sample is filtered through a 5 μ Millipore filter at 140° and immediately measured at 140°.

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Microscopy of Isotactic Polypropylene Crazed and Fractured in Liquid Nitrogen

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Crazing is commonly associated with glassy amorphous polymers.[1,2] The crazes are formed by highly localized drawing of the unoriented material. Such plastic deformation yields high molecular orientation of the material in the crazes. These are relatively thin, a few microns in the stress direction, but can grow laterally as long as the local stress concentration at the sharp tip of the craze is sufficient for propagation. Under homogeneous, one-dimensional tensile stress, each craze may extend through the whole cross-section of the sample, the craze plane being perpendicular to the stress direction. The growth of craze thickness occurs mainly by progressive plastic deformation of the already crazed material and not so much by conversion at the craze boundary of the unoriented polymer into crazed material. This thickness growth implies that the bulk density in the craze diminishes by longitudinal void formation. In this state, the craze consists of numerous fibrils bridging the gap between the uncrazed bulk material on each side of the craze. The high molecular orientation in the fibrils gives them a high tensile strength; therefore, the craze does not significantly weaken the sample although eventually a crack will nucleate in a craze and not, as a rule, in uncrazed material. The sequence of events leading from crack nucleation to crack propagation, and the important role played by the craze, have been described in great detail by Kambour[3] and by Murray and Hull.[4-8]

A few reports in the literature indicate that crazing can occur in crystalline polymers as well.[9-14] In particular, crystalline polypropylene (PP) was shown by van den Boogaart[11] to craze at room temperature and above. We recently observed extensive crazing in smectic polypropylene at low temperatures, in the range between −210 and 0°, and a pronounced dependence of crazing on the gaseous environment.[14] This last effect seems to be closely related to the environmental stress crazing of amorphous polymers recently reported by Parrish and Brown.[15]

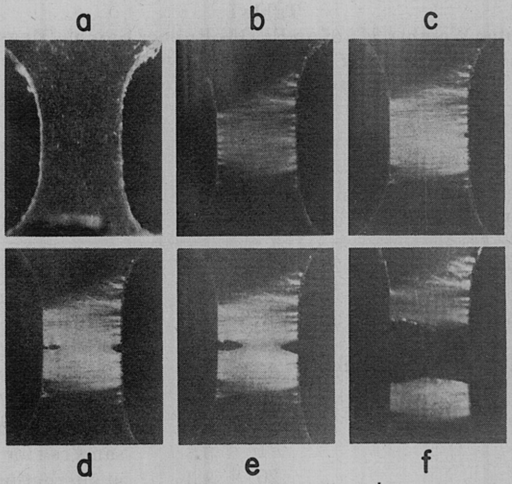

Figure 1. Optical micrographs at low magnification of crazing in PP while strained in liquid nitrogen (a) 0%, (b) 19%, (c) 33%, (d) 35%, (e) 49%, and (f) after rupture at approximately 50% strain. Illumination at about 45° to optical axis from behind the sample. Width of the sample was 0.5 cm.

The main feature of our observations was a dramatic increase of strain to break and of craze density at temperatures close to the boiling point of the surrounding gas (nitrogen, oxygen, carbon dioxide, and, as found recently, argon), *i.e.*, at high activity of the gas. In nitrogen at 1 atm the material, comparatively brittle between −50 and −140°, showed increasing toughness, ductility, and extent of crazing below −140°. The strain to break became a maximum at −196°, the boiling point of nitrogen, and did not change perceptibly down to the solidification point of nitrogen, the lowest temperature of our investigation. Thus, the extent of crazing and the concomitant strain to break seem to be related to the activity of the gas. When increasing the temperature above the boiling point, the gas activity rapidly decreases and so does the strain to break. At −140° no effect of the nitrogen is observable. The strain to break has reached the plateau value identical with that observed with the sample loaded under vacuum. Moreover, the vacuum data are identical with those in helium. Under atmospheric pressure, the activity of helium gas at liquid nitrogen temperatures is indeed so low that the environmental effect on plastic deformation of crystalline polypropylene can be neglected.

Isotactic PP in the smectic modification, crazed and fractured in liquid nitrogen, not only shows strain to break unusually high for a homopolymer, up to 60%, but also rather unique features of the fracture surface when examined by optical and scanning electron microscopy. Such microscopical observations are reported below.

As in the previous experiments,[14] a commercial film of isotactic polypropylene 0.125 mm thick (made by the Rexall Chemical Co.) was used. According to X-ray diagrams, the crystallites are in the so-called smectic form and randomly distributed, *i.e.*, the film is isotropic. Micrographs of crazing of smectic PP samples in liquid nitrogen are shown in Figure 1 as obtained at gradually increased strain, up to the final fracture of the specimen. The quality of the pictures is relatively poor since they were obtained by observation inside the low-temperature Dewar so that the light had to pass through two glass

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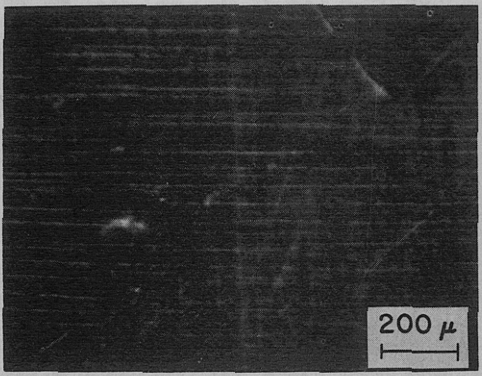

Figure 2. *Optical micrograph of crazes far from the fracture,* taken at room temperature under crossed polarizers and a first-order red gypsum plate.

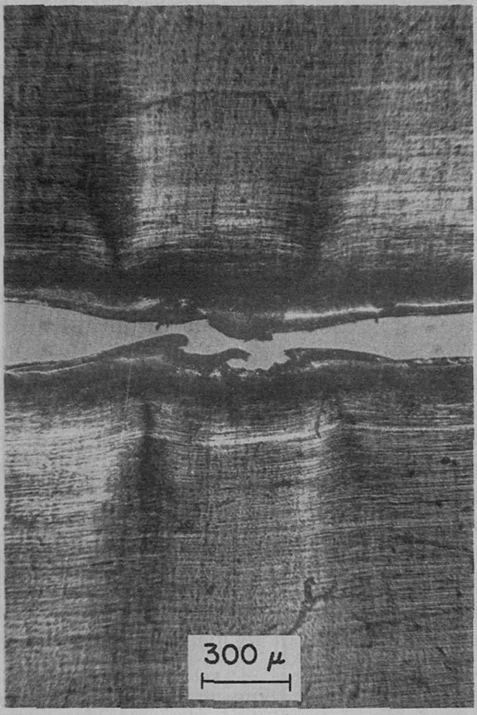

Figure 3. Optical micrograph of fractured sample, taken at room temperature between crossed polarizers and a first-order red gypsum plate.

walls of poor optical quality. The first crazes are observed to originate from flaws at the edges of the sample. Their number rapidly increases with strain. They grow in the direction perpendicular to the stress as crazes do in amorphous polymers. After a while, a craze at the edge of the sample opens into a crack with a well-rounded tip (Figure 1c). Propagation of this crack is noncatastrophic and comes to a halt when the strain rate is zero. Before the propagation of this first crack made much progress two new cracks appear, one at the opposite edge of the sample, the other a hole, on almost the same level as the first crack (Figure 1d). In Figure 1e, the secondary *cracks have* coalesced into a single crack. At this stage, with 49% overall strain, the crazes are extremely thick, up to 20 μ as es*timated from micrographs taken at higher magnification.* Finally, at 50% strain, fracture and subsequently considerable strain recovery occur (Figure 1e). There remains *substantial plastic deformation, however,* as will be seen below.

A view of the crazes at higher magnification can be obtained at room temperature. The sample crazed and fractured in liquid nitrogen was observed in an optical microscope between crossed polarizers and a first-order red gypsum plate. Since the fractured sample can freely retract the crazes can close. Thus, one observes only the traces of the crazes left after this contraction and not the crazes in their actual shape under stress in liquid nitrogen (Figure 2). But one still sees many important details. The crazes are rather smooth, extending over a fairly large section of the sample. Many extend indeed from one to the other lateral boundary. Figure 2 shows crazes far removed from the fracture surface. They are slightly curvilinear because the dumbbell shape of the sample distorts the stress field in this region from a strictly unidirectional one. The average separation between crazes is about 25 μ. In order to attribute plastic strains of 20–40%, *as typically obtained* in liquid nitrogen, entirely to crazing requires that the crazes grow in thickness up to 10 μ. This estimate is in *good agreement with the above mentioned maximal observed* craze thickness in the sample under strain.

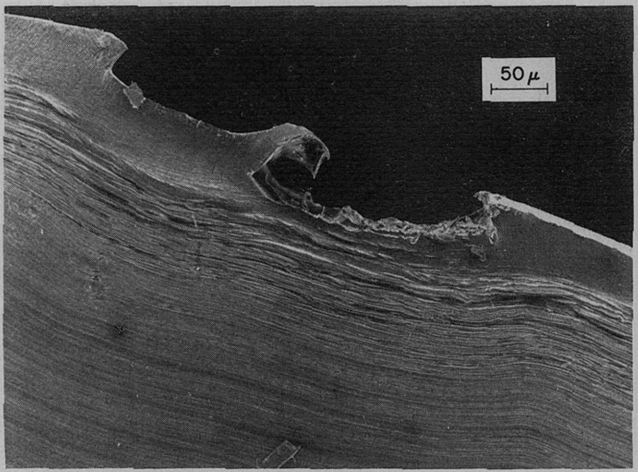

Figure 4. Scanning electron micrograph of the location of final rupture (see Figures 1 and 3).

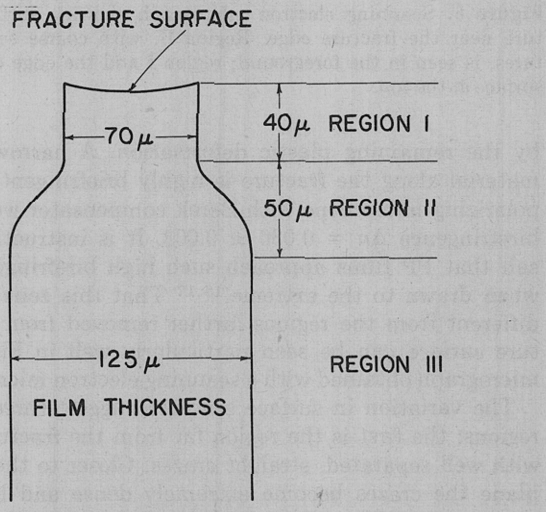

Figure 5. Cross-section of sample perpendicular to crack propagation.

Figure 3 is a micrograph taken under identical conditions as Figure 2. Whereas PP samples, crazed in liquid nitrogen to a strain short of crack initiation, will recover the entire strain upon warming to room temperature, such complete strain recovery clearly does not take place in a fractured sample. The two fracture surfaces do not match, and even far from the fracture the initially straight crazes have been permanently deformed into curvilinear shape

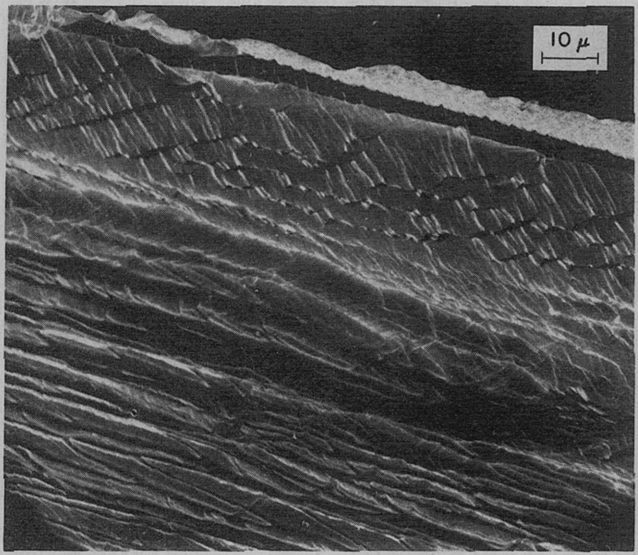

Figure 6. Scanning electron micrograph showing surface structure near the fracture edge. Region II, with coarse surface features, is seen in the foreground; region I and the edge of fracture surface at the top.

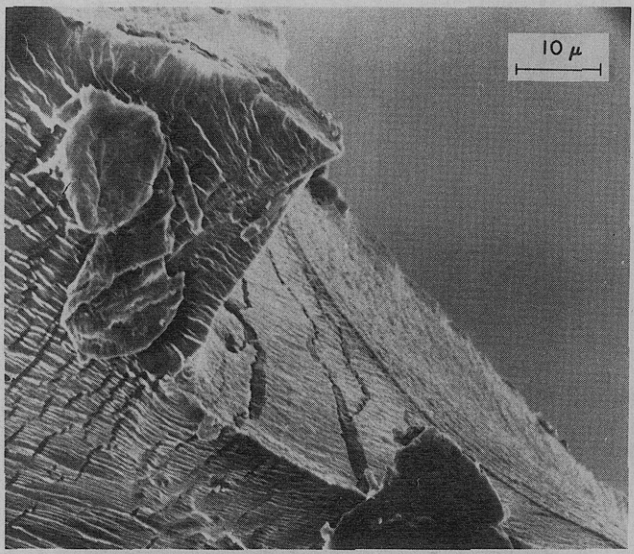

Figure 7. Scanning electron micrograph of the fracture surface in the neighborhood of catastrophic failure.

by the remaining plastic deformation. A narrow zone of material along the fracture is highly briefringent. Using a polarizing microscope with Berek compensator we found a birefringence $\Delta n = 0.030 \pm 0.003$. It is instructive to recall that PP films approach such high birefringence only when drawn to the extreme.[16,17] That this zone is rather different from the regions farther removed from the fracture surface can be seen particularly well in Figure 4, a micrograph obtained with a scanning electron microscope.

The variation in surface sructure suggest three distinct regions: the first is the region far from the fracture plane, with well separated, straight crazes. Closer to the fracture plane the crazes become extremely dense and highly interconnected. The average distance between adjacent crazes is only 2 μ and this is less than the craze thickness under stress in liquid nitrogen. The surface in this second region is very coarse. Considerable thinning of the sample occurs in this region. In the third region, in the already-mentioned narrow zone along the fracture, the surface is relatively smooth again. A schematic cross-section of the sample perpendicular to the crack propagation direction is shown in Figure 5. The dimensions given are average values.

The fracture surface is typically rather smooth where the single crack has propagated gradually, as can be seen at the right of Figure 4. The more rugged features in the fracture surface seen in Figure 4 are somewhat atypical and due to the catastrophic final rupture when the two cracks (Figure 1e) met. At the left of Figure 4 the crack which normally seems to follow a craze appears to have jumped a considerable distance (∼33 μ) to a neighboring craze.

The almost complete disappearance of crazes in the narrow zone along the fracture surface, with some fine isolated markings left, may permit the speculation that the crazes coalesced in the stress direction by complete transformation of the original matrix into a drawn material of void content somewhere between that of normal polymer and that of the single craze. This is probably made possible by the high density of crazes or, expressed another way, the small thickness of the layer of uncrazed material between crazes. At the crack tip, these thin layers may become drawn out and transformed into oriented fibrils. The lateral coalescence of craze voids may then account for the reduced thickness of the sample in this region.

At higher magnification, a new system of surface markings is resolved in the narrow zone along the fracture (Figure 6). This consists of fairly large steps whose edges subtend an angle of about 30° with the crack propagation direction, and, more or less perpendicular to these, a system of smaller steps. The bright object at the top in Figure 5 is a thin membrane of material such as can be frequently seen overhanging the edge of the fracture surface.

Figure 7 shows the jump in the fracture surface already seen in Figure 4, now at higher magnification. The catastrophic rupture that has taken place not far from this point has caused cracks in the fracture surface; such cracks are not present in regions of slow crack propagation.

In conclusion, the foregoing microscopic evidence shows that stress crazing and final fracture of smectic PP in liquid nitrogen involve considerable plastic deformation. When the polymer is stressed and fractured at the same temperature −196°, but under vacuum, it behaves brittly and practically no plastic deformation is observed. This further shows that liquid nitrogen acts as a plasticizer, as has been recently contended.[14]

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Characterization of Styrene–Isoprene Block Copolymers by Gel Permeation Chromatography

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The advent of anionic polymerization techniques, specifically those involving the organolithium systems, has made possible the preparation of many novel linear block

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