

that the full-scale intensity of the phase I diffractometer scan was considerably lower than either of the other two samples (100 cps full-scale for phase I versus 2000 cps for the other samples). Since low-pressure-crystallized phase I exists only in the oriented state, the intensity of peaks obtained by the diffractometer techniques will be greatly affected. The (001) reflection in phase I which occurs at 2.55 Å ( $2\theta = 35.16$ ) does not appear in the diffractometer scan due to this orientation. However, the peak positions should be correct for zero layer reflections of phase I, and, therefore, a comparison of peak positions in the three samples can be made. The (021) reflection does not appear in the scan of the high-pressure-crystallized sample in Fig. 2. This is undoubtedly also due to orientation in this sample, since the (021) reflection ( $d = 3.34$  Å; Table 1) appears in Debye-Scherrer photographs of samples crystallized at 5000 atm at high supercoolings. These scans point out the similarities between phases I and II and the high pressure crystallized PVF<sub>2</sub> samples in a manner that is much easier to interpret than if Debye-Scherrer photographs were compared. If, indeed, there is a mixture of phases I and II, then the fact that there are indications of two melting peaks for the high-pressure crystallized samples might be explained. It

TABLE 1  
Qualitative Comparison of Intensities of X-Ray  
Reflections Obtained from Debye-Scherrer Photographs<sup>a</sup>

Crystallization temperature (°C)	Degree of Supercooling (°C)	Intensity of peaks occurring near the following d spacings (Å) <sup>b</sup> :				
		5.00	4.81	4.45	4.27	3.34
—	Low-pressure- crystallized PVF <sub>2</sub> phase I	M	VS	VS	A	M
190	118	W	VS	VS	A	M
205	103	VW	S	VS	W	W
268	40	A	M	S	M	VVW
282	26	A	W	M	S	A
286	22	A	VW	W	VS	A
290	18	A	A	VVW	VS	A
	Low-pressure- crystallized phase I	A	A	A	VS	A

<sup>a</sup>All samples were crystallized at 5000 atm.

<sup>b</sup>A = absent, VVW = very very weak, VW = very weak, W = weak, M = medium, S = strong, VS = very strong.

has already been shown earlier in the discussion that if the copolymers are high-pressure crystallized, the resulting samples have a higher melting point. By varying the degree of supercooling on samples crystallized at 5000 atm, the relative size of the melting peaks occurring at 160° and 187°C changes. This is illustrated in Fig. 3.

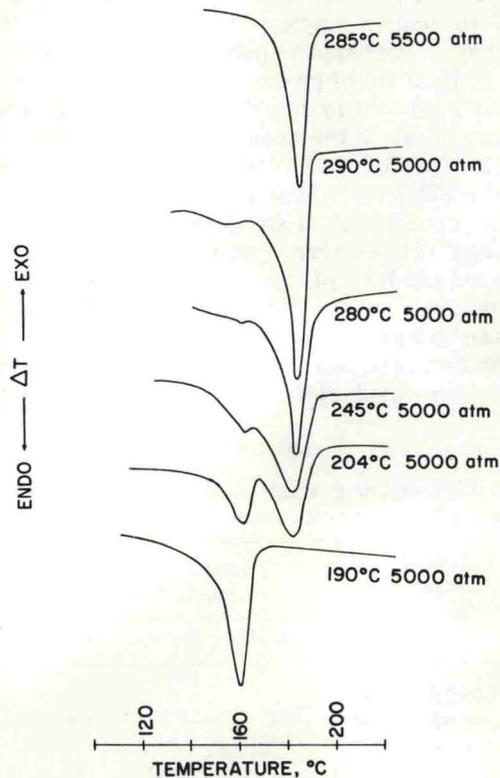


FIG. 3. DTA thermograms as a function of crystallization temperature for  $\text{PVF}_2$  samples crystallized at 5000 atm.

A sample which was heated to 190°C and pressure-crystallized at 5000 atm had a diffractometer scan which was nearly identical to that of phase II (scan I in Fig. 2). The DTA melting point of 160°C for this high-pressure crystallized sample was also identical with that of the atmospherically crystallized  $\text{PVF}_2$  phase II. The melting point thermogram for the sample which was heated to 280°C and pressure-crystallized at 5000 atm (scan 2 in Fig. 2) indicated melting endotherms at 160° and 187°C. The diffractometer scan for a