

TABLE 2
Comparison of the Melting Behavior at 500 Atm
for Samples That Crystallize in Phase I

Sample ^a	ΔS_m , cal g mole ⁻¹ °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

^aHPC = 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 VF₃ will probably increase slightly since a new group (CHF) is introduced. An entropy increase in the liquid state for the VF₂-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% VF₂-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% $\text{VF}_2\text{-VF}_3$ copolymer. However, as was shown for the 93-7 mole% $\text{VF}_2\text{-TFE}$ 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% $\text{VF}_2\text{-VF}_3$ 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% $\text{PVF}_2\text{-PVF}$ 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% $\text{VF}_2\text{-VF}_3$ 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	$\frac{\Delta S_m, \text{ cal}}{\text{g mole} \cdot ^\circ\text{K}}$	$\frac{\Delta H_m, \text{ cal}}{\text{g mole}}$	$T_m, ^\circ\text{C}$
Phase II (Kynar) LPC	2.45	1117	183
Radiation-polymerized PVF_2 LPC	1.80	842	195
91-9 mole% $\text{VF}_2\text{-VF}_3$ LPC	1.65	739	175

^a LPC = low-pressure-crystallized.