

LETTERS TO THE EDITORS

The Crystal Structure of Quenched Polytetrafluoroethylene

When polytetrafluoroethylene is cooled slowly from above its crystalline melting point ($327^{\circ}\text{C}.$) to $25^{\circ}\text{C}.$, it crystallizes in a hexagonal unit cell. Each chain is twisted to form a helix with 15 CF_2 groups per 180° turn.¹ Kilian and Jenckel² have concluded that this helical structure is not formed when the polymer is quenched rapidly from the melt.

A sheet of high molecular weight polytetrafluoroethylene 65 mils thick was constrained between two wire screens which prevented the sample from bending during heat treatment without application of pressure to the surface. The assembly was heated in an oven at $380^{\circ}\text{C}.$ for 1 hr. and then rapidly plunged into ice water to quench the polymer. A similar sample was heated at $380^{\circ}\text{C}.$ for 1 hr., and then cooled at $1^{\circ}\text{C./minute}$. The densities of these samples were 2.1485 and 2.200 g./cc. respectively.

An x-ray diffractometer scan made by reflection from the surface of the slow-cooled sample (Fig. 1a) showed four strong reflections. The (110) and (200) reflections are due to the lateral packing of the chains, and the (107) and (108) reflections are related to the helical structure of each chain. A similar scan from the quenched sample (Figure 1b) contained only the (110) and (200) reflections. This confirms the measurements reported by Kilian and Jenckel.

The diffractometer records x-rays scattered principally from the surface of the specimen, say 10 mils deep. When about 17 mils was removed from the surface of the quenched sample, the diffractometer scan shown in Figure 1c was obtained. The (107) and (108) peaks are clearly evident, but all of the peaks are lower in intensity than those in Figure 1a because of the lower degree of crystallinity and the roughness of the cut surface.

A section of the surface of the quenched specimen was

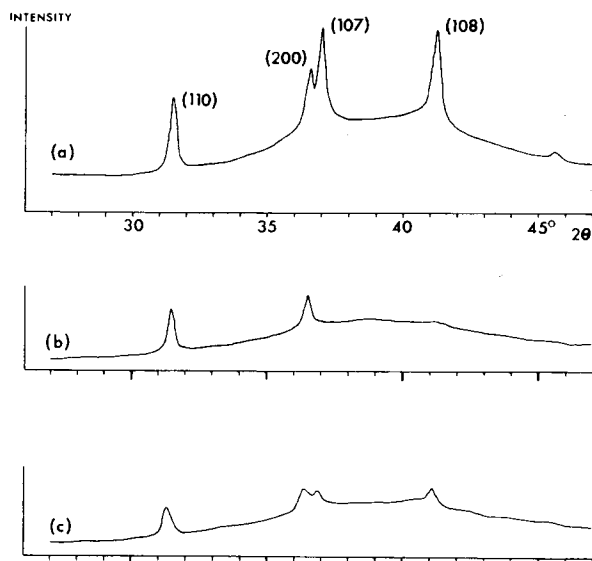


Fig. 1. X-ray diffractometer scans.

examined by x-ray photography. A photograph in which the x-ray beam was perpendicular to the surface plane shows no preferred orientation in the diffraction rings. On the other hand, a photograph in which the beam was parallel to the surface plane shows the rings broken into arcs. The equatorial reflections (100), (110), and (200) lie along a locus perpendicular to the surface. The (107) and (108) reflections lie in the quadrants on either side of the equatorial reflections. An idealization of this photograph is shown in Figure 2. The dotted line in Figure 2 shows the relationship between the diffractometer scan and the photograph. The diffractometer records only those reflections which lie in the plane perpendicular to the plane of the specimen. As Figure 2 shows, only the $(hk0)$ reflections lie in the perpendicular plane; the (107) and (108) reflections, although present, scatter out of this perpendicular plane and are not recorded on the counter. Thus the scan from the oriented surface is given by Figure 1b. The type of orientation of

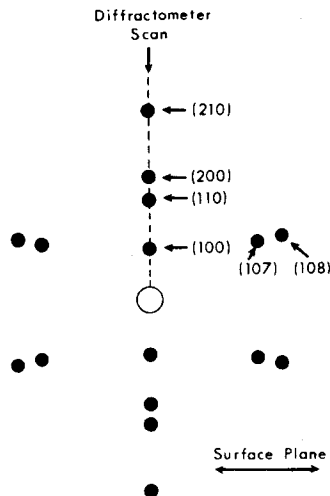


Fig. 2. Idealized x-ray photograph through edge of specimen.

the unit cells which produces the observed distribution of diffracted intensity is called planar orientation; a given crystal axis is parallel to a reference plane. In this case, the c (chain) axes lie in the surface plane of the quenched specimen. Figure 1c and additional x-ray photographs show that the interior of the quenched specimen is essentially unoriented.

Thus, three-dimensional x-ray data show that quenched polytetrafluoroethylene, although lower in crystallinity, possesses the same unit cell and helical chain structure as slow-cooled material. However, quenching produces a high degree of planar orientation on the surface, which strongly influences the nature of the diffractometer data.

References

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On the Discontinuity in the Flow Curve of Polyethylene

Bagley, Cabott, and West¹ report that in the extrusion of polyethylene there is a critical shear rate above which the extrudate becomes rough, twisted, and distorted, a phenomenon which has been termed melt fracture. Using a linear polyethylene, they found that there is a pressure region in which the output is double-valued and the extrudate filaments can be either smooth or rough, depending on the output value. This is illustrated in Figure 1.

In instruments that operate at constant volume displacement, the extruded filament will be smooth at all pressures below A. It will change to helical (wavy) or rough forms, or both, between A and B. At B, the discontinuity occurs. On further increase of rate of volume displacement, the filament will manifest various, continuous forms of distortion from smooth, to smooth and rough, to very rough. Pressure-sensitive devices will indicate corresponding changes in shear stress between A and B. By operating at different volume displacement rates, curves analogous to Figure 1 can be constructed.

A series of high-density polyethylenes have been characterized with respect to their molecular weight and a molecular weight distribution factor by a rheological method developed by one of us.² The data are summarized in Table I. A Baldwin tensile machine, modified to operate as an extrusion rheometer, was used to study the melt fracture properties of these resins. The experiments were carried out at 190°C. with a flat entry die having a radius of 0.035 cm. and a length of 1.05 cm. Results of a typical

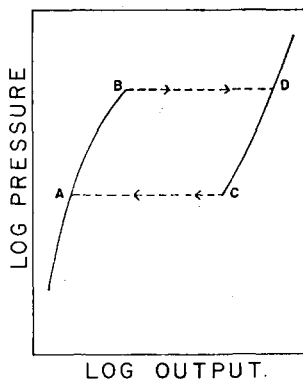


Fig. 1. Flow of a linear polyethylene through a capillary.

TABLE I
Flow Parameters of Resins^a Studied and Melt Fracture Behavior

| Resin | $\eta_0 \times 10^{-5}$, poises ^b | $K \bar{M}_w / \bar{M}_w$ $\times 10^8$ ^c | Type of melt fracture in cycle |
|-------|--|---|-----------------------------------|
| A | 18.0 | 13.1 | Rough-very rough-rough |
| B | 15.4 | 9.8 | Spiral-rough-spiral |
| C | 17.0 | 8.2 | Smooth-spiral-rough-smooth |
| D | 16.4 | 7.4 | Smooth-spiral-rough-smooth |
| E | 1.08 | 9.7 | No cycle |

^a Ethylene-butene-1 copolymers, 0.950 density.

^b Zero shear viscosity; see Ref. 2.

^c Rheological molecular weight distribution factor; see Ref. 2.

TABLE II
Typical Melt Fracture Data (Resin A)

| Dial ^a | Pressure, psi $\times 10^{-3}$ | Remarks |
|-------------------|-----------------------------------|------------------------|
| 45 | 1.55 | Smooth extrudate |
| 50 | 1.64 | Helical |
| 60 | 1.77 | Helical |
| 130 | 2.42 | Rough |
| 140 | 2.47 | Rough |
| 150 | 1.94-2.50 | Rough-very rough-rough |
| 160-200 | 1.96-2.50 | Rough-very rough-rough |
| 210 | 1.96 | Very rough |
| 270 | 2.14 | Very rough |

^a Corresponds to volume displacement rates.

run are reported in Table II. A physical description of the filament's appearance, as the pressure fluctuated between A and B, is given in Table I. Other data are graphically reported in Figure 2.

The strong dependence of filament distortion of the molecular weight distribution factor, aside from the expected dependence on molecular weight, is very interesting. High-pressure low-density polyethylenes are known to be of very wide molecular weight distribution. They show rough extrudates to a greater degree than high-density resins.³ This is in agreement with the data reported here. Similarly, the hysteresis area becomes smaller as the molecular weight distribution is broadened. A conventional low-density polyethylene with a zero shear viscosity of 1.7×10^5 poises did not yield a hysteresis loop.

The length of the extrudate between cycles was not found to be related to any known parameters. The length of individual sections, i.e., smooth, spiral, or rough, could not be easily defined and also could not be related to any known parameters. However, there were some differences between repeat units when resins A and B were compared with resins B and C.

Lastly, it was determined that the diameter of the extrudate changes little with the change from smooth to spiral flow. A large change occurs between the spiral and rough flows. It appears that the area of the hysteresis loop is a function of the difference in diameter between smooth and rough extrudates. If the difference in diameters is very