The Polymorphism of Poly(vinylidene fluoride) V. The Effect of Hydrostatic Pressure on the Melting Behavior of Copolymers of Vinylidene Fluoride*

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Summary

The high-pressure melting behavior of samples of vinylidene fluoride copolymerized with vinyl fluoride, trifluoroethylene, or tetrafluoroethylene indicate that the copolymers have a lower entropy of melting than the poly(vinylidene fluoride) homopolymers in the same phase. As the comonomer size increases, the entropy of melting decreases. High-pressure crystallization of copolymers of 91-9 mole% vinylidene fluoride-trifluoroethylene and 93-7 mole% vinylidene fluoride-tetrafluoroethylene results in a high-melting form of phase I (planar zig-zag).

INTRODUCTION

The effect of elevated hydrostatic pressure on the crystal structure, morphology, possible polymorphism, and physical properties of macromolecules has become the subject of intensive study within the past 15 years.

Wunderlich and Arakawa [1] and Geil et al. [2] demonstrated that upon pressure-crystallizing polyethylene (PE), they were able to obtain extended-chain crystals in the bulk rather than the normal folded-

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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 prepar-
ing new polymorphic forms of polymers with differing unit cells and
chain conformations. In addition to the polymorphic forms of PE dis-
cussed 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 γ 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]. Polytetrafluoroethyl-
ene (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$_2$) 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$_2$ normally contains 5-6% head-to-head linkages immediately
followed by tail-to-tail linkages [27-29]. Phase I of PVF$_2$ 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$_2$ has a trans-
gauche-trans-gauche' chain conformation with a crystalline density
of 1.90 g/cc [22,30]. When PVF$_2$ 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 crys-
tallized PVF$_2$ were oriented, then the remaining phase II was con-
verted 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$_2$.

PVF_2 crystallizes from most solvents in the TGTG' conformation; however, it has been shown that if PVF_2 is crystallized from dimethyl-sulfoxide (DMSO), it will crystallize as phase I' (disordered planar zig-zag) [32,33]. It has also been demonstrated that vinylidene fluor-ide-tetrafluoroethylene (VF_2-TFE), vinylidene fluoride-trifluoro-ethylene (VF_2-VF_3), and vinylidene fluoride-vinyl fluoride (VF_2-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_3, 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_2 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 VF_2-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_2-PVF was pre-pared by dissolving the two homopolymers in dimethylformamide (DMF) and casting a film on a glass plate. Phase I' was formed by dissolving PVF_2 in DMSO and casting a film on a glass plate. The 93-7 mole% VF_2-TFE and the 91-9 mole% VF_2-VF_3 copolymers were prepared by suspension polymerization and analyzed by the Diamond Shamrock Chemical Co.

In previous work it has been shown that PVF_2 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_2 at 50°C. This phase is characterized as having a planar zig-zag chain conformation. Prior to the high-pressure crystallization studies of PVF_2, this phase was only found in oriented films. As previously indicated, if PVF_2 is pressure crystallized at 285°C and

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 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$_2$ homopolymer and copolymers by the technique suggested by Van Krevelen and Hoftyzer [39]. The value obtained for the amorphous density of PVF$_2$ 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% VF_2-TFE and 91-9 mole% VF_2-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 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 ob-
tain the pure melting planar zig-zag form of the PVF_2 homopolymer
is limited, the degree of supercooling requirements for the copoly-
mer samples studied appear to be greatly relaxed. Throughout the
pressure range studied, both high-pressure forms of the copolymers
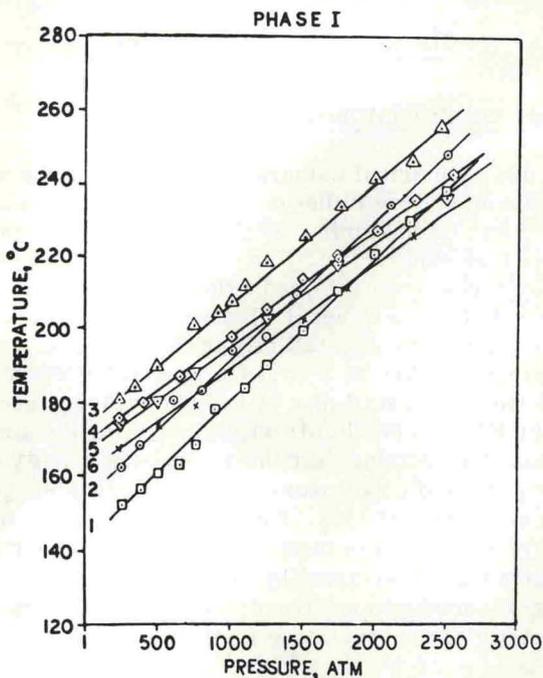
FIG. 1. Effect of pressure on the melting temperature of PVF_2 and copoly-
mers of VF_2 that crystallize in phase I. (1) 93-7 Copolymer VF_2-TFE(LPC);
(2) 93-7 copolymer VF_2-TFE(HPC); (3) 95-5 copolymer VF_2-VF; (4) 91-9
copolymer VF_2-VF_3 (HPC); (5) 95-5 blend PVF_2-PVF; (6) PVF_2 from DMSO.
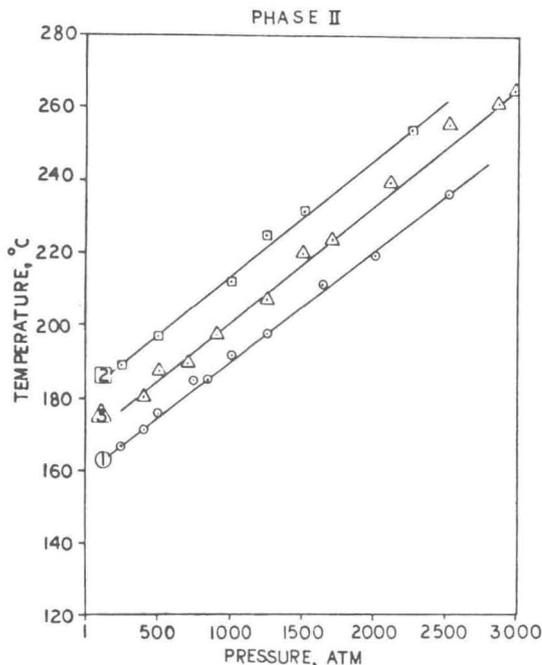
FIG. 2. Effect of pressure on the melting temperature of PVF$_2$ and copolymers of VF$_2$ that crystallize in phase II. (1) 91-9 Copolymer VF$_2$-VF$_3$(LPC); (2) radiation-polymerized PVF$_2$; (3) Kynar.

as well as the high-pressure-crystallized sample of PVF$_2$ have higher melting points than the corresponding low-pressure-crystallized samples. If these high-melting planar zig-zag forms are melted in the DTA and allowed to recrystallize under atmospheric pressure, they will return to the chain conformation and unit cell dimensions of the low-pressure-crystallized forms. Figures 1 and 2 indicate that within experimental error there exists a linear relationship between the melting temperature and applied pressure (up to 2500 atm) for all the samples examined. This linear behavior has also been previously observed for PVF$_2$ phase II and the high-pressure-crystallized mixture of phases I and II [23]. When copolymer samples were melted at pressures below 2500 atm, only a small amount of degradation occurred as evidenced by the samples turning light brown. Since there were no changes in the DTA or in X-ray photographs, it was assumed that the degradation must be minor. However, total decomposition of the sample occurred in numerous

experiments if the samples were subjected to the higher temperature necessary to melt samples at pressures much above 2500 atm.

The inverse of the slope of the $\Delta T_m/\Delta P$ line for each sample studied as well as the crystallinities as determined by both density and X-ray diffraction scans are presented in Table 1. By assuming

TABLE 1

Comparison of the Physical Properties of PVF_2
and Copolymers of VF_2

Sample [a]	Phase	T_m, °C	$\Delta P/\Delta T_m$	% Cryst. density	% Cryst. X-ray
93-7 mole% VF_2-TFE LPC	I	136	26.0	64.3	58.8
93-7 mole% VF_2-TFE HPC	I	156	26.0	73.1	65.4
91-9 mole% VF_2-VF_3 LPC	II	160	31.8	74.5	70.5
91-9 mole% VF_2-VF_3 HPC	I	163	33.4	56.5	71.5
Cocrystallized blend					
95-5 mole% PVF_2-PVF	I	158	34.5	39.4	52
95-5 mole% VF_2-VF LPC	I	174	29.8	67.2	63
Phase I'	I	156	33.6	40.7	52
Phase II [8]	II	160	29.8	–	68
High-pressure-crystallized PVF_2 (mixture of phases I and II) [8]		187	30.0	–	62

[a] LPC = low-pressure-crystallized; HPC = high-pressure-crystallized.

a two-phase model, the X-ray crystallinity can be determined. For most samples the diffraction patterns are sharp, and it is reasonably simple to determine the relative areas due to the crystalline and amorphous regions. However, for diffractometer scans of samples such as phase I' and the cocrystallized mixture of 95-5 mole% PVF_2-PVF, line broadening makes this determination more difficult. Figure 3 compares diffractometer scans for phase I', the 95-5 mole% PVF_2-PVF, and a copolymer of 93-7 mole% VF_2-VF_3 and indicates the line-broadening problem; density measurements were also made in order to check the X-ray crystallinity measurements. From De-bye-Scherrer powder photographs, it was possible to determine the unit cell dimensions. By knowing the unit cell dimensions, the number of atoms in a unit cell, and the composition, it was possible to calculate the crystalline density of the polymeric samples. The fluoroolefin samples cannot be quenched from the melt into a stable amorphous phase and, therefore, an accurate experimental determination of the amorphous density is extremely difficult. The empirical
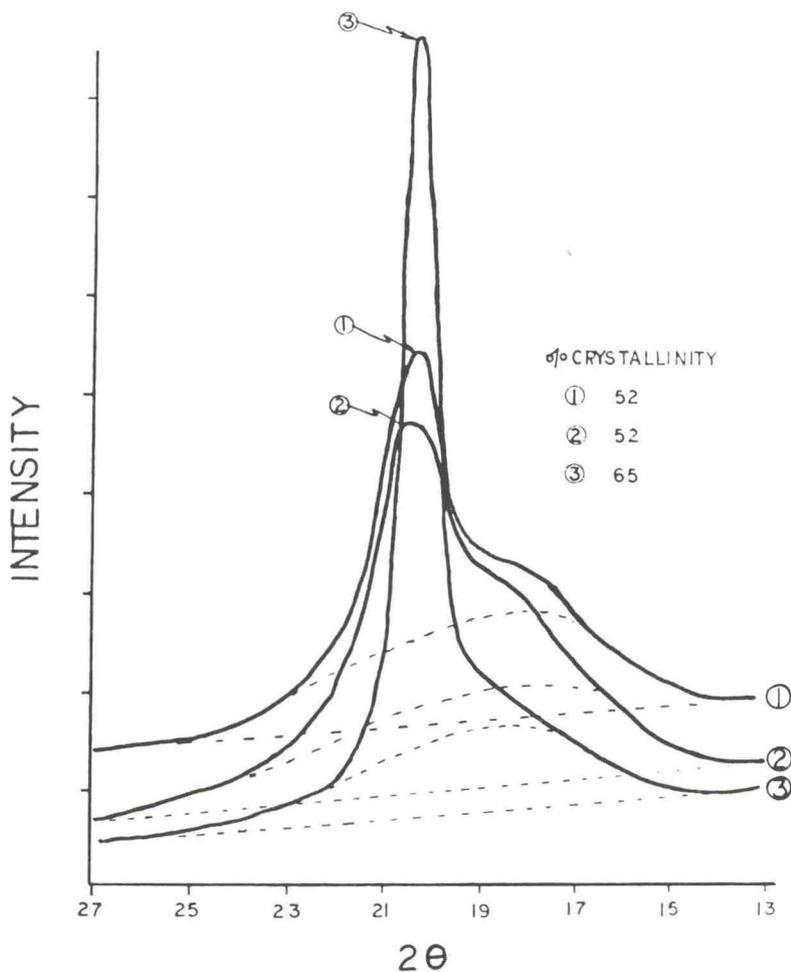
FIG. 3. Diffractometer scans indicating the line-broadening effect discussed in the text. (1) PVF$_2$ from DMSO; 95-5 blend of PVF$_2$-PVF; (3) 93-7 copolymer VF$_2$-TFE. 100 cps; 0.4°/min.

method of calculating amorphous density suggested by Van Krevelen and Hoftyzer [39] gave a value of 1.55 g/cm^3 for PVF$_2$. This value can be compared with an extrapolated value from an earlier paper by Doll and Lando [23] of 1.48 g/cm^3. Generally the crystallinities as determined by density measurements are higher than those determined by X-ray diffractometer scans. However, regardless of

which method is used to determine the crystallinity, the samples will maintain their same position on a scale that rates them from highest to lowest crystallinity.

The effect of pressure on the total entropy of melting for all samples that crystallize in phase I is shown in Fig. 4. Figure 5 indicates the same relationship for all samples which crystallize from the melt in phase II. The total change of entropy upon melting is corrected to 100% crystallinity on the basis of the X-ray diffractometer crystallinity measurements. The volume of melting curves and the total entropy of melting curves will have identical shapes since $\Delta P/\Delta T_m$ is a constant for these fluoroolefin samples, and it is assumed that the Clapeyron equation can be applied.
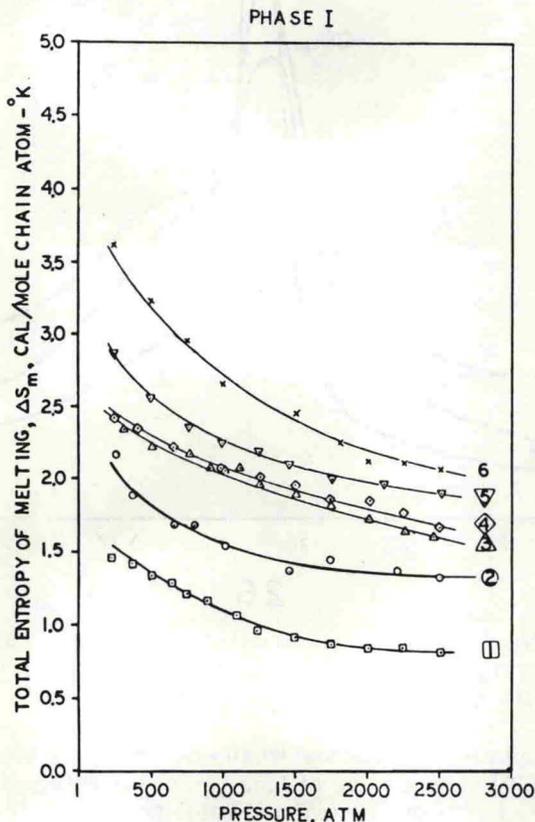
FIG. 4. Effect of pressure on the total entropy of melting for samples that crystallize in phase I. (1) 93-7 Copolymer VF_2-TFE(LPC); (2) 93-7 copolymer VF_2-TFE(HPC); (3) 95-5 copolymer VF_2-VF; (4) 91-9 copolymer VF_2-VF_3(HPC); (5) 95-5 blend PVF_2-PVF; (6) PVF_2 from DMSO.
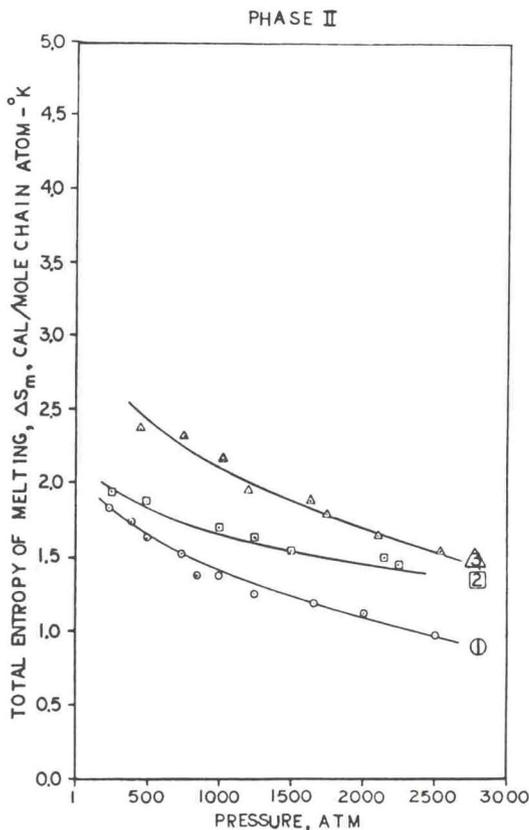
PHASE II

FIG. 5. Effect of pressure on the total entropy of melting for samples that crystallize in phase II. (1) 91-9 Copolymer VF$_2$-VF$_3$(LPC); (2) radiation-polymerized PVF$_2$; (3) Kynar.

If the total entropy of melting versus pressure curves is com-pared for the various polymorphic forms of the homopolymer of PVF$_2$ (Fig. 6), it can be observed that phase II has the lowest en-tropy of melting throughout the entire pressure range.

DISCUSSION

If the entropy of melting as a function of pressure for all samples which have a planar zig-zag conformation (phase I) are compared (Fig. 4), it can be observed that the copolymers of vinylidene fluoride have lower entropy of melting values than the homopolymer. Doll and
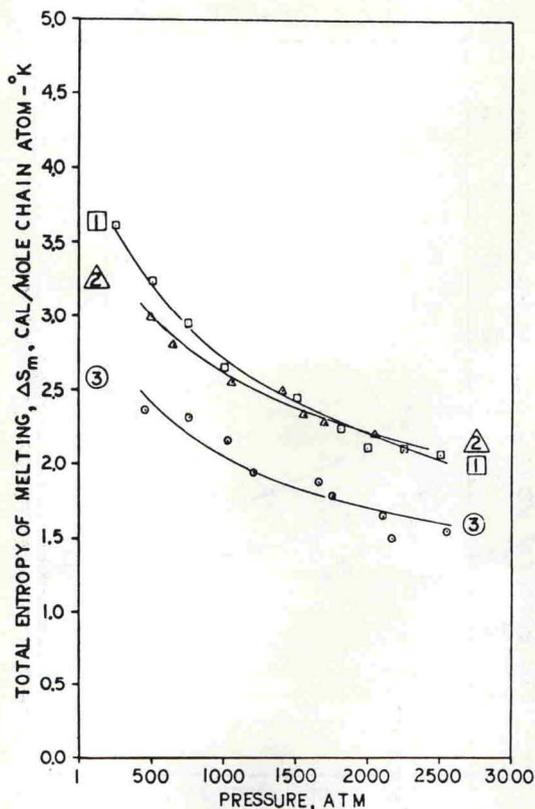
FIG. 6. Effect of pressure on the total entropy of melting for various phases of the homopolymer. (1) PVF_2 from DMSO (phase I); (2) PVF_2(HPC), 280°C and 500 atm; (3) PVF_2 (phase II).

Lando [21] have demonstrated that the comonomers can be incorporated in the vinylidene fluoride chain without a serious disruption of the crystalline structure. They have also shown that the comonomers of VF_3 and TFE act as pseudo head-to-head linkages.

From Fig. 4 it can be observed that the curves relating the entropy of melting at a given pressure do not cross one another at any point. Therefore, at any given pressure the samples will maintain their same position on a scale that rates them from highest to lowest entropy of melting. Thus the following analysis of data presented in Table 2 would be the same if a different pressure were chosen.

Since phase I′ is the only homopolymer sample, it was chosen as the standard. It can be observed that the entropy and enthalpy of

TABLE 2

Comparison of the Melting Behavior at 500 Atm
for Samples That Crystallize in Phase I

Sample[a]	ΔS_m, cal / g mole-°K	ΔH_m, cal / g mole	T_m, °C
Phase I'	3.25	1527	197
91-9 mole% VF$_2$-VF$_3$ HPC	2.40	1094	183
95-5 mole% VF$_2$-VF LPC	2.35	1088	190
93-7 mole% VF$_2$-TFE HPC	1.80	803	173
93-7 mole% VF$_2$-TFE LPC	1.40	599	155

[a]HPC = high-pressure-crystallized; LPC = low-pressure-crystallized.

melting for the copolymers decrease with increasing comonomer size. If the assumption is made that the enthalpy of the polymer in the melt is essentially the same for all the copolymer samples, then the enthalpy in the solid state must increase as the comonomer size increases. The entropy of the liquid state for the copolymers of VF and VF$_3$ will probably increase slightly since a new group (CHF) is introduced. An entropy increase in the liquid state for the VF$_2$-TFE copolymers would not be as large since tetrafluoroethylene linkages are already present in the homopolymer chain as a result of the head-to-head linkages. The entropy in the solid state would tend to increase since the different comonomer groups would disrupt the packing of the chains and, hence, somewhat disrupt the crystalline order. This analysis of the effect of comonomer size on the entropy of melting is in agreement with the curves in Fig. 4.

The 93-7 mole% VF$_2$-TFE copolymer remains in the planar zig-zag chain conformation whether it is crystallized under atmospheric pressure or at 5000 atm. For this copolymer there is a noticeable difference in the melting behavior as is indicated in Fig. 4 depending upon the pressure crystallization history of the sample. The high-pressure-crystallized samples have a greater entropy and enthalpy of melting. This could be indicative of greater perfection in the crystalline regions of the high-pressure-crystallized samples. Davidson and Wunderlich [5] have observed that the high-pressure-crystallized extended-chain crystals of polyethylene also exhibit a high melting point throughout the entire pressure range (1-4000 atm) when these samples are melted in a high-pressure DTA.

In Fig. 4 it can be observed that the only copolymer that does not follow the general trend of decreasing entropy of melting with in-

creasing comonomer size is the high-pressure-crystallized 91-9 mole% VF_2-VF_3 copolymer. However, as was shown for the 93-7 mole% VF_2-TFE copolymer, a high-pressure-crystallized sample has a higher entropy of melting value than the value obtained for the low-pressure-crystallized sample. Therefore, the 91-9 mole% VF_2-VF_3 high-pressure-crystallized copolymer is not really an exception to the rule.

The entropy of melting value for the cocrystallized blend of 95-5 mole% PVF_2-PVF would indicate that the cocrystallization of 5 mole% PVF does not seriously hinder the chain packing or crystalline order. It is interesting that 5 mole% PVF can stabilize the cocrystallized blend in the planar zig-zag chain conformation.

From Fig. 5, a similar analysis can be made for the samples that crystallize in phase II (Table 3). The commercial PVF_2 (Kynar) was chosen as the standard. From Table 3 it can be observed that values for the entropy and enthalpy of melting for the 91-9 mole% VF_2-VF_3 copolymer are smaller than those of the homopolymer. It would, therefore, appear that the same trend of decreasing enthalpy and entropy of melting with increasing comonomer size which was observed for the samples that crystallized in phase I also holds true for the samples that crystallize in phase II. The radiation-polymerized sample of PVF_2 phase II exhibits a higher-melting point, greater density, smaller entropy change upon melting, and increased crystallinity when it is compared with the normal homopolymer. Intrinsic viscosity measurements have indicated that the radiation-initiated polymerization of vinylidene fluoride in acetone results in polymers having much lower molecular weights than polymers resulting from the conventional suspension polymerization. For polyethylene samples of relatively low molecular weights (less than 10,000), Mandelkern [40] has observed that higher levels of crystallinity and density

TABLE 3

Comparison of the Melting Behaviors at 500 Atm for
All Samples That Crystallize in Phase II

Sample [a]	ΔS_m, cal / g mole-°K	ΔH_m, cal / g mole	T_m, °C
Phase II (Kynar) LPC	2.45	1117	183
Radiation-polymerized PVF_2 LPC	1.80	842	195
91-9 mole% VF_2-VF_3 LPC	1.65	739	175

[a] LPC = low-pressure-crystallized.

occur than would normally be expected. He considers the critical size in the chain direction for the crystalline nucleus to be of the same order of magnitude as that of the length of the chain for low molecular weight samples and, therefore, concludes that these crystals have essentially extended chains. A similar argument could be applied to the radiation-initiated PVF$_2$ using acetone as a solvent. Since the lower entropy of melting in this material is presumably related to a higher entropy in the solid state, the increased melting point and lower entropy of melting may be indicative of larger but less perfect crystallites when compared to suspension polymerized PVF$_2$. Defects in these presumably extended-chain crystals could produce higher densities than less crystalline samples having greater crystal perfection.

By comparing the melting behavior of all the phases of the homopolymer of PVF$_2$ (Fig. 6), it can be seen that phase II has the lowest change in entropy upon melting. These samples can be directly compared since they were all crystallized from the same homopolymer. The high-pressure-crystallized form of PVF$_2$ was originally designated as "phase III" by Doll and Lando [23], although it has since been shown that this high-pressure-crystallized form is in actuality a high-melting mixture of phases I and II [31].

Studies on the effect of pressure on the melting behavior of PVF$_2$ and its copolymers help to give some insight into the complexity of systems which are able to undergo isomorphous substitution. While the van der Waals radius of the fluorine atom is very similar to that of hydrogen (1.35 vs. 1.1 Å), the isomorphous substitution of a fluorine atom has a definite effect on the melting behavior. Since the melting point for most copolymers is not appreciably different than that of the homopolymer, although the entropy of fusion is reduced, the enthalpy of fusion must also be reduced. Therefore, by understanding the effects of this isomorphic substitution, copolymers having most of the properties of PVF$_2$ but which would require less thermal energy to process can be formulated.

Certain applications of PVF$_2$ require the polymer to have a particular chain conformation, and by the proper polymerization or copolymerization conditions one can obtain either the TGTG' conformation (phase II) or the planar zig-zag conformation (phase I) as the most thermodynamically favorable form.

CONCLUSIONS

High-pressure melting behavior obtained for samples of vinylidene fluoride copolymerized with vinyl fluoride, trifluoroethylene, or tetrafluoroethylene indicated that the copolymers have lower entropy and

enthalpy of melting values than poly(vinylidene fluoride) in the same phase. As the comonomer size was increased, the entropy and enthalpy of melting decreased.

For samples that have been high-pressure-crystallized the entropy and enthalpy of melting and the melting point all increase when compared with the corresponding values for the low-pressure-crystallized samples.

It has been previously shown [21] that fluoroolefin comonomers with vinylidene fluoride act as pseudo head-to-head linkages and, therefore, the copolymers of VF_2 tend to favor crystallization under atmospheric conditions in phase I. The data in this paper have indicated that high-pressure crystallization of the copolymers also favors crystallization in phase I.

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