

Molecular fractionation in melt-crystallized polyethylene: 3. Microscopy of solvent-treated samples

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Microscopy of melt-crystallized polyethylenes treated with hot *p*-xylene has revealed information concerning the morphology of the systems, in particular the distribution of the segregated low molecular weight material in the structure. It seems that this material, in accordance with earlier reports, is concentrated in the spherulite boundaries and between main lamellae within the spherulites. The effect of thermal treatment and the structure of the material on this morphological aspect is reported.

(Keywords: melt-crystallized polyethylene; microscopy; solvent treatment; molecular fractionation; morphology)

INTRODUCTION

This paper, the fourth in a series¹⁻³ dealing with molecular weight segregation in polyethylene (PE), deals with the effect of solvent treatment by *p*-xylene on the structure as studied by polarized light microscopy and scanning electron microscopy (SEM).

It is a well-established fact¹ that a sample isothermally crystallized from the melt (at a temperature T_c) and later quenched to a lower temperature shows a bimodal melting as recorded by differential scanning calorimetry (d.s.c.). The low temperature melting peak is associated with the fraction of the sample which has crystallized not at T_c but at a lower temperature¹. If the isothermal treatment is performed for a sufficiently long time, this fraction of the sample corresponds to the material (segregated component) which is unable to crystallize at T_c . It was shown by d.s.c.² that if an appropriate extraction temperature is chosen, the segregated component can be almost selectively dissolved in *p*-xylene leaving the rest of the sample unaffected. The selectivity is particularly high for samples with a high content of segregated component and for highly linear systems². The dissolved fractions were found to be of low molecular weight and to have a bimodal molecular weight distribution². Experimental support was provided² for the assignment of the low molecular weight peak to almost linear chains, indicating the occurrence of molecular weight segregation, and of the high molecular weight peak to molecules of a higher degree of chain branching, indicating the occurrence of a chain branch segregation. The present paper reports work in which the selective dissolution technique has been used to obtain morphological information regarding the distribution of the segregated component in the structure.

Solvent-etching, by refluxing solvent vapour of carbon tetrachloride⁴ for branched PE and toluene, benzene or *p*-xylene^{5,6} for linear PE, has been used since the early

1950's to permit the observation of spherulites in melt-crystallized samples. The condensed solvent vapour dissolves the material with some selectivity primarily for kinetic reasons and the spherulite structure can be observed by microscopy. A different technique has been used in more recent studies by Dlugosz *et al.*⁷ and Winram *et al.*⁸. Samples crystallized under isothermal conditions and quenched were prepared for microscopic work by treatment with hot *p*-xylene. The temperature of the solvent was chosen so that the segregated material was selectively dissolved. These investigators showed that the segregated low molecular weight material crystallizes in thin crystal lamellae localized primarily to the spherulite boundaries.

EXPERIMENTAL

Five PE's whose characteristics are given in Table 1, were treated either by isothermal crystallization (IC) from the melt for about 330 h at 393.2 K, 398.2 K or 401.2 K followed by quenching in water (50–80 K/min) or by annealing (A) for about 330 h at 393.2 K, 398.2 K or

Table 1 Polyethylenes investigated

Material	$\bar{M}_n \times 10^{-3} a$	$\bar{M}_w \times 10^{-3} a$	$MI_2 b$	Density ^c (kg m ⁻³)
7022	7.4	51	22	963
7006	8.4	90	7	960
2912	21.6	199	0.3	957
2215	22.0	286	0.05	953
6375	12.9	108	—	963

^a By gel permeation chromatography

^b Melt flow index according to ISO/R 292

^c On the material as obtained from the manufacturer according to ASTM D 1505-68

401.2 K of samples originally crystallized from the melt during a cooling to room temperature at a 1 K/min cooling rate, after which the samples were quenched as in the IC case. More detailed information concerning both the materials and the thermal treatments can be found in ref. 1.

Thin (20 μm) films treated as described above were studied by polarized light microscopy. Bulk samples treated in the same manner were handled as follows:

First, a planar surface with minimum smearing-out

effects was obtained by microtoming at liquid nitrogen temperature.

Secondly, an etched surface was obtained by *p*-xylene treatment in isothermal conditions for 48 h. The temperature of the solvent treatment was chosen so that the segregated component was selectively dissolved. This was checked by running d.s.c. scans before and after the *p*-xylene treatment as demonstrated in ref. 2. After they had been washed in fresh solvent at the extraction temperature, the samples were dried in vacuum. Finally, the

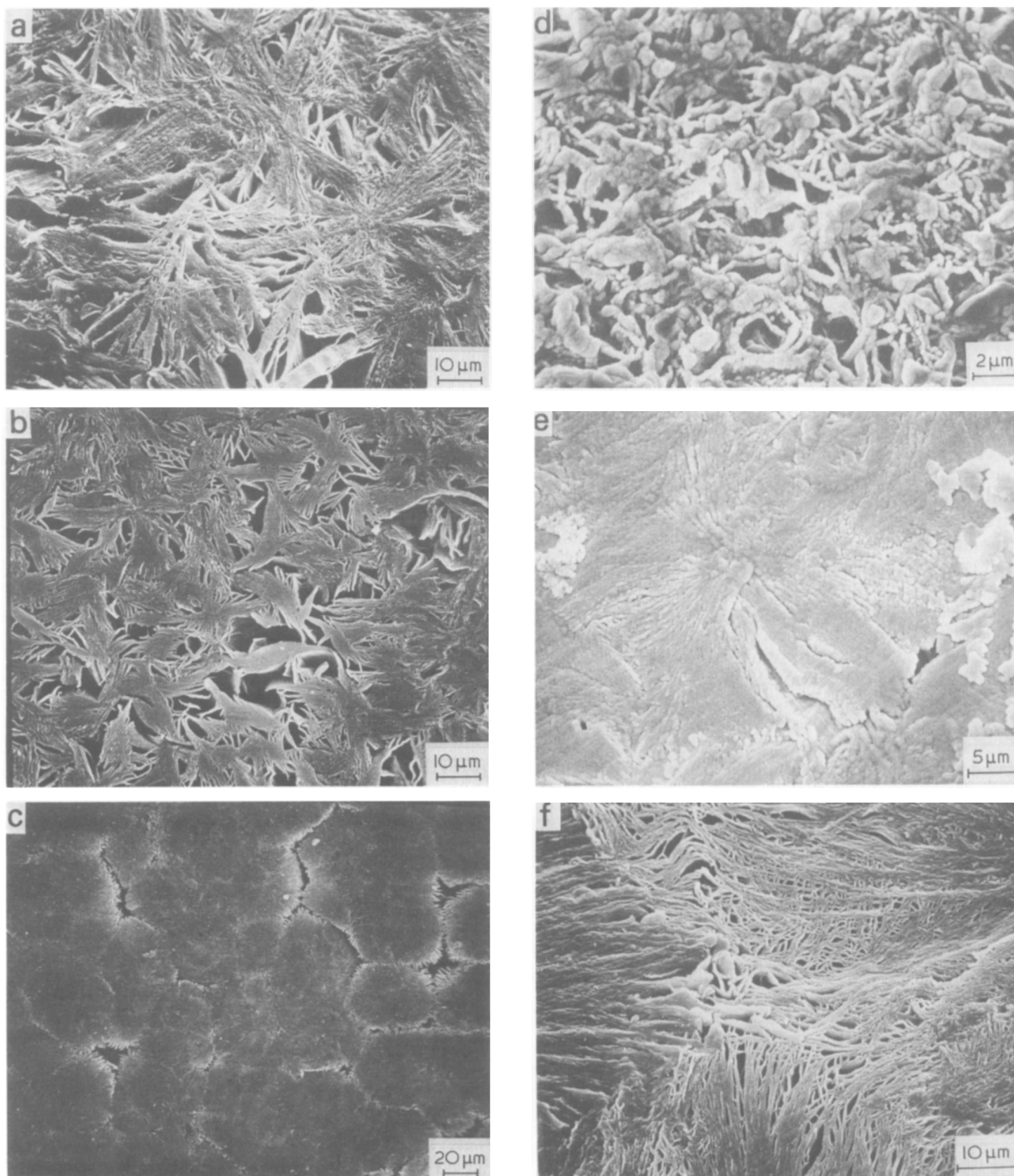


Figure 1 Scanning electron micrographs of solvent-treated samples: (a) 7022-IC-401.2 K (b) 7006-IC-401.2 K (c) 2912-IC-401.2 K (d) 2215-IC-401.2 K (e) 6375-IC-401.2 K (f) 7022-IC-398.2 K

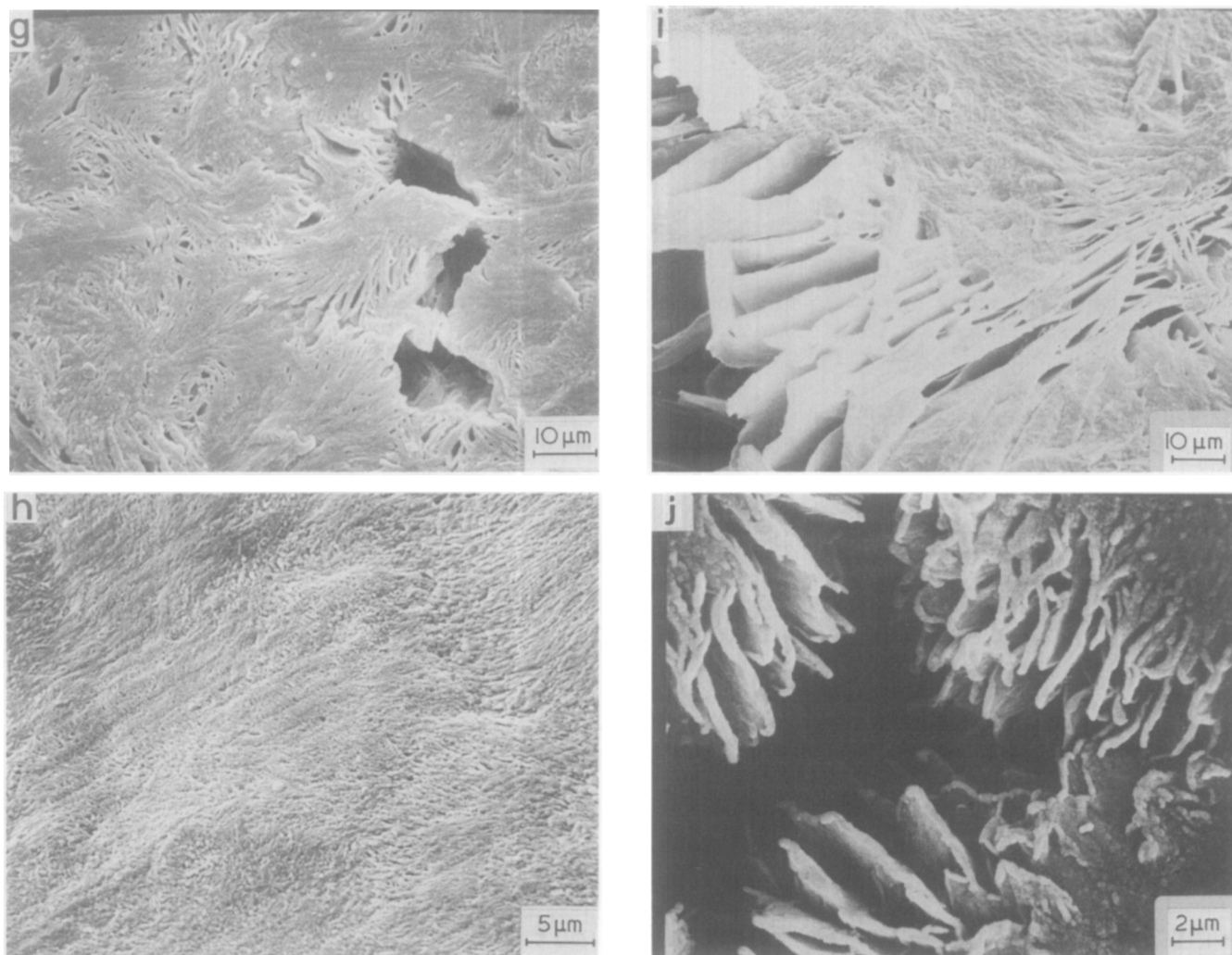


Figure 1 (contd) Scanning electron micrographs of solvent-treated samples: (g) 7006-IC-398.2 K (h) 7022-IC-393.2 K (i) 7022-IC-401.2 K (j) 2912-IC-401.2 K

samples were coated with gold and examined in an ISI Super Mini SEM.

RESULTS AND DISCUSSION

Figure 1 shows scanning electron micrographs of different IC samples treated with hot *p*-xylene. The holes in the etch-surfaces correspond to the original location of the segregated material. Occasionally, the swelling of the sample during the solvent treatment produced small cracks in the etch surface. The real morphological effects were however easily distinguished from these cracks. Another possible cause of artefacts is the recrystallization of dissolved polymer, in which case crystals of comparatively low melting point would be formed. No such effects were observed by d.s.c.² The only sign of recrystallized material was found in some solvent-etched fracture surfaces⁹. In these cases some recrystallization occurred in the mechanically formed fibrils.

The dissolved, segregated component is mainly concentrated to the boundary regions of 'spherulite-like' formations. In addition, the micrographs of Figures 1a, b, c, e, f and g show lamella-like formations, most probably stacks of almost parallel crystal lamellae, each stack separated from its neighbour by segregated material. The higher order magnifications (Figures 1i, j) show these lamellae in more detail. The concentration of holes

(segregated component) increases towards the peripheral parts of the spherulites. The void content in the etched surfaces increases with the concentration of segregated component (W_s) in the samples. This dependence becomes most apparent on comparison of the micrographs shown in Figure 1 with the following data obtained by d.s.c.: 7022-IC-401.2 K $W_s=0.56$; 7006-IC-401.2 K $W_s=0.46$; 2912-IC-401.2 K $W_s=0.32$; 2215-IC-401.2 K $W_s=0.75$; 6375-IC-401.2 K $W_s=0.13$. The calculations yielding these data consider the difference in crystallinity between the segregated and the non-segregated component in accordance with the treatment in ref. (1). The values of the volume fraction of voids in the etched samples as determined by the intercept method are in general significantly lower than the corresponding values of W_s . These discrepancies can be explained on the basis of the incomplete dissolution of the segregated component (according to ref. (2)) and to the thickening of all structures due to the gold sputtering of the samples.

The etched samples shown in Figures 1a, b and d all have a high concentration of segregated material, but they have very different morphologies:

- Sample 7022-IC-401.2 K (Figure 1a) has large spherulites with a high concentration of segregated material within the spherulites between the main lamellae.

● Sample 7006-IC-401.2 K (Figure 1b) has somewhat smaller sheaf-like spherulites with a lower concentration of segregated material within the spherulites than sample 7022-IC-401.2 K. The major part of the segregated material is concentrated in the inter-spherulite regions.

● Sample 2215-IC-401.2 K (Figure 1d) has a very different structure: The spherulites are very small and incomplete. They seem to be embryos of spherulites.

The size measurements of the spherulite formations observed in Figures 1a, b and d are in agreement with those obtained from the polarized light micrographs, see Table 2.

For IC samples crystallized at lower T_c 's, the concentration of segregated component is lower and it is more difficult to observe the distribution of the segregated component in the structure; compare Figures 1a, g and h. In addition, it seems that the segregated component is more evenly distributed in the samples crystallized at the lower temperatures.

The differences between samples treated according to IC and A can be seen by comparing Figures 1b, f and 2a, b. Although the mass fraction of segregated component is 0.46–0.32 for the IC samples and 0.34–0.24 for the A samples, it is evident that segregated component is more uniformly distributed in the A samples. The accumulation of segregated material in the spherulite boundaries is much more pronounced in the IC samples. In the micrographs of etched A-393.2 K samples with a minimum content of segregated component and relatively low selectively of extraction it is still possible to observe spherulites (see Figure 2c).

The polarized light micrographs shown in Figure 3 are in good agreement with the scanning electron micrographs of the etched samples with regard to the size of the spherulites. The spherulite size data are summarized in Table 2.

CONCLUSIONS

Selective solvent treatment can be used to study both molecular fractionation and higher order structures in

Table 2 Size of supermolecular structures as observed by s.e.m. and by polarized light microscopy

Sample	Spherulite diameter (μm)	
	a	b
7022-IC-401.2 K	50–100	—
7006-IC-401.2 K	20–30	25
2912-IC-401.2 K	20–60	15–25
2215-IC-401.2 K	<5	<5 ^c
6375-IC-401.2 K	30	30
7022-IC-398.2 K	30–60	40
7006-IC-398.2 K	20–30	20
2912-IC-398.2 K	20–30	20
2215-IC-398.2 K	<5	<5 ^c
6375-IC-398.2 K	—	20

a By SEM

b By polarized light microscopy

c Distinct maltese-cross patterns could not be observed in the photomicrographs of this sample. The quoted size corresponds to the period of the black and white pattern appearing in the photomicrograph

melt-crystallized high-density polyethylene. Both the spherulites and the arrangement of stacks of crystal lamellae in the spherulites can be observed by SEM after preparation of the samples by this solvent etching technique. These morphological structures can be studied without serious interference from artefacts caused by swelling or recrystallization. The selective dissolution of well-defined segregated material from the samples

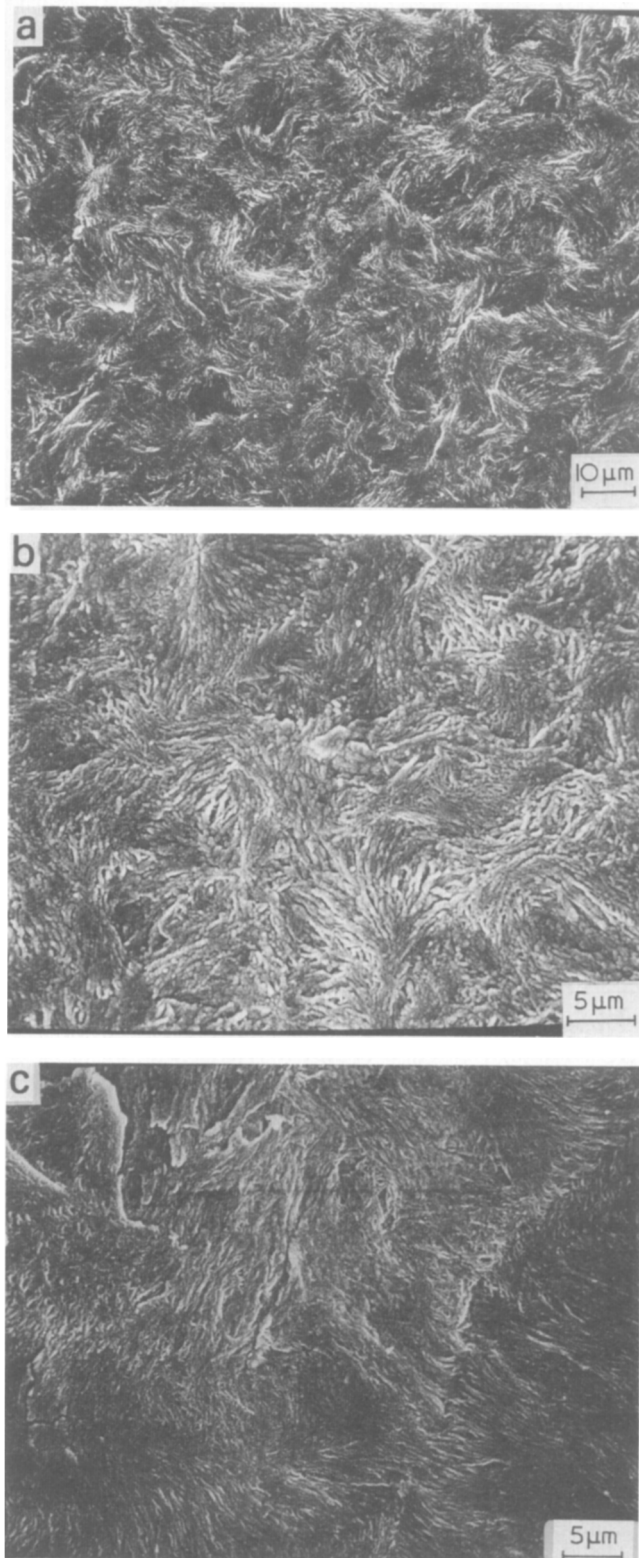


Figure 2 Scanning electron micrographs of solvent-treated samples: (a) 7006-A-401.2 K (b) 7006-A-398.2 K (c) 7022-A-393.2 K

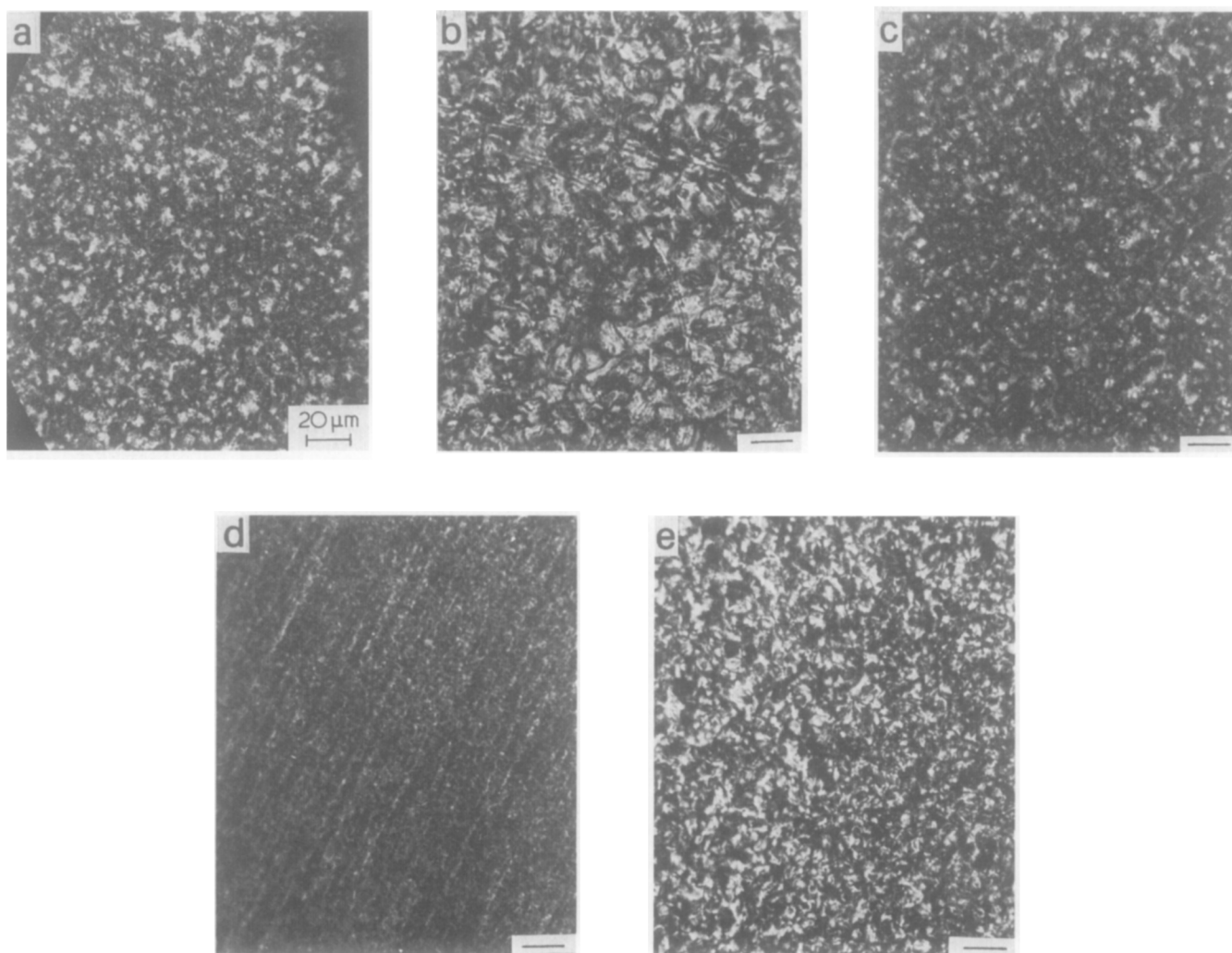


Figure 3 Polarized light micrographs of IC-398.2 K samples: (a) 7022 (b) 7006 (c) 2912 (d) 2215 (e) 6375 (all scale bars 20 μm)

demonstrated in detail in a previous report by d.s.c. measurements² forms the basis of this etching technique.

The segregated low molecular weight material is generally concentrated in the spherulite boundaries and between stacks of main crystal lamellae within the spherulites. Samples with a high concentration of segregated material and a low nucleation density (e.g. 7022 IC-401.2 K) have large 'open' spherulites with a considerable amount of segregated component within the spherulites, whereas samples with a lower concentration of segregated material and a higher nucleation density (e.g. 7006 IC-401.2 K) form smaller spherulites with less internal segregated material and a relatively larger portion of segregated material in the boundary regions.

The IC samples in general show a pronounced concentration of segregated material in the peripheral parts of the spherulites. The A samples, on the other hand, show a more uniform distribution of segregated material in the structure. Despite this 'unfavourable' distribution of segregated material, the spherulites can however be observed in the etched A samples.

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