

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.

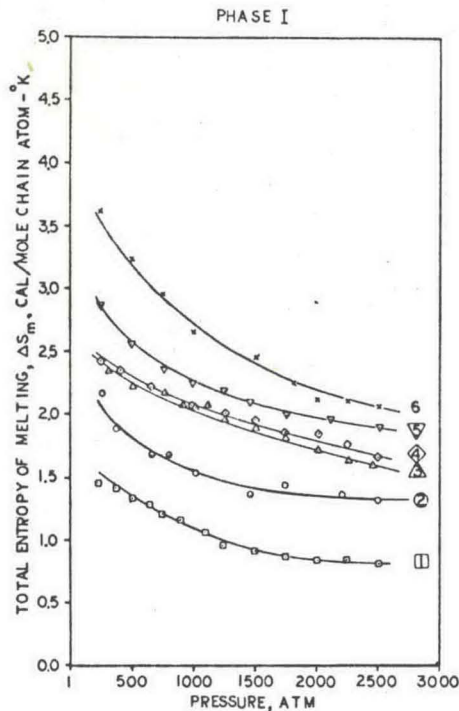


FIG. 4. Effect of pressure on the total entropy of melting for samples that crystallize in phase I. (1) 93-7 Copolymer  $\text{VF}_2$ -TFE (LPC); (2) 93-7 copolymer  $\text{VF}_2$ -TFE (1.PC); (3) 95-5 copolymer  $\text{VF}_2$ -VF; (4) 91-9 copolymer  $\text{VF}_2$ - $\text{VF}_3$  (HPC); (5) 95-5 blend  $\text{PVF}_2$ -PVF; (6)  $\text{PVF}_2$  from DMSO.

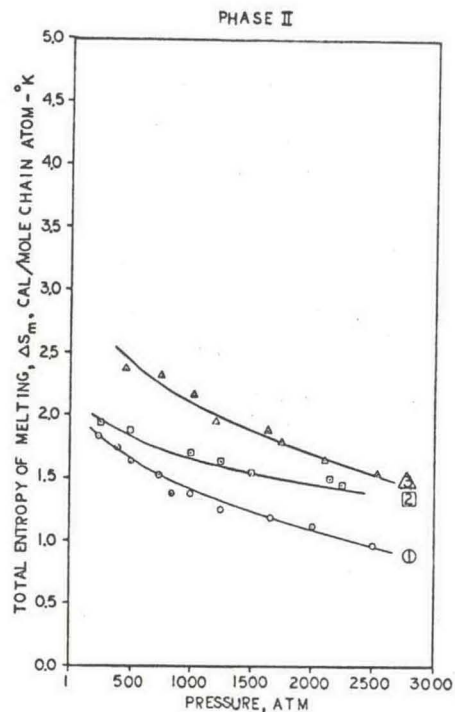


FIG. 5. Effect of pressure on the total entropy of melting for samples that crystallize in phase II. (1) 91-9 Copolymer  $\text{VF}_2$ - $\text{VF}_3$  (LPC); (2) radiation-polymerized  $\text{PVF}_2$ ; (3) Kynar.

If the total entropy of melting versus pressure curves is compared for the various polymorphic forms of the homopolymer of  $\text{PVF}_2$  (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