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High-Pressure Phase of Polytetrafluoroethylene

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Synopsis

The effect of hydrostatic pressure on the crystal structure of PTFE has been studied up to pressures of ca. 25 kbar by x-ray diffraction. The experimental method uses opposed diamond anvils of small surface area as transmitters of pressure with MoK α x-radiation propagating through these anvils. A small specimen of oriented polymer is held in place with a molybdenum gasket. Pressures are measured by change in lattice spacing of sodium chloride included with some specimens. It is found that above 4.5 kbar the PTFE changes to a high-pressure phase in which the molecules have transformed from their normal helical arrangement to that of a planar zigzag and that the planes of the molecules all lie parallel to one another. Further changes in the diffraction pattern on increase in pressure are attributed to slip and twinning in the high-pressure phase rather than to another phase change.

Introduction

The exceptional frictional behavior of polytetrafluoroethylene (PTFE) still attracts interest. As a means of understanding the nature of the deformation in frictional processes, a study of the effects of high hydrostatic pressure and shear stresses on the structure and morphology of PTFE has been undertaken. In this paper the structure of a high-pressure phase of PTFE is described.

Previous volume measurements over a wide range of temperature and pressure have established a phase diagram consisting of four solid phases and one liquid phase.^{1,2} Figure 1 shows the phase diagram. In phases I, II, and IV the molecule exists in the form of a helix.³ This helix may be derived from the planar zigzag arrangement (shown by polyethylene) by giving the molecule a 180° twist every $N \operatorname{CF}_2$ units, where N = 15 for phases I and IV, and N = 13 for phase II. The structure of phase III, which exists only at high pressures, is still largely unexplained. Brown⁴ found that the infrared spectrum of PTFE at pressures greater than 6 kbar was compatible with a planar zigzag conformation of the molecule. Hirakawa and Takemura,⁵ using an x-ray technique, have deduced, on the basis of extremely limited data, that the high pressure phase may be "closely packed but disordered with a 9 helical structure." Likewise, Newman and Pae⁶ have briefly reported a sharpening of lines and appearance of new lines

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Fig. 1. Phase diagram for PTFE.

at pressures in excess of 20 kbar. Beecroft and Swenson¹ have also found some evidence of another transition above room temperature at pressures near 11 kbar.

Experimental Methods

A high-pressure x-ray camera was constructed to the design of Piermarini and Weir.⁷ This camera uses opposed diamond anvils, the surface area of the smaller diamond being ca. 0.25 mm². X-radiation from a molybdenum target (zirconium-filtered) propagates through the diamonds perpendicular to the anvil faces. The diffraction pattern is recorded on a flat-plate film. The apparatus is provided with two film holders with specimen-to-film distances of 13 and 36 mm, respectively. The first is used for exploratory photographs of low resolution and short exposure (40 kV, 25 mA; ca. 1 hr) and the second for higher resolution photographs (exposure times at 40 kV, 25 mA; ca. 8 hr). In front of the second film holder it is possible to insert a rotatable quadrant sector screen whereby the diffraction pattern of a specimen at two distinct pressures can be recorded separately on the same film. The maximum value of θ which is detectable with this apparatus is 16°.

Owing to the soft nature of the material studied, a gasket was necessary to retain a sufficient amount of sample between the diamond anvils. The gasket was constructed from molybdenum (thickness 0.25 mm with a hole 0.32 mm in diameter) following the technique of Weir, Block, and Piermarini.⁸ All high-pressure experiments were carried out at room temperature (21°C).

Oriented samples of polymer were used. These were produced by drawing PTFE at 300°C to an extension ratio of 350%. The specimens were mounted in the diamond cell with the direction of drawing parallel to the

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