

ple at room temperature. However, this gradient vanished for the PVF<sub>2</sub> 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 fluoroolefins 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 PVF<sub>2</sub> homopolymer and copolymers by the technique suggested by Van Krevelen and Hoftyzer [39]. The value obtained for the amorphous density of PVF<sub>2</sub> by this method was in good agreement with an extrapolated value determined by Doll and Lando [23]. Van Krevelen and Hoftyzer'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.

## RESULTS

The techniques for determining the melting point and the change in specific volume of melting as a function of pressure have been previously described [23,38]. Figures 1 and 2 demonstrate the effect of pressure on the melting temperature for samples that crystallize in phases I and II, respectively. When the copolymer samples of 93-7 mole%  $\text{VF}_2$ -TFE and 91-9 mole%  $\text{VF}_2$ - $\text{VF}_3$  are heated to 225°C and pressure-crystallized at 5000 atm, high-melting planar zig-zag forms result. In a similar manner, if  $\text{PVF}_2$  is heated to 285°C and pressure-crystallized at 5500 atm, a high-melting planar zig-zag form results. Although the degree of supercooling necessary to obtain the pure melting planar zig-zag form of the  $\text{PVF}_2$  homopolymer is limited, the degree of supercooling requirements for the copolymer samples studied appear to be greatly relaxed. Throughout the pressure range studied, both high-pressure forms of the copolymers

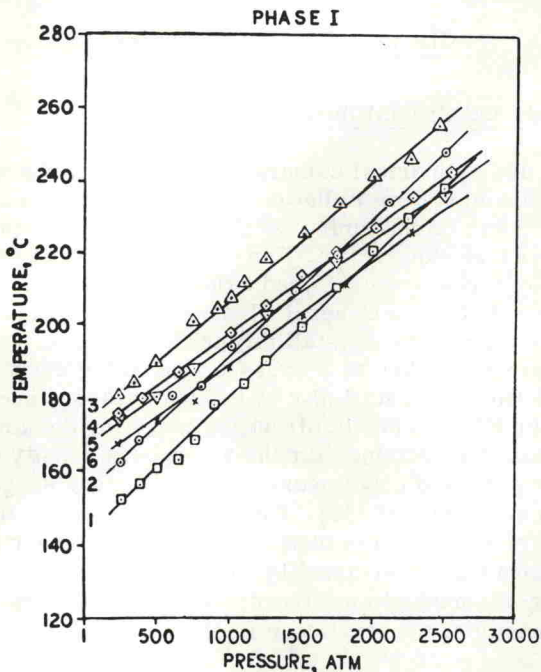


FIG. 1. Effect of pressure on the melting temperature of  $\text{PVF}_2$  and copolymers of  $\text{VF}_2$  that crystallize in phase I. (1) 93-7 Copolymer  $\text{VF}_2$ -TFE (LPC); (2) 93-7 copolymer  $\text{VF}_2$ -TFE (HPC); (3) 95-5 copolymer  $\text{VF}_2$ - $\text{VF}_3$ ; (4) 91-9 copolymer  $\text{VF}_2$ - $\text{VF}_3$  (HPC); (5) 95-5 blend  $\text{PVF}_2$ - $\text{PVF}$ ; (6)  $\text{PVF}_2$  from DMSO.