

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 <sup>a</sup>	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

<sup>a</sup> 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 Debye-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 fluorolefin 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

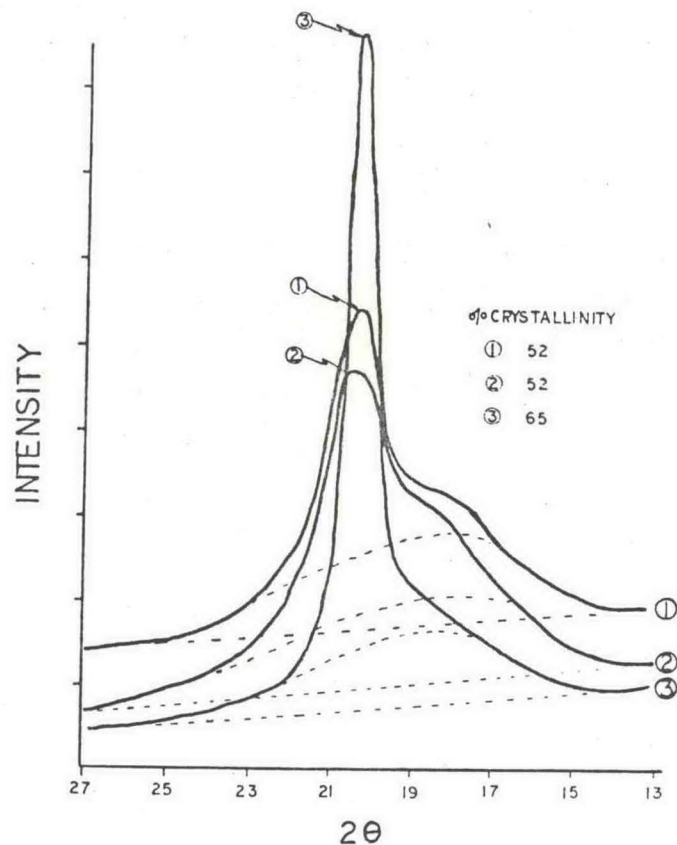


FIG. 3. Diffractometer scans indicating the line-broadening effect discussed in the text. (1)  $PVF_2$  from DMSO; 95-5 blend of  $PVF_2$ -PVF; (3) 93-7 copolymer  $VF_2$ -TFE. 100 cps; 0.4°/min.

method of calculating amorphous density suggested by Van Krevelen and Hoftyzer [39] gave a value of 1.55 g/cm<sup>3</sup> for  $PVF_2$ . This value can be compared with an extrapolated value from an earlier paper by Doll and Lando [23] of 1.48 g/cm<sup>3</sup>. Generally the crystallinities as determined by density measurements are higher than those determined by X-ray diffractometer scans. However, regardless of