

## Nitric Acid Attack on Polypropylene. Weight and Density Changes and Blister Formation During the Initial Stages

V. J. ARMOND\* and J. R. ATKINSON, *Department of Metallurgy, University of Leeds, Leeds LS2 9JT, Yorkshire, England*

### Synopsis

Weight loss and density change results are presented to indicate the manner in which fuming nitric acid at 70°C attacks three grades of polypropylene of different crystallinity. The phenomenon of surface blistering is discussed in relation to the spherulitic structure at the surface of the bulk specimen.

### INTRODUCTION

The selective attack and embrittlement of polyethylene by fuming nitric acid was first reported by Palmer and Cobbold<sup>1</sup> who showed that the acid preferentially attacks and removes the less-ordered material thereby embrittling the sample. Reports of its use to study the ordered-disordered structural relationships in polyethylene have been made for single crystals<sup>2,4</sup> thin films,<sup>5</sup> drawn samples,<sup>6,7</sup> unoriented bulk samples,<sup>8</sup> and also for unoriented bulk samples of polypropylene.<sup>9,10</sup>

Recently, Hinton and Keller<sup>11</sup> have described the surface blistering which occurs during the initial stages of fuming nitric acid attack on unoriented bulk samples of polyethylene. The formation of blisters is reported to be related to the presence of columnar spherulites in a transcrystalline surface layer, although the blistering layer was appreciably thicker than the columnar skin.

Part of our work on structure-property relationships in bulk polymers has been concerned with the effect of fuming nitric acid on unoriented bulk samples of polypropylene. The route taken by an acid-induced crack through the spherulitic microstructure has been described elsewhere<sup>10</sup> and a brief mention was made of the blister formation which preceded cracking. This latter phenomenon will now be discussed in detail and results will be presented for weight and density changes during the attack.

### Experimental

**Materials.** Two annealed samples and one quenched sample of compression-moulded, isotactic polypropylene in the form of 3.2-mm-thick sections

\* Present address: Fulmer Research Institute, Stoke Poges, Bucks, England.

were supplied by I.C.I. Plastics Division, Welwyn Garden City, Herts., U.K. An additional commercial grade of polypropylene was obtained from G.H. Bloore Ltd., Stanmore, Middlesex, U.K. Some properties of the materials are listed in Table I. The nitric acid was 95%–98% fuming nitric acid supplied by B.D.H.

TABLE I  
Some Properties of Materials Used

Sample	Density $\times 10^{-3}$ , kg/m <sup>3</sup>	X-ray crystallinity	Weight average MW
Annealed-1	0.9135	63%	ca. 190,000
Annealed-2	0.9130	ca. 63%	ca. 190,000
Quenched	0.9060	58%	ca. 190,000
Bloore	0.9047	—	—

**Weight Changes.** After treatment with fuming nitric acid at 70°C, the reaction mixture was poured into excess distilled water and the polypropylene sample was removed, washed with more water, and then extracted with acetone in a Soxhlet apparatus for 6 hr. The sample was then dried and reweighed.

**Density Determinations.** Density measurements were made in a density gradient column made up with isopropanol and distilled water and maintained at 23°C.

**Microscopy.** The Reichert MeF light microscope was used to examine sections, ca. 20  $\mu\text{m}$  thick, cut from the bulk sample with a sledge microtome. The thin sections invariably curled up and the section edges, which were of interest, were cut from the curled section without flattening it, in order to minimize handling and possible destruction of the fragile surface regions.

## Results

### Initial Microstructures

The annealed-1 material showed large spherulites, 50–100  $\mu\text{m}$  in diameter, which extended to the surface (see Fig. 1). Spherulites nucleated at or near the surface assume a hemispherical shape. The annealed-2 material had, on average, a smaller spherulite size and some regions where columnar spherulites were present at the surface (see Fig. 2). In other regions spherulites extended to the surface as for the annealed-1 material.

The quenched sample had a similar microstructure to the annealed-2 sample, but the spherulites were on average smaller (10–40  $\mu\text{m}$  in diameter). In some regions columnar spherulites formed a 10- to 30- $\mu\text{m}$ -thick transcrystalline surface layer.

The commercial grade of polypropylene (Bloore) also showed a definite surface layer, 35–45  $\mu\text{m}$  thick, but it was not possible to resolve any spherulites in this region or in the bulk region below using the light microscope (see Fig. 3).



Fig. 1. Microtome section of annealed-1 polypropylene. Transmitted light and crossed polars.



Fig. 2. Microtome section of annealed-2 polypropylene. Transmitted light and crossed polars.

### Weight and Density Changes During Nitric Acid Attack

Experiments to follow the weight and density changes occurring during treatment with fuming nitric acid at 70°C were conducted using three grades of polypropylene: the annealed-1 sample, the quenched sample,

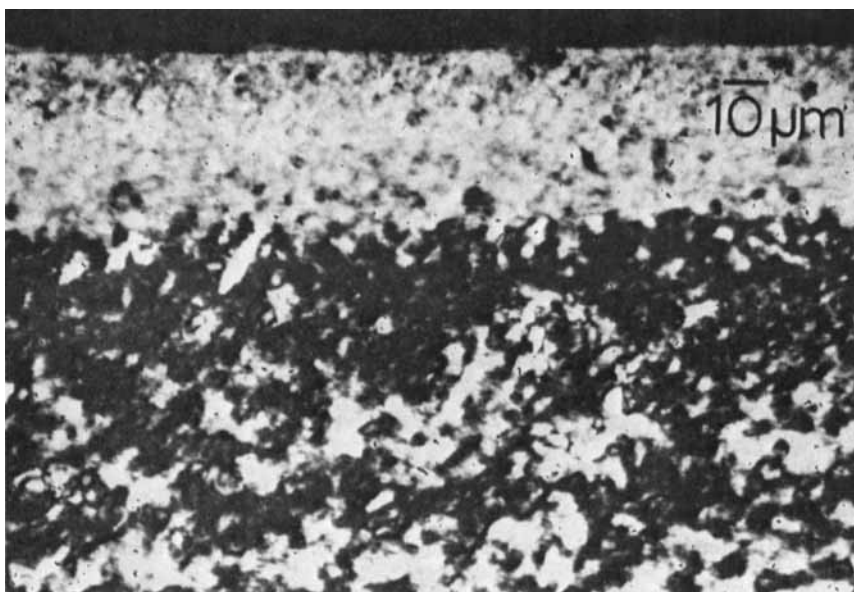


Fig. 3. Microtome section of Bloore polypropylene. Transmitted light and crossed polars.

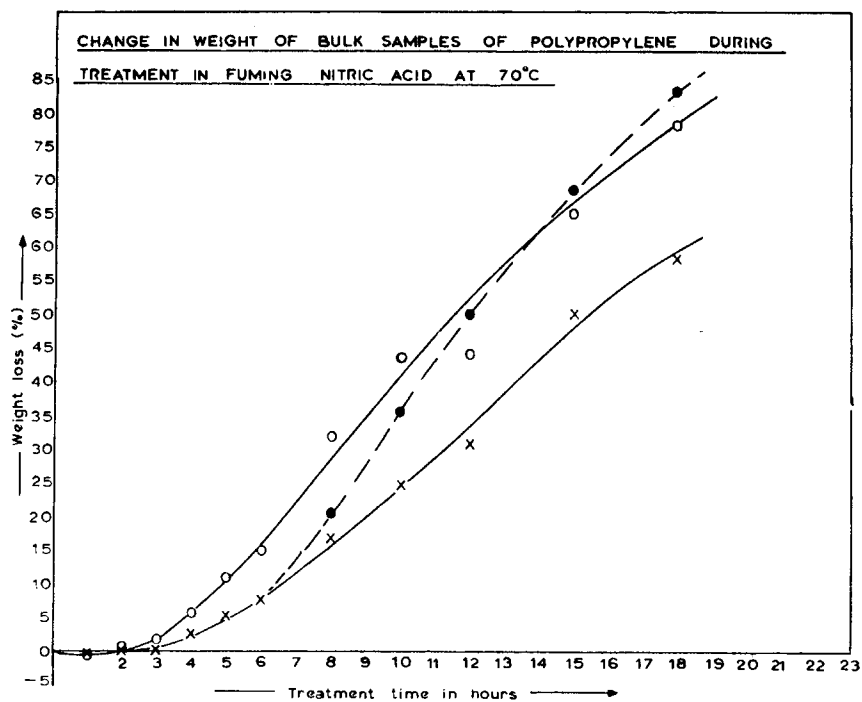


Fig. 4. Graph showing percentage weight loss of bulk samples of polypropylene during treatment in fuming nitric acid at 70°C: (X) annealed-1 sample; (●) quenched sample; (○) Bloore sample.

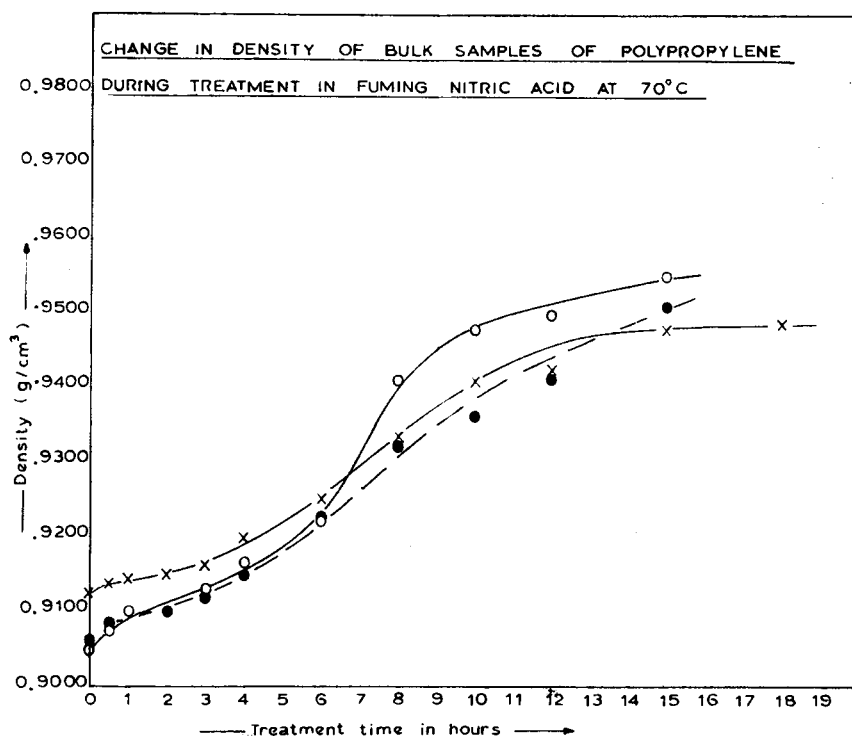


Fig. 5. Graph showing change in density of samples during treatment in fuming nitric acid at 70°C. Symbols as in Fig. 4.

and the Bloore sample. Tests showed that within the limits of experimental accuracy the results were identical for the annealed-1 and annealed-2 samples. All samples were cut to be as nearly as possible the same size, i.e.,  $3.2 \times 5.0 \times 5.0$  mm. The weight change results are presented graphically in Figure 4. Figure 5 shows how the densities changed during treatment in fuming nitric acid.

The appearance of the curves in Figure 4 indicates that the samples have all undergone a similar mode of weight change, the difference being in the rate of loss of weight. In the initial stages of treatment, up to approximately 2 hr, all three samples gained in weight. The maximum gain, by the quenched material, was 0.53%. This weight gain has been explained<sup>4,12</sup> as due to the attachment of heavy end groups ( $\text{NO}_2$ ,  $\text{COOH}$ ) onto the polymer chain. This attachment causes a rapid gain in weight in the early states of treatment and then, when the accessible disordered regions have been attacked, a gradual increase in weight caused by slow attack on lamellae. The effect of this addition will be noticeable only in the early stages as it will later be masked by the much larger weight loss due to the removal of material. Furthermore, in the case of bulk samples it is quite probable that in the early stages of treatment the acid has penetrated

into the bulk to some extent, but finds it difficult to remove oxidation products until further attack occurs. Both factors would contribute to the small increase in weight observed.

For treatment times greater than 2 hr, the loss of weight increased rapidly. After 18 hr the bulk samples were very fragile and often disintegrated on handling. Similar weight change experiments reported by Hook<sup>12</sup> showed that his bulk samples of polypropylene lost weight rapidly but then the weight remained constant. Our results show that the rapid weight loss, although diminishing somewhat at longer treatment times, continues up to the point when the sample is too fragile to handle. The weight loss at this time was ca. 60% for the annealed-1 sample and ca. 80% for the quenched and Bloore samples. An explanation put forward by Blundell and Keller<sup>4</sup>



Fig. 6. Microtome section from a bulk sample of annealed-1 polypropylene treated for  $\frac{1}{2}$  hr in fuming nitric acid at 70°C. Transmitted light and crossed polars.

for single crystals of polyethylene appears to fit our results. They divide the attack into two components: interlamellar attack, which is expected to proceed relatively quickly to an asymptotic value, and crystalline attack, which is expected to be slower but which will continue and have a linear dependence on time.

Figure 5 shows density values plotted against time. This graph shows that the Bloore material, which initially has the lowest density value (and therefore crystallinity), undergoes the largest density increase after 15 hr, while the annealed-1 material, with the highest initial density, undergoes the smallest change. These results confirm that the Bloore material (and the quenched material) contain more of the less dense disordered material which is preferentially attacked and removed by the acid.

After longer treatment times, ca. 10 hr for the Bloore material (ca. 43% weight loss) and ca. 13 hr for the annealed-1 material (ca. 38% weight loss, the density approached a fairly constant value. Thus most of the disordered or amorphous material had been removed and the final density value was that of the more highly crystalline residue. The final state was not achieved with the quenched sample whose density was still increasing after 15 hr.

## Blister Formation

### *The Annealed-1 Material*

The first sign of fuming nitric acid attack was the formation of surface blisters. These were observed after  $1/2$  hr of treatment at  $70^{\circ}\text{C}$ . A typical blister is shown in Figure 6. The material raised in the blister appears to have been detached along the radial arms of a large bulk spherulite. This shows that the presence of a transcrystalline surface layer is not essential for blister formation, contrary to the conclusions of Hinton and Keller.<sup>11</sup>

After having penetrated through the surface, the acid spreads into the surrounding regions by reacting with any available less-ordered material. This is indicated by the appearance of small internal cracks running approximately parallel to the surface. Figure 7 shows a section from a sample treated for 1 hr. A chunk of surface material has become detached, probably during sectioning, and a series of small cracks can be seen in the

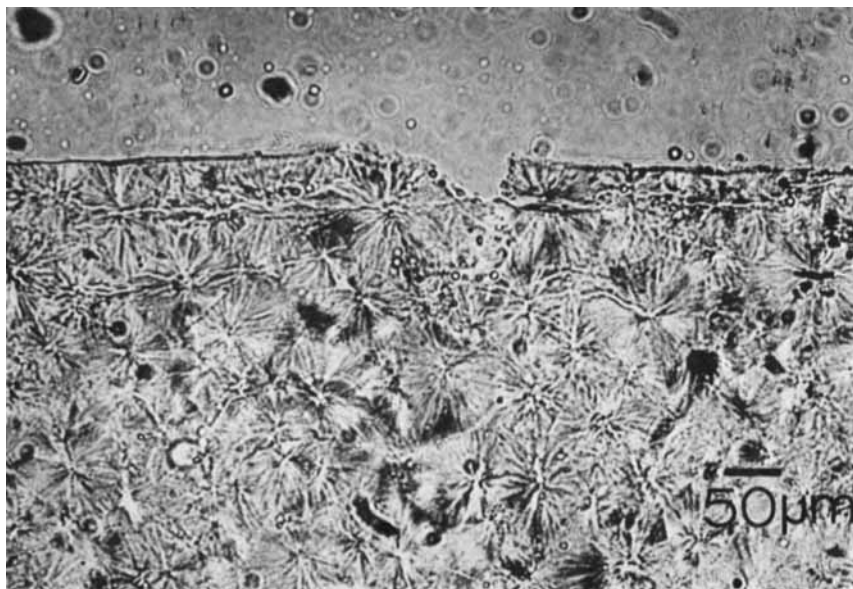


Fig. 7. Microtome section of annealed-1 polypropylene treated for 1 hr in fuming nitric acid at  $70^{\circ}\text{C}$ . Transmitted light and crossed polars but with the microscope analyzer partly removed.



Fig. 8. Higher magnification view of the cavity in Fig. 7, showing a large crack running from center to center of neighboring spherulites. Transmitted light and crossed polars.

material surrounding the cavity. These cracks follow radial paths through bulk spherulites. The micrograph has been obtained with the microscope analyzer partly removed in order to highlight the cracks. The area to the left of the cavity is shown in Figure 8 viewed with crossed polars.

The blisters increased in number and size during further treatment and after 2 hr were between 100 and 400  $\mu\text{m}$  in diameter and often covered several spherulites. After 3 hr of treatment the surface began to crack and after 4 hr it was covered by a crazy-paving network of cracks. These cracks have been shown previously<sup>10</sup> to follow radial routes through the bulk spherulites.

#### *The Annealed-2 Material and the Quenched Material*

These two materials will be considered together since their initial microstructures were very similar. In both cases thin internal cracks were observed for treatment times less than  $\frac{1}{2}$  hr and before any blistering occurred. These cracks ran approximately parallel to the surface through the first layer of spherulites below the transcrystalline surface region. During further treatment the cracks spread deeper into the bulk though still remaining nearly parallel to the surface. Figure 9 shows a section of annealed-2 material and Figure 10 a section of quenched material, in both cases after  $\frac{1}{2}$  hr of treatment with fuming nitric acid. Cracks are seen running below the transcrystalline surface layer and travelling along radial paths from center to center of bulk spherulites. Figure 11 shows annealed-2 material which possesses a relatively thick (ca. 35  $\mu\text{m}$ ) transcrystalline layer. Again cracks may be seen to run along radial paths through the



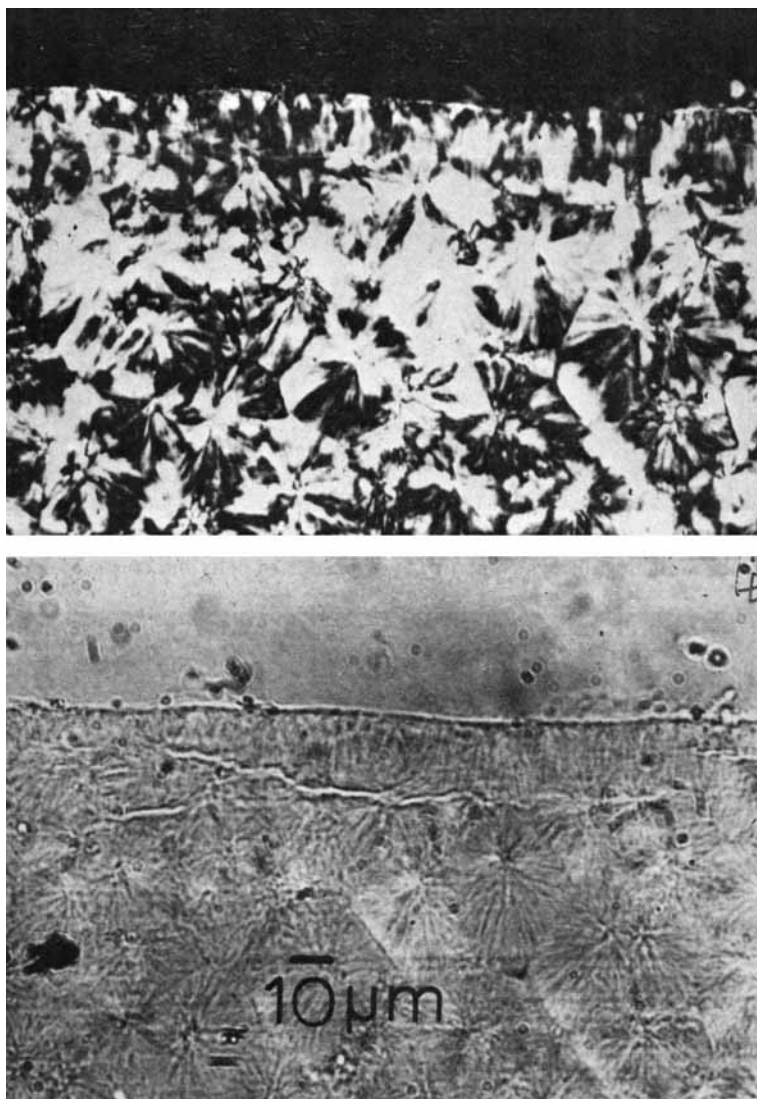


Fig. 9. Microtome section from a bulk sample of annealed-2 polypropylene treated for  $\frac{1}{2}$  hr in fuming nitric acid at  $70^\circ$ . Top picture was obtained using transmitted light and crossed polar. In bottom picture, the microscope analyzer has been partly removed and cracks can be seen below the surface running nearly parallel to the surface.

first layer of bulk spherulites except occasionally, when a crack follows the transcrystalline boundary.

Both materials suffered blister formation during subsequent acid treatment ( $\frac{1}{2}$  to 2 hr). The rate of blister formation was greater for the quenched samples, a not unexpected result in view of the greater content of disordered material in these samples. Figure 10 shows a symmetrical blister in the quenched material after  $\frac{1}{2}$  hr of treatment. Material ca. 13

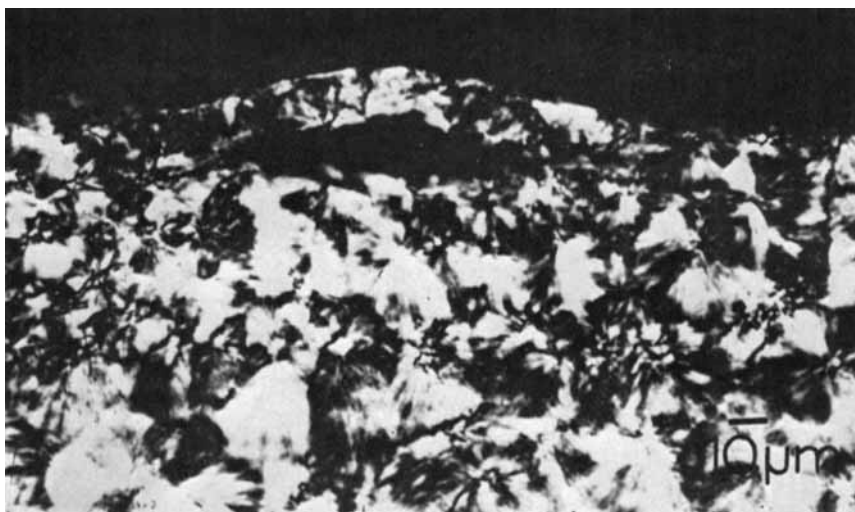


Fig. 10. Microtome section from bulk sample of quenched polypropylene treated for  $\frac{1}{2}$  hr in fuming nitric acid at  $70^{\circ}\text{C}$ . Transmitted light and crossed polars.

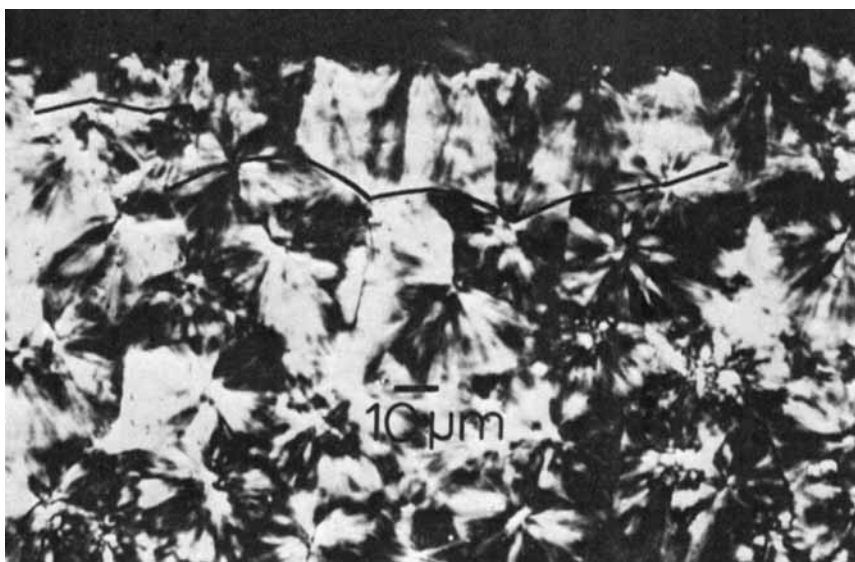


Fig. 11. Microtome section from a bulk sample of annealed-2 polypropylene treated for  $\frac{1}{2}$  hour in fuming nitric acid at  $70^{\circ}\text{C}$ . The crack path has been marked in. Transmitted light and crossed polars.

$\mu\text{m}$  in thickness has been raised up. Figure 12 shows a nonsymmetrical blister on the same material which has raised up material ca.  $13\ \mu\text{m}$  thick on one side and ca.  $25\ \mu\text{m}$  thick on the other. A point to note is that the raised material shown in Figure 10 is not transcrystalline, and the thinner raised-up material shown in Figure 12 does not appear to possess a transcrystalline



Fig. 12. Microtome section from a bulk sample of quenched polypropylene treated for  $\frac{1}{2}$  hr in fuming nitric acid at  $70^{\circ}\text{C}$ . Transmitted light and crossed polars.

structure. The material raised on the thick side of the blister in Figure 12 appears to have been detached at the boundary of the transcrystalline layer. In general, however, the thickness of the blistered material was slightly greater than the depth of the transcrystalline surface layer.

#### *The Bloore Material*

Weight loss and density change results showed that acid attack on this material was more rapid than attack on the annealed and quenched samples.

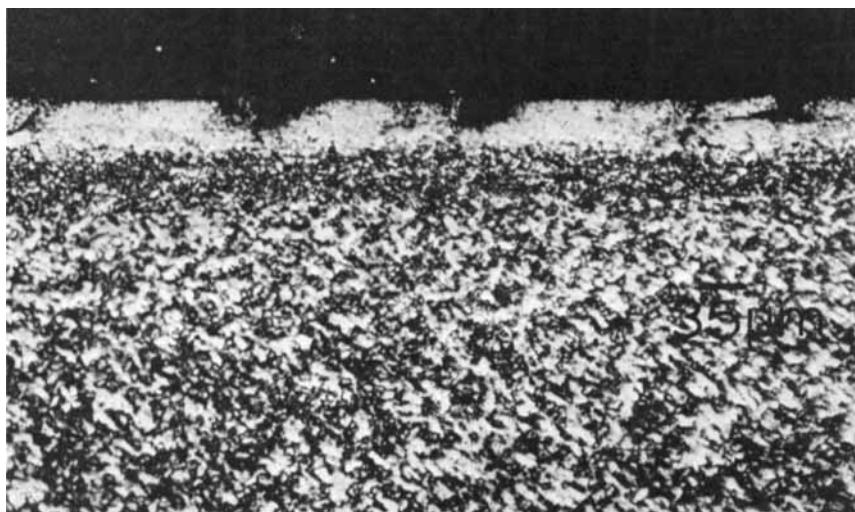


Fig. 13. Microtome section from a bulk sample of Bloore polypropylene treated for 2 hr in fuming nitric acid at  $70^{\circ}\text{C}$ . Transmitted light and crossed polars.

However, the internal cracks and blisters associated previously with the early stages of attack were not observed. Examination of thin sections by transmission microscopy indicated that no blisters occurred at any stage of the treatment. This was confirmed by an examination of the surface of the bulk sample using reflection optics. After 3 hr the surface was covered with a network of cracks and was severely embrittled.

Figure 13 shows a transmitted light micrograph of a section from a sample treated for 2 hr. Chunks of material have been removed from the surface. The depth of attack is less than the thickness of the surface layer. Examination of the sections with the microscope analyzer partly removed did not reveal any of the small internal cracks which were prominent in the annealed and quenched spherulitic samples.

### Discussion

The weight loss and density change results confirm that polypropylene is attacked by fuming nitric acid in the accepted manner. For all three samples studied (annealed-1, quenched, and Bloore), an initial small weight gain was followed by a rapid weight loss and an almost equivalent density increase. For all three samples the weight loss continued but at a somewhat diminished rate until the samples were too fragile to handle. These results are at variance with those of Hock<sup>12</sup> whose polypropylene samples initially lost weight rapidly but then attained a constant weight, but can be explained by a theory of Blundell and Keller.<sup>4</sup> Weight loss and density change results show that the material of lowest crystallinity initially is attacked most rapidly and undergoes the largest increase in density.

It is instructive to compare the modes of nitric acid attack on the four samples of polypropylene investigated. In the annealed-1 material, where bulk spherulites extended to the surface and a transcrystalline layer was not observed, small blisters were formed and then cracking occurred parallel to the surface along radial paths through spherulites. In the annealed-2 and quenched samples, both possessing regions of columnar spherulites in a transcrystalline skin, larger blisters (in the sense of thickness of raised material) were formed and were preceded by networks of thin cracks running parallel to the surface through bulk spherulites. In the commercial (Bloore) sample, which displayed a pronounced surface region though no spherulites could be resolved in the light microscope, no blisters were observed.

Thus it appears that a requirement for blisters to form is that a region containing spherulites must be present near to or at the surface. The nitric acid can travel through this region and penetrate the material in directions approximately parallel to the surface. Initially the acid diffuses into the bulk material via any possible routes. Figures 9 and 11 suggest that initial penetration most readily occurs through a transcrystalline layer, but it can also occur via radial paths through bulk spherulites situated at the surface (Fig. 6). Ease of penetration through spherulites will depend upon the extent of interfibrillar linking. In our materials, as discussed previously, we believe that the disordered atactic and low molecular weight material is

concentrated between fibrils and, as a result, these are more fibrillar links across spherulite boundaries than between fibrils. Hence nitric acid will penetrate between the fibrils rather than at spherulite boundaries. After penetration, the acid spreads out through the material by attacking interfibrillar links and by leaching out disordered material from the bulk spherulites, and in doing so creates a series of radial cracks in the spherulites. These cracks effectively loosen surface layers and it is suggested that the stresses exerted by the buildup of acid and of gaseous oxidation products within the cracks cause localized swelling of the weakened surface. Cracks form more easily parallel to the surface rather than perpendicular to it, because the surface can blister to accommodate the reaction products.

The commercial (Bloore) polypropylene possesses no spherulites of sufficient size for the acid to penetrate easily into the interior. However this material will contain a greater amount of the more readily attacked amorphous material and probably also more interfibrillar links because of the generally less-ordered structural arrangement. The material is therefore attacked at a relatively rapid rate. Blistering does not occur because the acid cannot penetrate to the boundary of the surface layer.

In conclusion, it has been shown that for blistering to occur, a region containing spherulites must be present near to or at the surface. Blistering involves, first, the penetration of acid into the interior; second, the severing of interfibrillar links in bulk spherulites and consequent cracking approximately parallel to the surface along radial routes through spherulites; and third, the raising up of surface layers due to a buildup of acid and oxidation products within the cracks produced. Penetration of acid into the interior is influenced by the crystalline texture of the surface and is most rapid through a transcrystalline layer.

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Received February 26, 1970

Revised March 30, 1970