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

experiments if the samples were subjected to the higher temperature necessary to melt samples at pressures much above 2500 atm.

The inverse of the slope of the $\Delta T_m/\Delta P$ line for each sample studied as well as the crystallinities as determined by both density and X-ray diffraction scans are presented in Table 1. By assuming

TABLE 1

Comparison of the Physical Properties of PVF_2
and Copolymers of VF_2

Sample [a]	Phase	T_m, °C	$\Delta P/\Delta T_m$	% Cryst. density	% Cryst. X-ray
93-7 mole% VF_2-TFE LPC	I	136	26.0	64.3	58.8
93-7 mole% VF_2-TFE HPC	I	156	26.0	73.1	65.4
91-9 mole% VF_2-VF_3 LPC	II	160	31.8	74.5	70.5
91-9 mole% VF_2-VF_3 HPC	I	163	33.4	56.5	71.5
Cocrystallized blend					
95-5 mole% PVF_2-PVF	I	158	34.5	39.4	52
95-5 mole% VF_2-VF LPC	I	174	29.8	67.2	63
Phase I'	I	156	33.6	40.7	52
Phase II [8]	II	160	29.8	–	68
High-pressure-crystallized					
PVF$_2$ (mixture of phases I					
and II) [8]		187	30.0	–	62

[a] LPC = low-pressure-crystallized; HPC = high-pressure-crystallized.

a two-phase model, the X-ray crystallinity can be determined. For most samples the diffraction patterns are sharp, and it is reasonably simple to determine the relative areas due to the crystalline and amorphous regions. However, for diffractometer scans of samples such as phase I' and the cocrystallized mixture of 95-5 mole% PVF_2-PVF, line broadening makes this determination more difficult. Figure 3 compares diffractometer scans for phase I', the 95-5 mole% PVF_2-PVF, and a copolymer of 93-7 mole% VF_2-VF_3 and indicates the line-broadening problem; density measurements were also made in order to check the X-ray crystallinity measurements. From De-bye-Scherrer powder photographs, it was possible to determine the unit cell dimensions. By knowing the unit cell dimensions, the number of atoms in a unit cell, and the composition, it was possible to calculate the crystalline density of the polymeric samples. The fluoroolefin samples cannot be quenched from the melt into a stable amorphous phase and, therefore, an accurate experimental determination of the amorphous density is extremely difficult. The empirical