

PVF₂ crystallizes from most solvents in the TGTG' conformation; however, it has been shown that if PVF₂ is crystallized from dimethylsulfoxide (DMSO), it will crystallize as phase I' (disordered planar zig-zag) [32,33]. It has also been demonstrated that vinylidene fluoride-tetrafluoroethylene (VF₂-TFE), vinylidene fluoride-trifluoroethylene (VF₂-VF₃), and vinylidene fluoride-vinyl fluoride (VF₂-VF) copolymers and cocrystallized blends of the homopolymers will form crystalline phase I or II, depending upon the comonomer or second homopolymer present and its concentration [20,21,34-36].

The purpose of this paper will be to report on some further studies on the effect of pressure on the melting behavior of phase I. The effect of small amounts of VF, VF₃, and TFE comonomer on the polymorphism of vinylidene fluoride copolymers as a function of pressure will also be reported.

EXPERIMENTAL

Polymer Samples

Two different homopolymer samples of PVF₂ were studied. A commercial grade of Kynar (Pennwalt Chemicals Co.) which had been used in the previous high-pressure work [23] was used. Vinylidene fluoride in an acetone solution was polymerized in a pressure vessel using γ -radiation as an initiator. A 95-5 mole% copolymer of VF₂-VF was also prepared by the same radiation-initiated solution technique. The molar concentration of VF was determined by using the Schoniger combustion technique for determining the amount of fluorine present [37]. The cocrystallized blend of 95-5 mole% PVF₂-PVF was prepared by dissolving the two homopolymers in dimethylformamide (DMF) and casting a film on a glass plate. Phase I' was formed by dissolving PVF₂ in DMSO and casting a film on a glass plate. The 93-7 mole% VF₂-TFE and the 91-9 mole% VF₂-VF₃ copolymers were prepared by suspension polymerization and analyzed by the Diamond Shamrock Chemical Co.

In previous work it has been shown that PVF₂ exhibits several different polymorphic forms depending upon sample preparation and copolymer content; therefore, a brief description of the sample preparation is included.

Phase I may be obtained by the uniaxial drawing of a sample of PVF₂ at 50°C. This phase is characterized as having a planar zig-zag chain conformation. Prior to the high-pressure crystallization studies of PVF₂, this phase was only found in oriented films. As previously indicated, if PVF₂ is pressure crystallized at 285°C and

5500 atm, a high-melting form of phase I results [31]. By crystallizing PVF_2 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% VF_2 - VF_3 (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 PVF_2 -PVF also crystallize in phase I.

Phase II is the phase in which PVF_2 normally crystallizes from the melt. Its chain conformation has been determined to be TGTG' [30]. As previously stated, the copolymer of 91-9 mole% VF_2 - VF_3 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 PVF_2 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 KNO_3 , AgNO_3 , 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 $\pm 0.5^\circ\text{C}$.

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 PVF_2 sample, it was observed that there was a 20-30-atm pressure gradient between the top and bottom of the sam-