TABLE I

Sr. no.	Composition used GaAs (mol %)	GaP (mol %)	Composition obtained after growth GaAs (mol %)	GaP (mol %)	Mode of preparing source	Doping if any	Result
1	—	—	83	17	GaAs$_x$ P$_{1-x}$ powdered and pressed in graphite block	Nil	Single crystalline layer
2	50	50	53	47	Powdered GaAs and GaP mixed and pressed in graphite block	Te present in GaAs source	Single crystalline layer
3	50	50	45	55	Remainder of no. 2	,,	,,
4	0	100	0	100	Powdered GaP pressed in graphite block	Nil	,,
5	30	70	35	65	Powdered GaAs and GaP mixed and pressed in graphite block	Te present in GaAs source	,,
6	30	70	35	65	Remainder of no. 5	,,	,,
7	50	50	54	46	Powdered GaAs and GaP mixed and pressed in graphite block	,,	Matt structure
8	50	50	45	55	,,	Nil	Needle growth
9	50	50	52	48	Remainder of no. 8	Nil	Single-crystal
10	50	50	50	50	Remainder of no. 9	Nil	Single-crystal
11	70	30	—	—	Powdered GaAs and GaP mixed and pressed in graphite block	Te present in GaAs source	Polycrystalline
12	90	10	—	—	Powdered GaAs and GaP mixed and pressed in graphite block	,,	Partly single-crystal
13	100	0	100	0	Powdered GaAs pressed in graphite	,,	Single crystalline layer
14	—	—	42	58	Powder pressed of GaAs$_x$ P$_{1-x}$	,,	,,

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The Effect of Chromic Acid on Polypropylene

Polypropylene is an important plastic because of its good combination of strength and rigidity over a relatively wide temperature range. It has been predicted [1] that it will eventually overtake high density polyethylene to become the second largest tonnage polyolefin. Successful use of this material requires data on the influence of cooling rate from the melt on the microstructure, and on the way in which the microstructure deforms under stress. Few data are available however because previously the only ways of revealing the microstructures of bulk test specimens were either by fracturing and examining fracture surfaces or by microtome sectioning. Research at Leeds has shown that the microstructures of bulk polypropylene specimens can be revealed non-destructively using a chromic acid etchant. This means that surface studies can be carried out using conventional reflection microscopy techniques and that now it should be possible to study microstructures at different stages in the deformation of a test specimen. This letter describes the etching technique used.

All experiments were carried out using annealed, compression-moulded, isotactic polypropylene supplied in the form of 0.32 cm thick sheets by ICI Plastics Division, Welwyn Garden City, Herts, UK. Initial properties of this material were: density 0.9135 g/cm^3; crystallinity (from X-ray diffraction) 63%; molecular weight (weight average) ca 190,000. The 6M chromic acid was prepared by dissolving 600 g chromic oxide (CrO_3) flake, supplied by the Associated Chemical Company, Harrogate, Yorks, UK, in 1000 cm^3 of aqueous solution. The polypropylene specimens (0.32 × ca 0.5 × ca 0.5 cm) were kept under the surface of the chromic acid solution in test tubes maintained at 70° C in a thermostat tank for times ranging up to 1000 h. The optimum treatment time for etching was found to be 96 h. On removal, the specimens were washed thoroughly with distilled water and acetone.

Fig. 1 is a typical view of the surface of the polypropylene in the "as received" state. Fig. 2 shows the surface after 50 h treatment in the 6M chromic acid solution at 70° C, whilst fig. 3 shows a fully-etched surface after 96 h treatment. Figs. 4 and 5 show a bulk specimen, which has been microtomed to half thickness, before and after the 96 h chromic acid treatment. Fig. 6 is another micrograph of a fully-etched surface, this time obtained using a scanning electron microscope.

Comparison of the shapes and sizes of the spherulites revealed by chromic acid etching, with those observed in microtomed sections of the material viewed using transmission optics and crossed polars, gives perfect agreement. This indicates that the observations seen in reflection represent genuine texture effects, and not some surface deposition due to the chromic acid itself, or some degradation product resulting from the attack. This is further substantiated by the Stereoscan observations in which, due to the large depth of field possible, certain spherulites are seen to have depressed central regions from which the radiating fibrils appear to emerge. This indicates that for these particular spheru-

Figure 1 Polypropylene surface before treatment showing scratches and moulding marks (reflected light × 700).

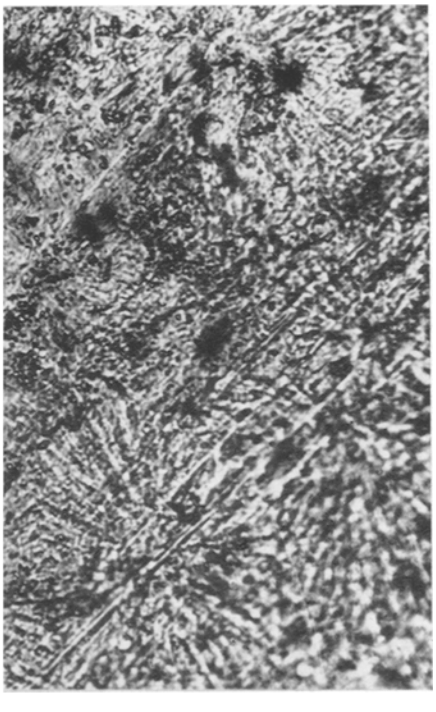

Figure 2 Polypropylene surface after etching for 50 h showing the partially-revealed spherulitic microstructure (reflected light × 700).

Figure 3 Polypropylene surface after etching for 96 h. The spherulitic microstructure is now fully revealed (reflected light × 700).

lites the spherulite centres are below the surface and that the chromic acid has revealed this phenomenon by a preferential etching action.

In order to gain information on the mode of the chromic acid attack, weight, thickness, density and infrared analysis measurements were made for treatment times up to 1000 h.

(i) The weight results showed a small, steady, rate of removal of ca 6×10^{-6} g polypropylene per hour. After the normal treatment time of 96 h, the weight loss from a bulk specimen of 0.10 g was ca 0.6%.

(ii) Thickness measurements, obtained using a micrometer gauge, gave no indication of any swelling, but showed a steady thinning down of the specimen at a rate of ca 0.15 μm per hour.

(iii) The densities were measured in a density gradient column made up with isopropanol and distilled water and maintained at 23° C. The density initially was 0.9135 g/cm^3, and this remained constant over all treatment times up to 1000 h. No measurements were made after this time.

(iv) The infrared analysis was carried out on microtomed sections of the polypropylene, ca 150 μm thick, which were examined initially and at various stages during treatment with the

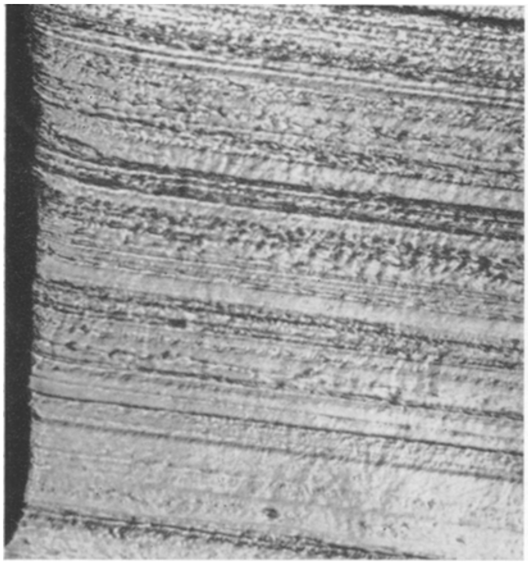

Figure 4 Interior surface of polypropylene produced by microtome sectioning. Scratches indicate cutting direction. A reference mark inscribed on the surface is seen as a thick black line on the left-hand side of the picture (reflected light × 555).

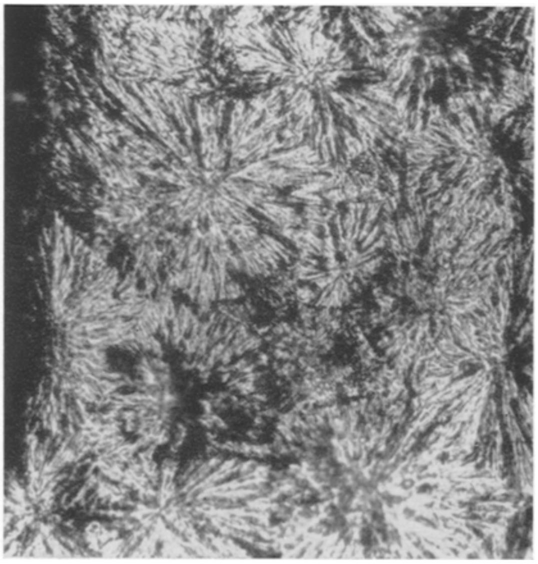

Figure 5 Identical surface (to fig. 4) after etching (reflected light × 555).

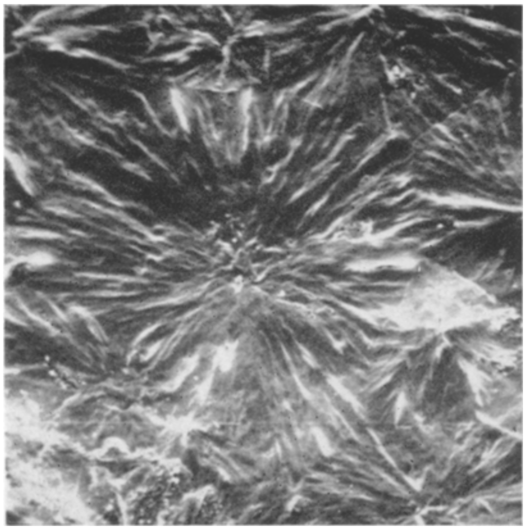

Figure 6 Fully etched polypropylene surface viewed with the Cambridge Instrument Company Stereoscan (×830).

chromic acid. The initial specimens gave spectra agreeing in detail with the results published by Snyder and Schachtschneider [2] and there was no change in the spectra after 500 h treatment with the chromic acid solution.

Discussion

The observations show that 6M chromic acid at 70° C can be used to etch crystalline polypropylene. Treatment times are of the order of 100 h. Chromic acid appears to attack crystalline and amorphous regions at approximately the same rate, thereby removing layers of polypropylene uniformly and revealing the microstructure of the interior. There is no change in density of the bulk specimens after extensive chromic acid treatment, implying that there is no change in percentage crystallinity. The infrared measurements show that there is no obvious change in overall chemical composition.

The chromic acid results are encouraging, for they suggest that it may now be possible to study the microstructures of bulk polypropylene test specimens as they undergo deformation, and hence determine deformation mechanisms. Such a programme of work is under way in the Metallurgy Department at Leeds. Chromic acid etching has also enabled us to determine the mode of fuming nitric acid attack on polypropylene. The results of this work will be published shortly.

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Electrical Conductivity during Hydrogen Reduction of Barium Titanate Single Crystals

In recent years, considerable research effort has been directed to a better understanding of electrical processes in oxygen-deficient barium titanate [1-7] and particularly in single crystals grown by the process described by Remeika [8]. It is well established that single crystals grown by this technique suffer from the incorporation of appreciable concentrations of impurities, notably potassium and fluorine from the solvent.

It has been recently shown by Arend *et al* [7] that these impurities play an important role in the chemical processes which take place during the early stages of the hydrogen reduction of these single crystals. The method employed by Arend involved chemical analysis of crystals reduced in hydrogen at temperatures of 900° C and above for periods from a few minutes to a few hours. This established that there are three regions in which different chemical processes are involved.

Initially, the hydrogen reacts with fluorine present in the crystal to produce hydrogen fluoride. This results in the fast liberation of electrons into the conduction band of the material.

Subsequently, a slower process of volatilis-