sample heated to 285° C and pressure-crystallized at 5500 atm is very similar to that of a PVF_2 phase I sample (scan 3 in Fig. 2). The DTA melting point, however, is 27° C higher for the high-pressure-crystallized sample. The intensities of various X-ray reflections for high-pressure-crystallized PVF_2 samples as a function of supercooling are compared in Table 1. It can be observed that as the degree of supercooling is reduced, the peak occurring at about 4.2 Å increases in intensity whereas the other peaks decrease. When the samples were heated above 290° C and pressure-crystallized at 5000 atm, they decomposed.

If the qualitative X-ray results of Table 1 are correlated with the corresponding DTA thermograms of Fig. 3, it would appear that as the reflections due to phase II decrease in intensity, the lower melting endotherm also diminishes in size. When the pressure and temperature conditions are such that only phase I X-ray reflections remain, the lower melting peak no longer appeared in the thermogram. However, the possibility that some contribution to the higher-melting point is made by phase II cannot be discounted without further studies.

It would, therefore, appear that the previously reported phase III of PVF_2 [3] is actually a mixture of low- and high-melting phases II and I rather than a new polymorphic form. Since phase I has a higher density than phase II (2.0 vs. 1.90 g/cm^3), it is reasonable that pressure crystallization should favor crystallization in the polymorphic form having the greater density. No observable long-period spacings have been obtained from small-angle photographs for the low-pressure-crystallized or the high-pressure crystallized PVF_2. However, electron microscopy of fracture surfaces of high-pressure crystallized PVF_2 revealed step heights on the order of 680 Å [3]. Chain-folding theories would predict a higher-melting point for samples that have longer fold periods, and the high-pressure crystallized PVF_2 has a 27° increase in its melting point when compared with the normal low-pressure phase I. Davidson and Wunderlich [5] have observed that when polyethylene is pressure-crystallized at 5000 atm, extended chain crystals with an increased melting point result.

CONCLUSIONS

The following results have been demonstrated in this paper:

1. The postulated new high-pressure-crystallized polymorphic form of PVF_2, phase III [3], is a mixture of low-melting phase II and high-melting phase I.
2. With crystallization pressures greater than 5000 atm, the higher-melting planar zig-zag form alone results.

3. Orientation of the high-pressure-crystallized samples which are a mixture of phases I and II results in the polymorphic transition to phase I of any material which was originally phase II. The resulting oriented sample has a melting point of 187°C which is 27° higher than the phase I samples resulting from orienting of low-pressure-crystallized films of PVF_2.

4. To obtain the high-pressure-crystallized planar zig-zag form (phase I) of the copolymers, less stringent supercooling requirements are required than those required for the PVF_2 homopolymer.

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