

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

If the total entropy of melting versus pressure curves is compared for the various polymorphic forms of the homopolymer of PVF<sub>2</sub> (Fig. 6), it can be observed that phase II has the lowest entropy 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

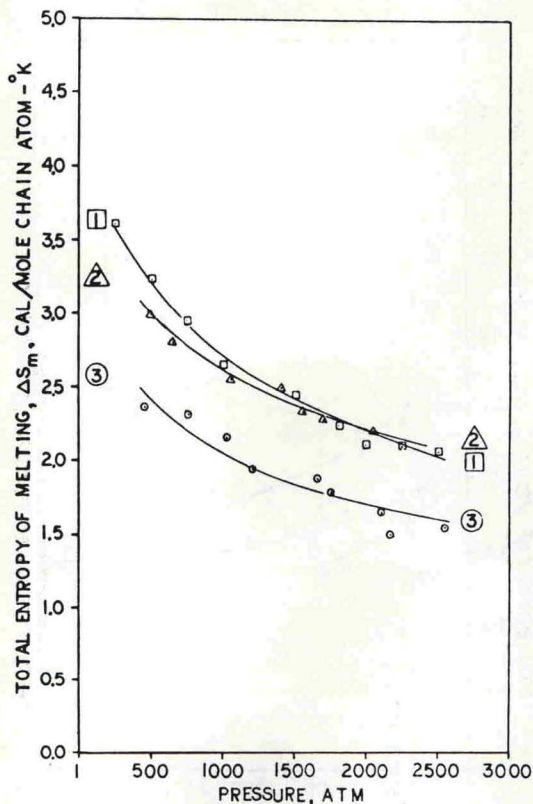


FIG. 6. Effect of pressure on the total entropy of melting for various phases of the homopolymer. (1)  $\text{PVF}_2$  from DMSO (phase I); (2)  $\text{PVF}_2$ (HPC),  $280^\circ\text{C}$  and 500 atm; (3)  $\text{PVF}_2$  (phase II).

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  $\text{VF}_3$  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