

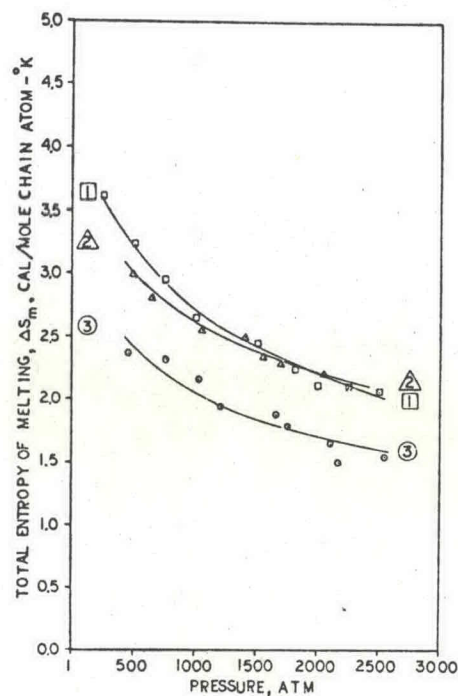


FIG. 6. Effect of pressure on the total entropy of melting for various phases of the homopolymer. (1) PVF_2 from DMSO (phase I); (2) PVF_2 (HPC), 280°C and 500 atm; (3) PVF_2 (phase II).

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

^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 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-