

FIG. 1. Debye-Scherrer powder photographs of phases I and II and the high-pressure-crystallized form of PVF₂.

ple would fracture brittlely at a very low draw ratio when orientation experiments were performed, rather than draw uniformly. Therefore, the fiber photographs were difficult to interpret since there was only a low degree of preferred orientation. However, it was evident that, although what was considered to be phase III had two strong X-ray reflections of nearly equal intensity in the 4.0-4.5 Å region, oriented samples of this material exhibited only one intense reflection. When DTA scans were taken of the unoriented high-pressure crystallized samples, there was a shoulder at 160°C whereas the major melting peak occurred at 187°C. As previously stated the samples were drawn successfully at a draw ratio of 2.5 to 1. These oriented samples also had a melting point of 187°C; however, the shoulder at 160°C was no longer present. The X-ray fiber photographs of the oriented material were identical with ones observed for phase I. It should be noted that low-pressure-crystallized phase II also converts to phase I upon drawing at 25°C. A comparison of in-

frared spectra of the oriented samples of high-pressure crystallized PVF_2 and phase I indicated no differences in band positions.

If a copolymer of 93-7 mole% VF_2 -tetrafluoroethylene, which normally crystallizes from the melt in phase I, is heated to 225°C and pressure-crystallized at 5000 atm, X-ray powder photographs indicate that the resulting samples are still phase I rather than phase III. This high-pressure-crystallized copolymer sample had a melting point of 158°C which is 19° higher than the normal melting point of the copolymer. Similarly, if a copolymer of 91-9 mole% VF_2 - VF_3 , which normally crystallizes from the melt in phase II, is heated to 225°C and pressure-crystallized at 5000 atm, X-ray photographs indicate that phase I again results rather than phase III. This high-pressure-crystallized phase I also has an elevated melting point of 170°C which is 10° higher than the melting point of the normal low-pressure-crystallized samples.

Since the high-pressure-crystallized samples of both copolymers studied crystallized in phase I with a higher melting point rather than in phase III, the possibility that phase III for the homopolymer might be a mixture of phase II and phase I had to be considered. Diffractometer scans of phases I and II and the high-pressure crystallized material are presented in Fig. 2. It should be noted in Fig. 2

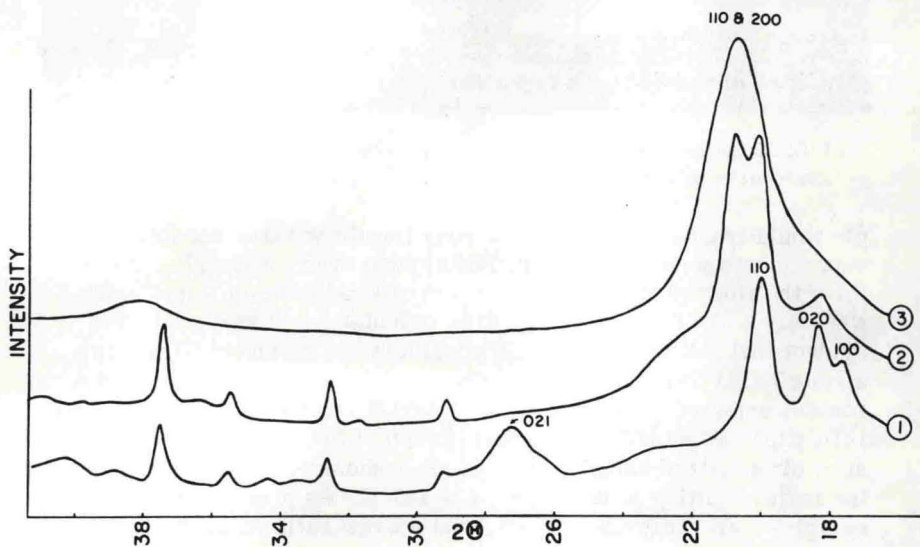


FIG. 2. X-ray diffractometer scans of phases I and II and the high-pressure-crystallized form of PVF_2 . (See note in text concerning relative intensities.) (1) Phase II, (2) high-pressure-crystallized PVF_2 , (3) phase I.