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