

chain morphology. Holdsworth and Keller [3] observed that a small amount of the triclinic form of PE originally suggested by Turner-Jones [4] was present in samples which were pressure crystallized at 4000 atm. High-pressure differential thermal analysis (DTA) studies have been performed on both folded-chain and extended-chain PE crystals from 1 to 4000 atm [5]. These high-pressure DTA studies indicated that the extended-chain crystals melt at a higher temperature than the corresponding folded-chain crystals at the same pressure, as is suggested by theory [6].

High pressure would appear to be a promising method of preparing new polymorphic forms of polymers with differing unit cells and chain conformations. In addition to the polymorphic forms of PE discussed above, the rate of transformation of polybutene-1 from form II to form I has been found to increase as a function of pressure [7,8]. The  $\gamma$  form of polypropylene results from crystallization at 5000 atm. This polymorphic form of the polymer is not commonly found after crystallization at atmospheric pressure [9-11]. Polytetrafluoroethylene (PTFE) undergoes several solid-solid polymorphic transitions when subjected to varying thermal and elevated pressure conditions [12-19]. Several studies have been made on the effect of pressure on the melting behavior of PTFE [18,19].

The homopolymer of poly(vinylidene fluoride) (PVF<sub>2</sub>) exhibits at least two polymorphic phases under atmospheric conditions [20-26]. Head-to-head linkages play a large role in determining which phase will form upon crystallization. Crowding along the chain for phase II becomes more severe with increasing head-to-head content, whereas crowding decreases with increasing head-to-head content for phase I [21]. Nuclear magnetic resonance (NMR) studies have demonstrated that PVF<sub>2</sub> normally contains 5-6% head-to-head linkages immediately followed by tail-to-tail linkages [27-29]. Phase I of PVF<sub>2</sub> has been shown to have a planar zig-zag chain conformation and an X-ray crystalline density of 2.0 g/cc [7]. Phase II of PVF<sub>2</sub> has a trans-gauche-trans-gauche' chain conformation with a crystalline density of 1.90 g/cc [22,30]. When PVF<sub>2</sub> is pressure-crystallized at 280°C and 5000 atm, it has been previously shown [31] that a mixture of phase II with a melting point of 160°C and a planar zig-zag phase with an increased melting point of 187°C resulted. The samples crystallized under these conditions consisted mainly of the planar zig-zag form. As the degree of supercooling was increased, the amount of phase II increased. If samples of the high-pressure crystallized PVF<sub>2</sub> were oriented, then the remaining phase II was converted to the high-melting planar zig-zag form. Doll and Lando had originally designated as phase III the material which resulted from the high-pressure crystallization of PVF<sub>2</sub>.

PVF<sub>2</sub> crystallizes from most solvents in the TGTG' conformation; however, it has been shown that if PVF<sub>2</sub> 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 (VF<sub>2</sub>-TFE), vinylidene fluoride-trifluoroethylene (VF<sub>2</sub>-VF<sub>3</sub>), and vinylidene fluoride-vinyl fluoride (VF<sub>2</sub>-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, VF<sub>3</sub>, 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 PVF<sub>2</sub> 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  $\gamma$ -radiation as an initiator. A 95-5 mole% copolymer of VF<sub>2</sub>-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% PVF<sub>2</sub>-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 PVF<sub>2</sub> in DMSO and casting a film on a glass plate. The 93-7 mole% VF<sub>2</sub>-TFE and the 91-9 mole% VF<sub>2</sub>-VF<sub>3</sub> copolymers were prepared by suspension polymerization and analyzed by the Diamond Shamrock Chemical Co.

In previous work it has been shown that PVF<sub>2</sub> 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 PVF<sub>2</sub> at 50°C. This phase is characterized as having a planar zig-zag chain conformation. Prior to the high-pressure crystallization studies of PVF<sub>2</sub>, this phase was only found in oriented films. As previously indicated, if PVF<sub>2</sub> is pressure crystallized at 285°C and