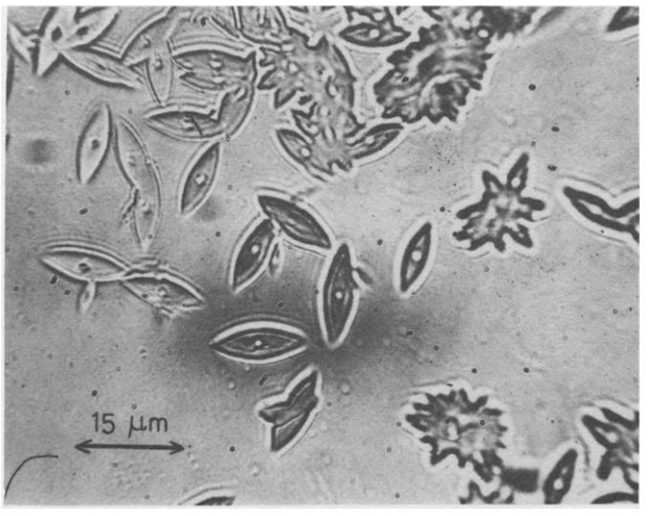

Figure 1a Entities produced by physical ageing of polymer-rich globules *dispersed* in chloroform

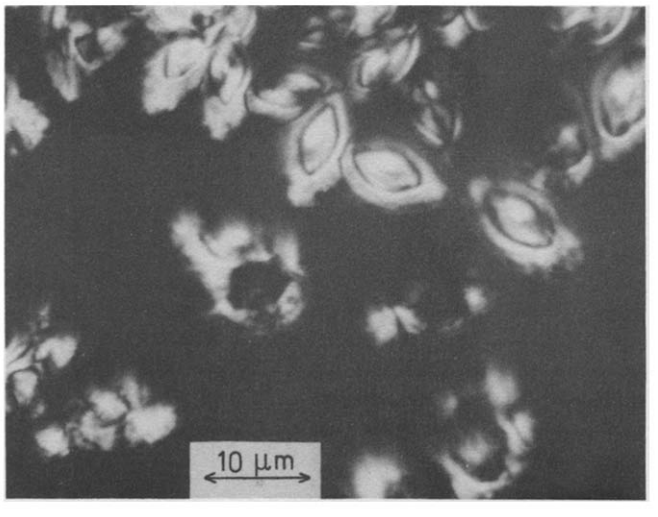

Figure 1b As *Figure 1a* but viewed between crossed polars

and see whether, under appropriate conditions, crystallinity can be detected.

MATERIALS

Polymer

The polymer used in this work was polyethersulphone grade 200P, kindly supplied by ICI Plastics Division. The sample was specified as having a glass transition temperature of 220°C and a density of 1370 kg/m^3.

Solvents

Chloroform and dichloromethane were both of AR grade and used as received.

RESULTS AND DISCUSSION

The behaviour of solvent-saturated polymer has been studied using specimens in three distinct size categories.

(1) If polymer-rich globules are dispersed in a large volume of chloroform so that aggregation does not occur, unusual changes can be observed in each globule. A dispersion of 0.1 wt% polymer was transferred to a cavity in a microscope slide and covered with a slip. During storage at 15°C in the continuing presence of solvent, ovoids appeared gradually over a period of 2 weeks. The rate of formation of these strange entities is markedly dependent upon temperature. *Figure 1* shows their appearance under the optical microscope and the effect of crossed polars is shown in *Figure 1*.

(2) A film of PES a few μm in thickness can be cast from chloroform solution on a glass plate[2] to which it is sufficiently strongly attached to remain in place even when immersed bodily in chloroform. The changes occurring under such conditions are quite unlike those associated with globules. *Figure 2* shows an array of spherulitic structures observed with the electron microscope which are typical of many crystalline polymers. *Figure 2* shows the birefringence of the spherulites still immersed in solvent and the familiar Maltese crosses are in evidence.

(3) Yet another morphology results from the deliberate agglomeration of globules to form a viscous phase. This viscous liquid was allowed to stand at 15°C for 2 weeks and by then it had become a whitened, tough material. The sol-

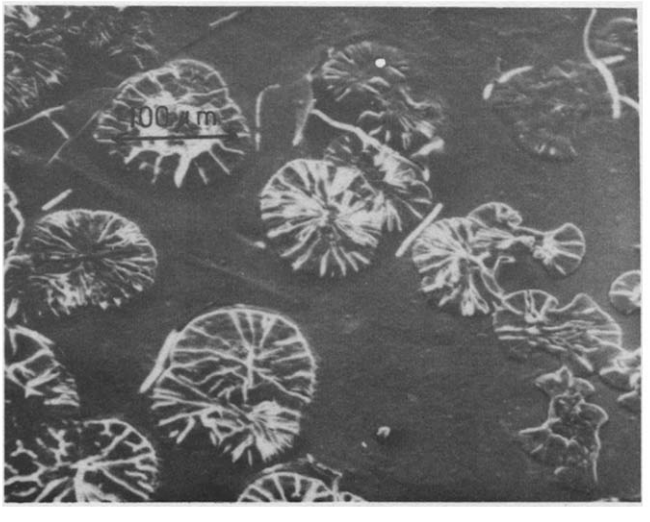

Figure 2a Spherulitic structures in PES *film* aged in chloroform

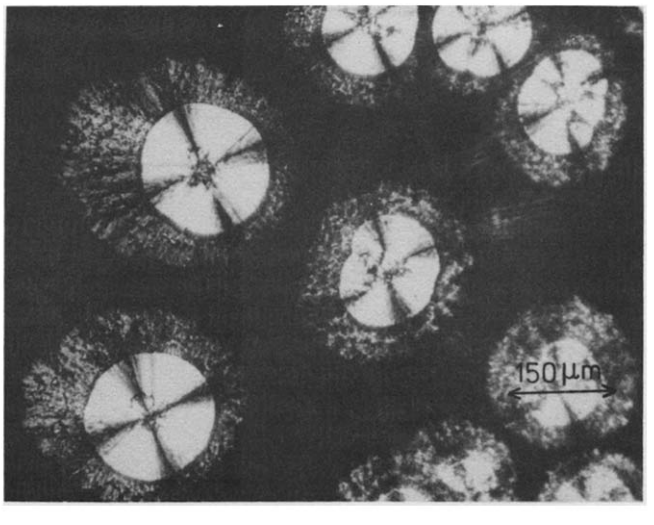

Figure 2b As *Figure 2a* but viewed between crossed polars

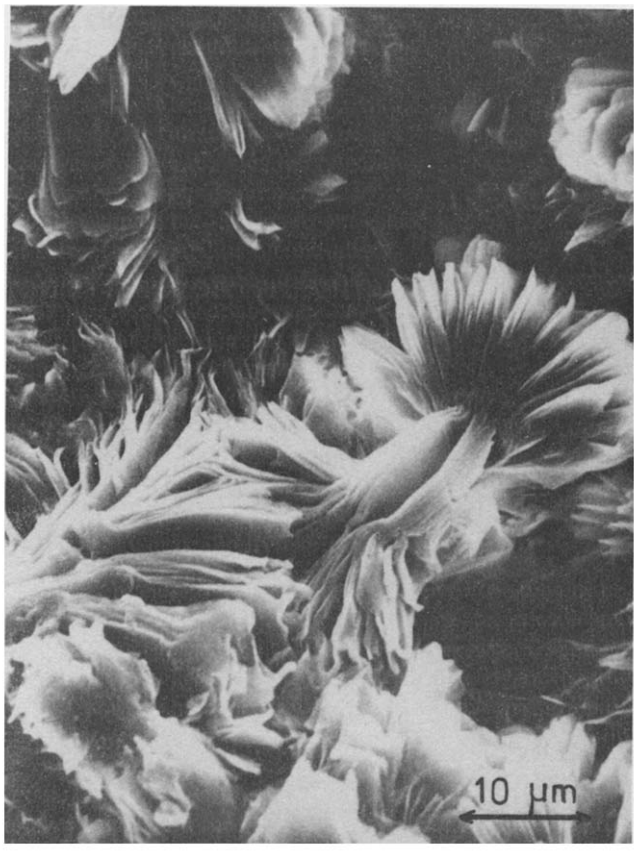

Figure 3 Texture of PES produced by ageing *agglomerated* polymer-rich globules in chloroform

vent was evaporated as far as possible under vacuum at room temperature for several days before electron micrographs were taken (*Figure 3*) to show the details of typical structures.

The physical changes which occur in all three systems include whitening and hardening, during which time some solvent is rejected. The physical changes become slower, at a given temperature, on passing from system (1) to (2) to (3), but this may be little more than a consequence of increasing bulk and a smaller surface to volume ratio. Temperature has some effect on the rate of the changes but in the negative sense. Two days at 5°C produce the same changes as 14 days at 25°C.

No evidence of X-ray crystallinity was found in any of the specimens which, in view of the other evidence for crystallinity, is surprising. However, there remains the possibility that X-ray crystallinity exists only around some critical polymer–solvent composition, since the specimens examined in this work were either solvent-saturated or vacuum-dried. In any event there is evidently a fundamental problem to be solved here because to describe a specimen as crystalline is normally a statement of sufficient precision. In the present context, however, it seems necessary to say that the PES is undoubtedly crystalline on the evidence of outward appearances, yet can be bereft of that repeated internal regularity which gives rise to X-ray diffraction patterns associated with crystalline materials.

At a deeper level one might ask if the PES–chloroform complex is ever possessed of X-ray crystallinity like the PES–dichloromethane system which certainly does, or if it is an example of a new kind of system which cannot attain to that degree of regularity even though it has many properties of a well-crystallized solid. No answers can be given to these questions in the meantime but the experimental observations are being published to draw attention to the problem of defining crystallinity in the PES–chloroform system.

ACKNOWLEDGEMENTS

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