

5500 atm, a high-melting form of phase I results [31]. By crystallizing PVF₂ from a DMSO solution, a disordered planar zig-zag conformation, designated as phase I', will result. A copolymer of 93-7 mole% VF-TFE will crystallize from the melt in phase I. If a sample of 91-9 mole% VF₂-VF₃ (this material normally crystallizes from the melt in phase II) is heated to 225°C and pressure-crystallized, it will crystallize in phase I. Copolymers with small amounts of VF and cocrystallized blends of homopolymers of PVF₂-PVF also crystallize in phase I.

Phase II is the phase in which PVF₂ normally crystallizes from the melt. Its chain conformation has been determined to be TGTG' [30]. As previously stated, the copolymer of 91-9 mole% VF₂-VF₃ will crystallize from the melt in phase II.

High-Pressure Dilatometry

The construction and use of the high-pressure dilatometer has been described previously [23,38]. An insert made of Dynacut steel (Latrobe Steel Co.) was precision machined and hardened and fitted inside the high-pressure dilatometer. Earlier studies of PVF₂ had shown that upon decomposition, one of the resulting products was hydrogen fluoride which would seriously pit the inside of the bomb [23]. This insert was, therefore, made so that it could be removed and a new one inserted in its place without requiring the entire bomb to be remade. Intensifier rods and pistons were also made from Dynacut steel so that all close-fitting parts would have the same coefficient of thermal expansion. Electrical heating elements encased in a cylindrical ceramic block were placed around the sample bomb in order to allow rapid heating of the system.

The calibration of the high-pressure cell was accomplished by utilizing known solid-solid polymorphic transitions in inorganic salts throughout the temperature and pressure range to be studied. The salts used in the calibration experiments included KNO₃, AgNO₃, AgI, and RbBr, and the results obtained were accurate within ±15 atm for a given nitrogen pressure on the low-pressure piston. The temperature of the high-pressure cell and sample was measured using a chromelalumel thermocouple embedded in the high-pressure cell immediately below the sample chamber. The temperature measurements were accurate to ±0.5°C.

When using the high-pressure dilatometer, it was assumed that the sample was quite plastic so that the pressure was essentially hydrostatic. By placing a thin layer of salt first on the bottom and then on the top of a PVF₂ sample, it was observed that there was a 20-30-atm pressure gradient between the top and bottom of the sam-

ple at room temperature. However, this gradient vanished for the PVF₂ samples above 110°C indicating that, at temperatures much above 100°C, the pressure was essentially uniform throughout the sample. Since the lowest-melting point encountered in the melting behavior studies of the fluorolefins was 140°C, all the samples were essentially under hydrostatic conditions.

Pressure crystallization of the copolymer samples was accomplished by heating them in the high-pressure dilatometer under very low pressure (pressure just sufficient to set the Bridgman type seal) to the desired temperature and then applying pressure in order to crystallize the sample at the desired pressure and degree of supercooling. The degree of supercooling was defined as the difference in temperature between the crystallization temperature and the melting point of the particular copolymer under the same pressure. The samples were then slowly cooled to room temperature and the pressure removed.

Characterization of Samples

X-Ray Methods and Crystallinity Determination

Flat-plate and cylindrical camera X-ray photographs were taken with nickel-filtered copper radiation. A flat-plate photograph was generally sufficient to determine which phase was present as a result of the pressure experiment. For accurate d spacings, Debye-Scherrer photographs were obtained using chromium radiation. Diffractometer scans from a General Electric XRD 6 diffractometer were used to estimate the crystallinity of the samples. Density measurements were also taken as a cross-check on the crystallinity. The determination of crystallinity by density measurements is hampered by the inability to obtain directly a value for the amorphous density. Values were obtained for the amorphous density of the PVF₂ homopolymer and copolymers by the technique suggested by Van Krevelen and Hoftzyer [39]. The value obtained for the amorphous density of PVF₂ by this method was in good agreement with an extrapolated value determined by Doll and Lando [23]. Van Krevelen and Hoftzyer's method was, therefore, used to determine the amorphous density of the vinylidene fluoride copolymer samples.

Differential Thermal Analysis

DTA scans of the samples were made using a du Pont 900 differential thermal analyzer with a heating rate of 10°/min.