

RESULTS

The techniques for determining the melting point and the change in specific volume of melting as a function of pressure have been previously described [23,38]. Figures 1 and 2 demonstrate the effect of pressure on the melting temperature for samples that crystallize in phases I and II, respectively. When the copolymer samples of 93-7 mole% VF_2 -TFE and 91-9 mole% VF_2 - VF_3 are heated to 225°C and pressure-crystallized at 5000 atm, high-melting planar zig-zag forms result. In a similar manner, if PVF_2 is heated to 285°C and pressure-crystallized at 5500 atm, a high-melting planar zig-zag form results. Although the degree of supercooling necessary to obtain the pure melting planar zig-zag form of the PVF_2 homopolymer is limited, the degree of supercooling requirements for the copolymer samples studied appear to be greatly relaxed. Throughout the pressure range studied, both high-pressure forms of the copolymers

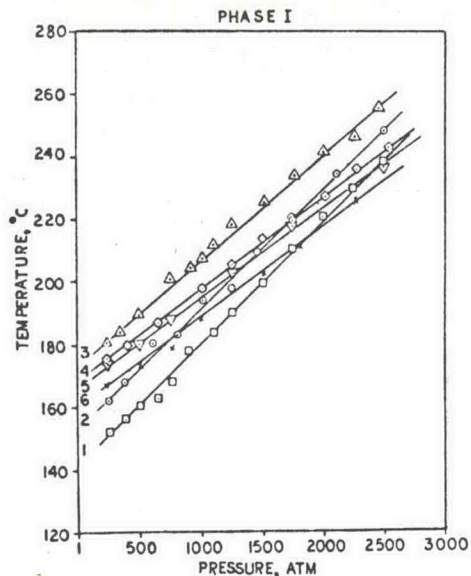


FIG. 1. Effect of pressure on the melting temperature of PVF_2 and copolymers of VF_2 that crystallize in phase I. (1) 93-7 Copolymer VF_2 -TFE (LPC); (2) 93-7 copolymer VF_2 -TFE (HPC); (3) 95-5 copolymer VF_2 -VF; (4) 91-9 copolymer VF_2 - VF_3 (HPC); (5) 95-5 blend PVF_2 -PVF; (6) PVF_2 from DMSO.

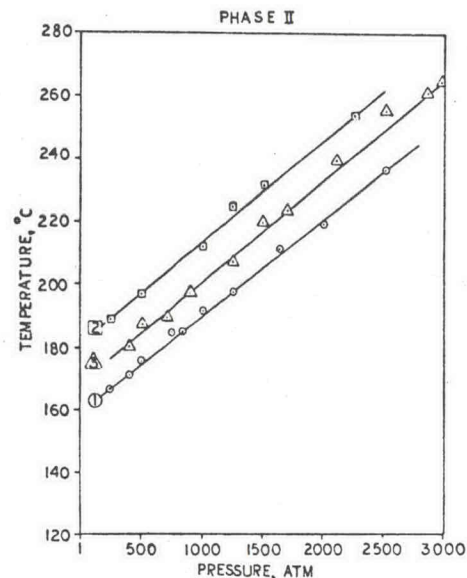


FIG. 2. Effect of pressure on the melting temperature of PVF_2 and copolymers of VF_2 that crystallize in phase II. (1) 91-9 Copolymer VF_2 - VF_3 (LPC); (2) radiation-polymerized PVF_2 ; (3) Kynar.

as well as the high-pressure-crystallized sample of PVF_2 have higher melting points than the corresponding low-pressure-crystallized samples. If these high-melting planar zig-zag forms are melted in the DTA and allowed to recrystallize under atmospheric pressure, they will return to the chain conformation and unit cell dimensions of the low-pressure-crystallized forms. Figures 1 and 2 indicate that within experimental error there exists a linear relationship between the melting temperature and applied pressure (up to 2500 atm) for all the samples examined. This linear behavior has also been previously observed for PVF_2 phase II and the high-pressure-crystallized mixture of phases I and II [23]. When copolymer samples were melted at pressures below 2500 atm, only a small amount of degradation occurred as evidenced by the samples turning light brown. Since there were no changes in the DTA or in X-ray photographs, it was assumed that the degradation must be minor. However, total decomposition of the sample occurred in numerous