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The Polymorphism of Poly(vinylidene fluoride) IV. The Structure of High-Pressure-Crystallized Poly(vinylidene fluoride)*

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Summary

A detailed study of high-pressure-crystallized poly(vinylidene fluoride) has indicated that a mixture of low-melting phase II and high-melting phase I is present, rather than a new crystalline phase (phase III) as originally suggested.

The relative amounts of phase I and phase II resulting from crystallization under pressure are a function of pressure and the degree of supercooling. Pressure crystallization at 285°C and 5500 atm results in samples which were pure phase I with an increased melting point of 187°C.

INTRODUCTION

The crystal structures of phase I [1] and phase II [2] of poly(vinylidene fluoride) have recently been determined. These crystalline forms are prepared under atmospheric pressure. Doll and Lando [3] have demonstrated that if poly(vinylidene fluoride), PVF₂, is heated to 280°C and pressure-crystallized at 5000 atm, a new and different X-ray pattern appeared which they designated phase III. When the degree of supercooling is held to a small value, this diffraction pattern has also been observed in samples which were crystallized at pressures as low as 3000 atm. This high-pressure-crystal-

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lized sample had a melting point of 187°C which is about 27° above that of the normally crystallized phase II of PVF₂. At the time this high-pressure sample was obtained, efforts to orient it were generally unsuccessful. Without an oriented sample it was impossible to determine the lattice constants unambiguously. In this paper some of the recent results which have been obtained on the high-pressure-crystallized PVF₂ will be discussed.

EXPERIMENTAL

The PVF₂ used was a commercial grade of Kynar (Pennwalt Chemical Co.). The samples were pressure-crystallized in a high-pressure dilatometer which has been previously described [3,4]. In a previous paper [3], the effect of pressure on the melting behavior of PVF₂ has been discussed. By knowing the melting point under a given hydrostatic pressure, it was possible to determine the degree of supercooling of a sample. Supercooling is defined as the difference between the melting point and crystallization temperature at a given pressure. Interplanar spacings were determined from Debye-Scherrer photographs. Fiber patterns of oriented samples prepared as below were obtained by using a 70-mm-diameter cylindrical camera. Reflections from planes perpendicular to the chain axis were obtained by taking 180-deg oscillation photographs with the draw direction aligned perpendicular to the oscillation axis. Diffractometer scans were taken on a GE XRD-6 diffractometer, and differential thermal analysis (DTA) scans were made on a du Pont 900 DTA. PVF₂ pressure-crystallized in the high-pressure dilatometer resulted in samples having a cylindrical shape 0.25 in. in diameter. These cylindrical samples were turned down on a lathe to form dumbbell-shaped samples which could be oriented by using the Instron tensile tester. Pin vise grips were used to hold the sample in the jaws of the tensile tester. With this experimental arrangement, samples crystallized at high pressure could be drawn to a ratio of 2.5 to 1.

RESULTS AND DISCUSSION

Figure 1 depicts the Debye-Scherrer powder photographs for the three polymorphic phases of PVF₂ as originally presented by Doll and Lando [3]. As can be seen in Fig. 1, if photographic techniques alone are used, the phase III Debye-Scherrer photograph resembles neither phase I nor II. Any attempts to orient phase III resulted in a polymorphic transition to a phase having an X-ray fiber pattern very similar to that of PVF₂ phase I. In general, however, the sam-