5500 atm, a high-melting form of phase I results [31]. By crystalliz-
ing PVF$_2$ from a DMSO solution, a disordered planar zig-zag confor-
mation, designated as phase I', will result. A copolymer of 93-7
mole% VF-TFE will crystallize from the melt in phase I. If a sam-
ple 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-crystal-
lized, 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 en-
cased 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 tem-
perature 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 measure-
ments 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 PVF$_2$ 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
PVF$_2$ 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 accom-
plished 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 super-
cooling. The degree of supercooling was defined as the difference
in temperature between the crystallization temperature and the melt-
ing point of the particular copolymer under the same pressure. The
samples were then slowly cooled to room temperature and the pres-
sure 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 re-
sult of the pressure experiment. For accurate d spacings, Debye-
Scherrer photographs were obtained using chromium radiation. Dif-
fractometer scans from a General Electric XRD 6 diffractometer
were used to estimate the crystallinity of the samples. Density mea-
surements were also taken as a cross-check on the crystallinity.
The determination of crystallinity by density measurements is ham-
pered by the inability to obtain directly a value for the amorphous
density. Values were obtained for the amorphous density of the
PVF$_2$ homopolymer and copolymers by the technique suggested by
Van Krevelen and Hoftyzer [39]. The value obtained for the amor-
phous density of PVF$_2$ by this method was in good agreement with
an extrapolated value determined by Doll and Lando [23]. Van Kreve-
len 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 differ-
ential thermal analyzer with a heating rate of 10°/min.