# The structure of polyethylene, as revealed by solvent extraction

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When high density polyethylene (HDPE) is crystallized from the melt at low super-cooling, quenched, and then treated with xylene at ~100° C, part of it dissolves. The remaining part is that which crystallized at the low supercooling. Scanning electron microscopy of the spherulite boundaries in the treated sample shows very clearly the open lamellar structure which was the growth front at the time of quenching.

## 1. Introduction

Polymers tend to fractionate during crystalliz-ation, with high molecular weight material crys-tallizing preferentially. It has been shown that in the case of HDPE crystallizing at low supercooling, some significant low molecular weight fraction of the material will not crystallize at all, either from solution [1] or from the melt [2, 3]. Uncrystal-lized material in solution can be separated by hot filtration. Surprisingly, uncrystallized material can be separated from the solid, by quenching it, and extracting with hot solvent [2, 3]. At the correct temperature of extraction the originally uncrystal-lized material is dissolved, and the rest is not. Some structural consequences of the procedure have been investigated [4]. It was found that the quenched specimens contained a double popu-lation of lamellae: large thick lamellae formed isothermally, and smaller thin ones, which formed during cooling. After extraction, the smaller thin lamellae disappeared leaving voids. The purpose of the present work was to examine how voiding, and thus the underlying molecular weight segregation, relates to the spherulitic texture [5]. It has be-come apparent that as a result of voiding the tex-ture is "loosened up", affording an unexpectedly revealing insight into the internal morphology of the bulk sample. The main purpose of the present note is to illustrate this.

## 2. Experimental preparation and results

A sample of Shell Carlona 60050 HDPE was sealed in an aluminium pan, as used in the differential scanning calorimeter (DSC), melted, then crystal-lized at 128.8 ± 0.2° C for 31 h. On removal from the oil bath it was quenched in ice water. Sections about 30 $\mu$m thick were cut from the sample, using a sledge microtome at room temperature. Indi-vidual sections were then placed in a wire gauze basket and immersed in xylene at 101.5° C for 24 h, with occasional agitation. After rinsing in hot solvent and drying, the section was studied by op-tical microscopy, and then after coating with carbon and gold, by scanning electron microscopy.

To find the best preparation conditions, which are those described above, samples were prepared in a variety of ways and analysed in the DSC [2, 3, 5]. After crystallization at 128.8° C and quench-ing, the samples show two melting peaks. The low temperature peak corresponds to material crystal-lized on quenching, and the size of this peak de-creases with increasing crystallization time (Fig. 1). Crystallization for more than 30 h causes no further change, so the low temperature melting peak then comes from material which will not crystallize at 128.8° C. Dissolution in xylene at temperatures above 101.5° C reduced the size of both peaks, and more material dissolved with in-creasing time. At 101.5° C the low temperature peak was removed and there was no effect on the high temperature peak, which remained unchanged even when the dissolution time was increased. Analysis by gel permeation chromatography of both extract and residue (as in [4]) confirmed that low molecular weight material was removed by the solvent.
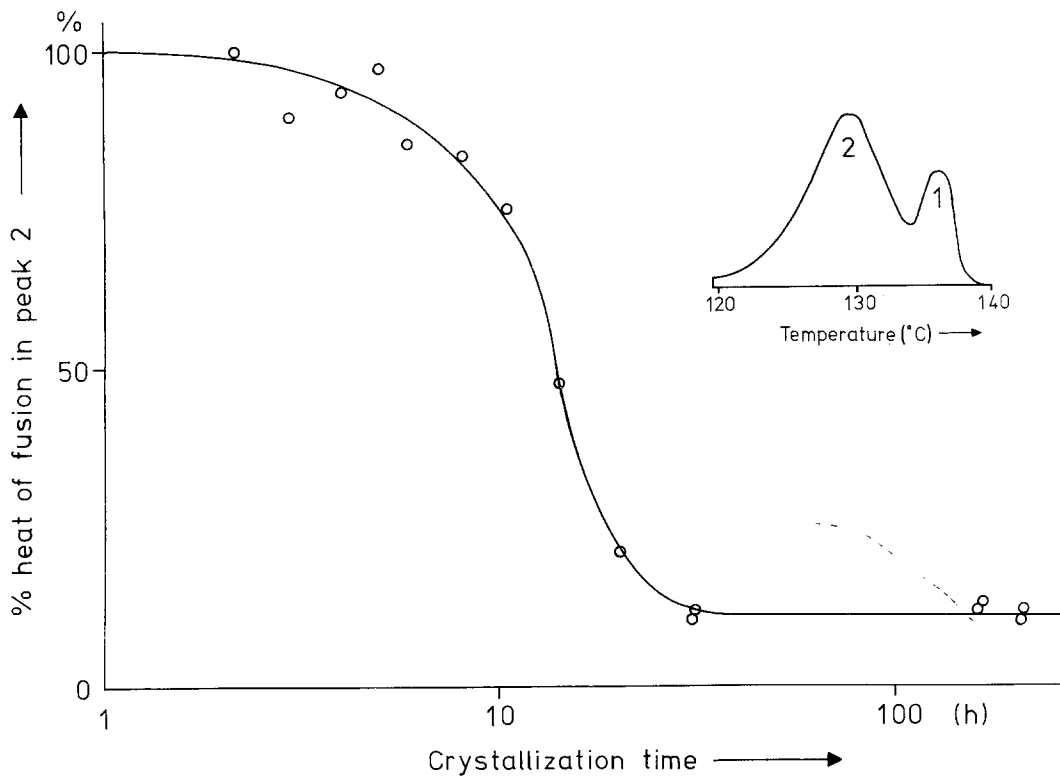
*Figure 1* Analysis of DSC melting traces for polyethylene crystallized at 128.8° C. The graph shows the variation with crystallization time of the size of the low temperature melting peak, peak 2. Inset is a DSC trace of a specimen crystallized for 10 h, showing the size and positions of the two peaks.
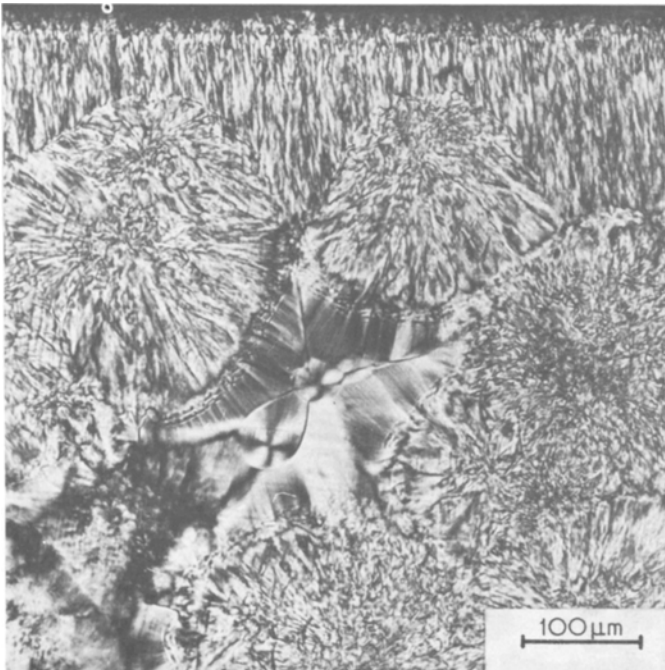


*Figure 2* Optical micrograph taken with crossed polarizers, of a 40 μm thick section of polyethylene crystallized for 31 h at 128.8° C, then quenched. There are large, coarse textured spherulites, with an occasional island of fine textured material, crystallized on quenching.

Fig. 2 is an optical micrograph, taken between crossed polarizers, of part of a section before extraction. The spherulities in Fig. 2 have the coarse texture typical of polyethylene crystallized at high temperatures, and they are large because the polymer used, Carlona 60050, has an unusually low nucleation density. Occasionally between the spherulities there is an island of fine textured material, as in the centre of Fig. 2. This consists entirely of material which has crystallized on quenching, much of it nucleated by the existing spherulite boundaries. Fig. 3 shows part of a similar section after extraction. Each spherulite is now outlined with a grey band where detail is obscured,
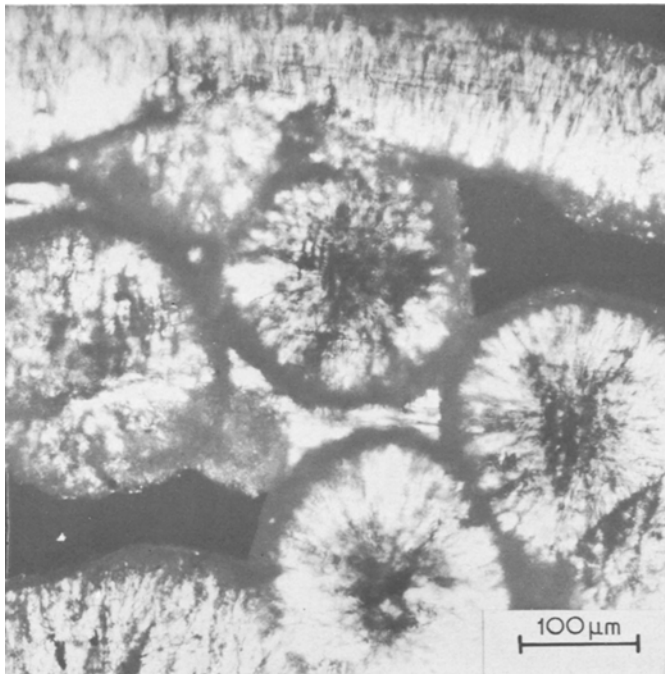


*Figure 3* Optical micrograph as Fig. 2, but after extraction in xylene at 101.5° C. The grey edges to the spherulites are due to the scattering of light by many small voids. The fine textured material has been removed leaving occasional large voids.
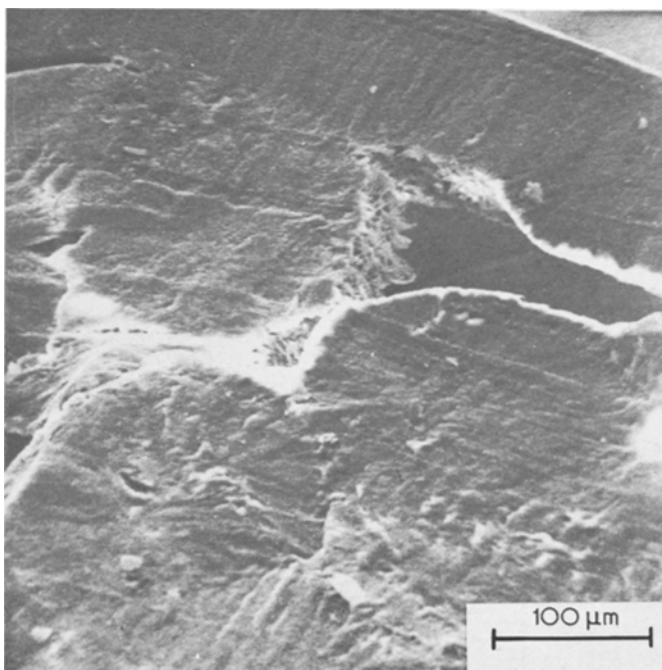


*Figure 4* Scanning electron micrograph of the area in Fig. 2, with the specimen tilted 45° about a horizontal axis. The comparatively featureless top surface has been affected by the cutting process.

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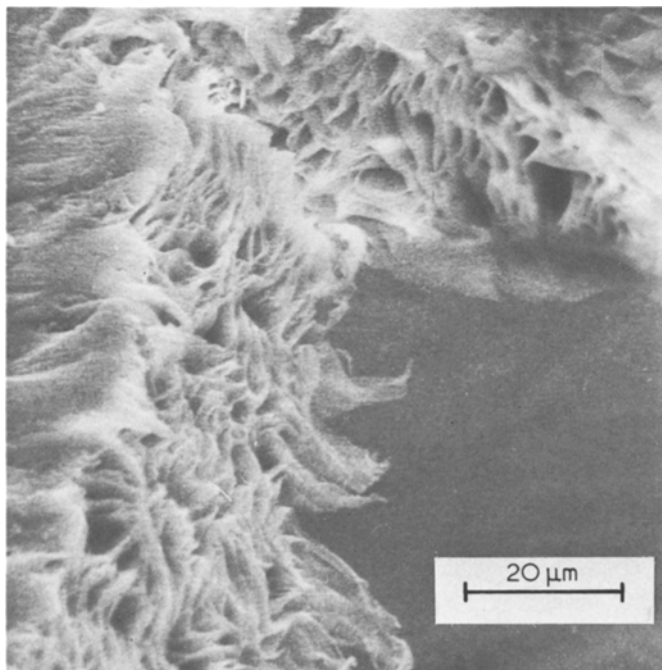
*Figure 5* Scanning electron micrograph of the upper central area of Fig. 3, showing the contrast between the featureless top surface and the highly structured spherulite edges.

and there are occasional large voids between spherulites.* When a suitable immersion fluid such as xylene is added to a section after extraction the grey bands become transparent and the radial birefringent structure of the spherulites becomes very like that before extraction (Fig. 2) even where the grey bands had been. The observation that the grey bands disappear when an immersion fluid is used shows that the opacity is due to scattering of light by voids within the spherulite structure. Thus extraction in xylene causes small voids within the peripheral zones of the spherulites and some large voids between spherulites, where before extraction there was material crystallized on quenching.
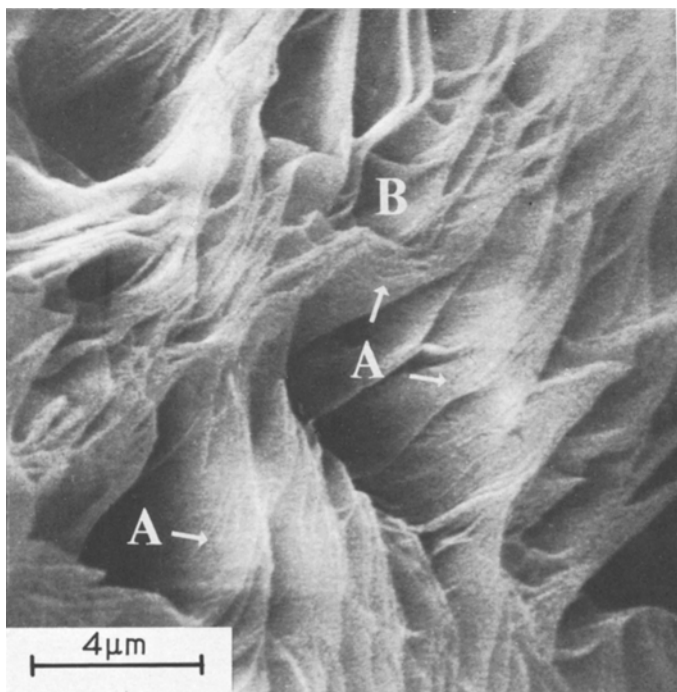
Fig. 4 is a scanning electron micrograph of the same area as in Fig. 3 at a similar magnification. Although some structural features can be seen on the cut surface of the section, most of it is featureless or shows only knife marks. This means that sectioning at room temperature has produced a smooth deformed layer at each surface. We can see the undisturbed spherulitic structure by looking at the surfaces within the section, adjacent to voids. Figs. 5 and 6 are views at increasing magnification of such a surface at the centre of Figs. 3 and 4. Voids are clearly visible, and they are of a size that will strongly scatter visible light as was

implied by the optical experiments using immersion fluid. The material present is in the form of large distinct sheets. When the flat surface of one of these sheets is visible, it is covered with fine bright lines (A in Fig. 6). These lines indicate steps, and their width is 70 to 90 nm. The sharpest edges of individual sheets (B in Fig. 6) have the same width. The lamellar thickness of material crystallized 60 h at 128.5° C is 70 nm [4], so clearly the steps and the thinnest sheets are single lamellae.

## 3. Discussion
In accord with preceding work [1—4] the present study has demonstrated that molecular weight segregation occurs during crystallization. At low supercoolings, low molecular weight material is like an uncrystallizable impurity, it is rejected by the growing crystals and will crystallize only at lower temperatures on subsequent cooling. The fact that this segregation is distinct enough to allow removal of one component by solvent extraction may appear surprising. Even more surprising is the fact that the location of the low molecular weight material can be identified by light microscopy as described above. Two types of segregation have been found: (a) the segregated material remains within the confines of the grow-

*Some voids form during crystallization, but most during extraction.

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*Figure 6* Scanning electron micrograph of a central area from Fig. 4. The spherulite edges are made up of large thin sheets enclosing voids in the micron size range. The arrows A point to fine lines, interpreted as steps 70 to 90 nm high. This is the expected thickness of individual crystal lamellae in this preparation. Separate sheets of this thickness can occasionally be seen, as at B.

ing spherulite, (b) it is ejected from the spherulite. In case (a) it becomes part of the spherulitic texture on subsequent crystallization during cooling. In case (b) material accumulates, eventually forming islands which remain molten until the specimen is cooled, when they crystallize with a fine texture distinct from the rest of the material. Some influence of the isothermally grown spherulites may still remain but only through the secondary effect of surface nucleation. We have seen before that a crystalline polymer with the usual broad molecular weight distribution can be a composite where the components are of differing molecular weights and of correspondingly different lamellar textures [4]. The present work reveals an additional differentiation, according to whether the two kinds of lamellar textures are intermeshed, with the coaser one forming the skeleton of the spherulite, or whether each forms distinct regions on its own. Similar effects were seen some years ago in systems containing deliberately added uncrystallizable impurities [6].

When the segregated material is removed by solvent extraction, the structure of the last material to crystallize at the high temperature is revealed. The structure is very open, because of the high concentration of "impurities", and the open structure allows the lamellae to be seen clearly. Optical microscopy shows that voids large enough to scatter light do not occur near to the centre of the spherulite. However, there will be *some* low molecular weight "impurities" present throughout the sample, and in any poly-disperse material crystallized slowly. The visible structure should then be typical, except for the size of the voids.

There is always the danger of introducing artefacts by treating samples with hot solvents. For example it is probable that surface tension effects will cause lamellae separated by small voids to come together, leaving some large voids. The more serious possibilities are that dissolved material might re-precipitate on the samples, or that material which does not dissolve undergoes substantial reorganization. Both possibilities are largely ruled out by the DSC [5] and Raman [4] observations on samples before and after solvent extraction. As mentioned above, on extraction the low temperature melting peak disappears and the high temperature melting peak is very little affected in size, shape or position. Reprecipitated material would have a low melting point, and reorganization of the original material would cause changes in the shape or position of the higher melting peak. Analagous results come from the Raman LAM spectra of similar specimens [5].

After extraction, no thin lamellae (such as would be precipitated from solution) are detected, and the lamellar thickness of the undissolved material is the same as it was before treatment with solvent.

Accepting that the undissolved material is not seriously affected by the extraction process, Figs. 5 and 6 show, in a striking three-dimensional manner, the structural arrangement of the crystalline material at the crystallization temperature. Thus we have obtained a new method for characterizing the internal crystal morphology which should be capable of further development.

The highly organized large scale structures visible in Figs. 5 and 6 tend to reaffirm that lamellae are the representative structural units in melt crystallized polymers. The visible lamellae must have grown largely as spatially separate entities, with limited molecular interconnections. These lamellae were the last to grow at the high crystallization temperature, so when they grew a large fraction of the material was uncrystallizable. This would naturally give rise to large separations between adjacent lamellae making molecular connection unlikely. The situation becomes similar to growth from solution, where the proportion of crystallizable material is low, with the "solvent" consisting of the lower molecular weight poly-ethylene which crystallizes only on quenching*. The sample here is crystallized from the melt, and not from solution. Although it was obtained at a very low supercooling, it will not be entirely atypical; all samples crystallized slowly from a poly-disperse melt will contain lamellae separated by material which crystallized after the lamellae did. Any generalized description of the structure of melt-crystallized polyethylene must take into account the structural effects of segregation.

## References

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*A step structure is visible along the outermost lamellar surfaces in Fig. 6, and these growth steps seem to define lozenges with curving prism faces. It should be noted that this growth habit is characteristic of polyethylene crystallized from paraffinic solvents [7] and also seems to be typical of the melt crystallized polyethylenes obtained by slow crystallization in thin films by Kovacs [8]. However surface features such as these steps are most susceptible to artefacts which may be introduced during solvent extraction (dissolution and re-precipitation), and the arguments given above against such artefacts do not preclude their presence on a small scale.