation normally encountered in lamellar crystals of

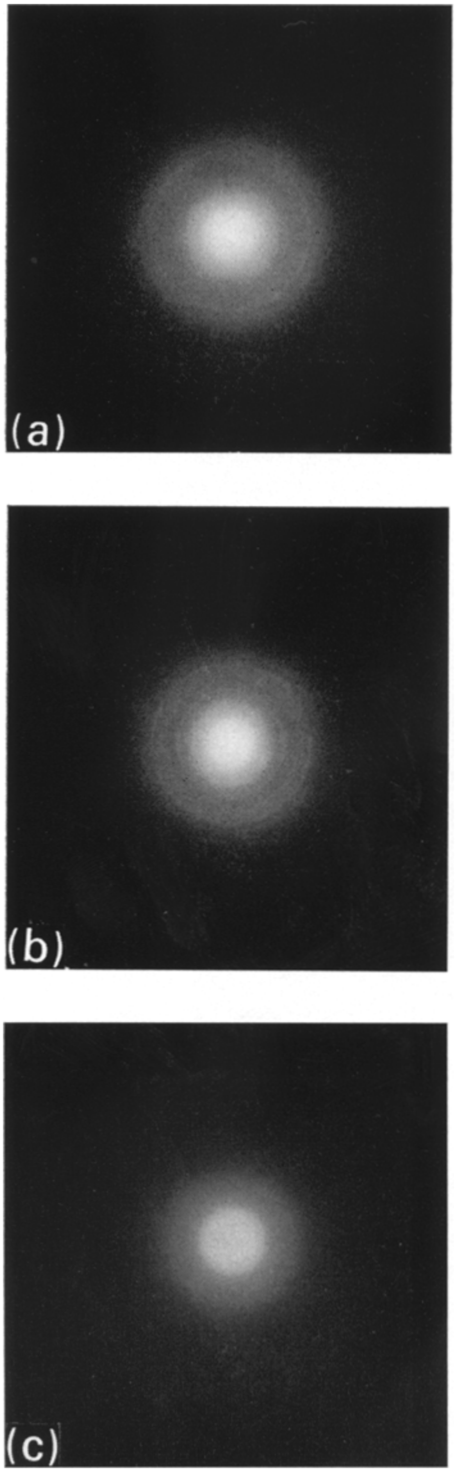

*Figure 2* Electron diffraction patterns of (a) the high pressure phase, (b) normal spherulitic growth, (c) the amorphous phase

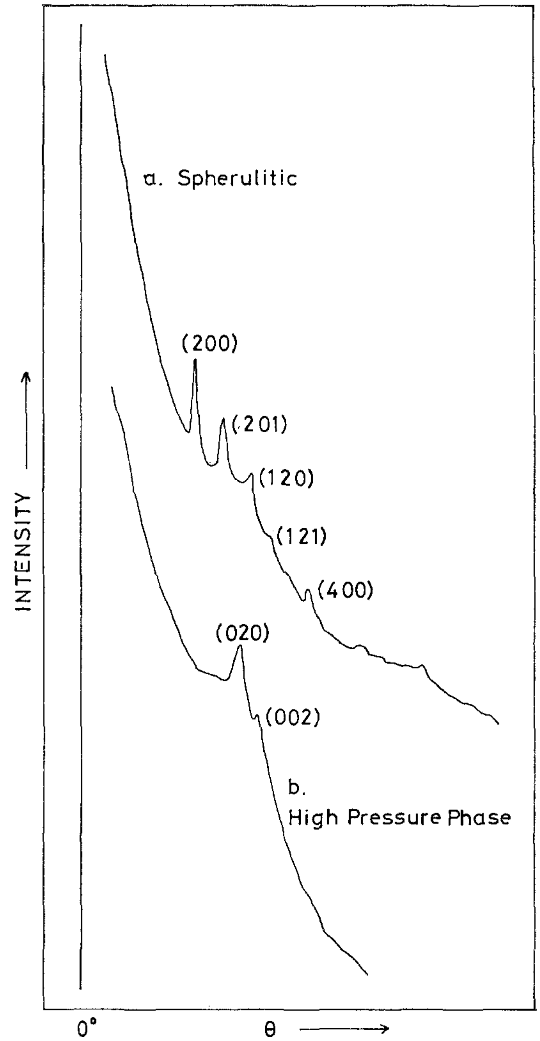

*Figure 3* Microdensitometer traces of electron diffraction patterns characteristic of (a) the high pressure phase, (b) normal spherulitic growth.

polymers. An additional reflection is found in the low-angle X-ray region corresponding to the layer thickness. This particular structural classification would seem to best approximate our system, with the proviso that our crystals are monolayers with layer thickness corresponding to the thin dimension apparent in micrographs (Fig. 1).

Since the phase is less stable than the normal metastable folded-chain lamellae [10] which grow into and replace it at longer times, the concept of a partially ordered, although more dense, phase is acceptable. A fully ordered hexagonal phase of higher density than the normal crystal structure would be at variance with such an observation.

There is a remarkable similarity emerging between our postulated structure and observed morphology and that of the fringed micelle thought in the past to be characteristic of crystal structures in polymers. A fully ordered structure was associated with the fringed micelle, but an alternative way of describing our high pressure phase could be as fringed micelles in which the chains have packed together in an approximately uniaxial fashion. We are, of course, unable to comment on the molecular structure of the end surfaces.

The reported diffraction pattern for the high pressure phase in polyethylene [5] is consistent with our proposed model, even though it was interpreted as a fully-ordered hexagonal phase. In shape, the species in both polymers are remarkably similar although the nucleation densities and sizes are very different. Indeed, it has been suggested [9], on the basis of *in situ* crystal growth studies, that the phase in polyethylene is liquid crystalline in nature. The suggestion made was that a nematic was the correct classification, but this would not be consistent with the X-ray data [5].

We would suggest that in view of the remarkably similar crystalline and morphological structures there is a possibility that this disordered hexagonal or liquid crystalline phase may be a general occurrence in crystalline polymers at sufficiently high pressures if nucleation and growth of lamellar crystals is severely inhibited.

## Acknowledgement

We would like to thank the Science Research Council for financial support.

## References

1. P. J. PHILLIPS and E. H. ANDREWS, *J. Polymer Sci. B* **10** (1972) 321.
2. B. C. EDWARDS and P. J. PHILLIPS, *Polymer* **15** (1974) 491.
3. D. C. BASSETT and B. TURNER, *Phil. Mag.* **29** (1974) 285.
4. *Idem, ibid* **29** (1974) 925.
5. D. C. BASSETT, S. BLOCK and G. J. PIERMARINI, *J. Appl. Phys.* **45** (1974) 4146.
6. A. SKOULIOS, *Adv. Coll. Interface Sci.* **1** (1967) 79.
7. G. H. BROWN, J. W. DOANE and V. D. NEFF, "A Review of the Structure and Properties of Liquid Crystals" (Butterworths, London, 1971).
8. R. DE GENNES, "Physics of Liquid Crystals" (Oxford University Press, 1974).
9. M. YASUNIWA and T. TAKEMURA, *Polymer* **15** (1974) 661.
10. P. J. PHILLIPS and B. C. EDWARDS, *J. Polymer Sci.* to be published.

*Received 4 December 1974*
*and accepted 27 January 1975*

B. C. EDWARDS*
P. J. PHILLIPS†
*Department of Materials*
*Queen Mary College,*
*University of London, UK*

---

*Present address: Metallurgy Division, AERE, Harwell, Oxon., UK.
†Present address: Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, NY 14214, USA.

---

## *On the mode of chipping fracture in brittle solids*

Chipping processes in brittle solids, despite their unquestionable relevance to a diversity of technologies from ceramics finishing to geological engineering, are not well understood at the fundamental level. Some recent studies of microfracture patterns beneath standard hardness indenters do, however, provide some insight into the problem [1, 2], and it is our objective here to indicate how this insight may be applied to construct a physical model of chipping fracture. Essentially, the picture which emerges is that depicted in Fig. 1. (i) Upon *loading* the indenter, a confined zone of irreversible (plastic) deformation forms about any sharp points or corners (thereby accounting for the residual hardness impression), from which "median vent" cracks first initiate and subsequently propagate radially outward along suitable planes of symmetry (e.g. as defined by the diagonals of a pyramid indenter, or by preferred cleavage planes) containing the contact axis. (ii) Upon *unloading* the indenter, the median vents close up but, just prior to complete removal, "lateral vent" cracks initiate and extend laterally from the deformation zone toward the specimen surface. Of the two types of cracking, it is clearly the second which relates more directly to brittle chipping.

However, up to now a detailed fracture