

The Polymorphism of Poly(vinylidene fluoride)

IV. The Structure of High-Pressure-Crystallized Poly(vinylidene fluoride)*

W. W. DOLL AND J. B. LANDO
Division of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio

Summary

A detailed study of high-pressure-crystallized poly(vinylidene fluoride) has indicated that a mixture of low-melting phase II and high-melting phase I is present, rather than a new crystalline phase (phase III) as originally suggested.

The relative amounts of phase I and phase II resulting from crystallization under pressure are a function of pressure and the degree of supercooling. Pressure crystallization at 285°C and 5500 atm results in samples which were pure phase I with an increased melting point of 187°C.

INTRODUCTION

The crystal structures of phase I [1] and phase II [2] of poly(vinylidene fluoride) have recently been determined. These crystalline forms are prepared under atmospheric pressure. Doll and Lando [3] have demonstrated that if poly(vinylidene fluoride), PVF₂, is heated to 280°C and pressure-crystallized at 5000 atm, a new and different X-ray pattern appeared which they designated phase III. When the degree of supercooling is held to a small value, this diffraction pattern has also been observed in samples which were crystallized at pressures as low as 3000 atm. This high-pressure-crystal-

*This research was supported by the National Science Foundation under NSF Grant 6P-21301.

lized sample had a melting point of 187°C which is about 27° above that of the normally crystallized phase II of PVF₂. At the time this high-pressure sample was obtained, efforts to orient it were generally unsuccessful. Without an oriented sample it was impossible to determine the lattice constants unambiguously. In this paper some of the recent results which have been obtained on the high-pressure-crystallized PVF₂ will be discussed.

EXPERIMENTAL

The PVF₂ used was a commercial grade of Kynar (Pennwalt Chemical Co.). The samples were pressure-crystallized in a high-pressure dilatometer which has been previously described [3,4]. In a previous paper [3], the effect of pressure on the melting behavior of PVF₂ has been discussed. By knowing the melting point under a given hydrostatic pressure, it was possible to determine the degree of supercooling of a sample. Supercooling is defined as the difference between the melting point and crystallization temperature at a given pressure. Interplanar spacings were determined from Debye-Scherrer photographs. Fiber patterns of oriented samples prepared as below were obtained by using a 70-mm-diameter cylindrical camera. Reflections from planes perpendicular to the chain axis were obtained by taking 180-deg oscillation photographs with the draw direction aligned perpendicular to the oscillation axis. Diffractometer scans were taken on a GE XRD-6 diffractometer, and differential thermal analysis (DTA) scans were made on a du Pont 900 DTA. PVF₂ pressure-crystallized in the high-pressure dilatometer resulted in samples having a cylindrical shape 0.25 in. in diameter. These cylindrical samples were turned down on a lathe to form dumbbell-shaped samples which could be oriented by using the Instron tensile tester. Pin vise grips were used to hold the sample in the jaws of the tensile tester. With this experimental arrangement, samples crystallized at high pressure could be drawn to a ratio of 2.5 to 1.

RESULTS AND DISCUSSION

Figure 1 depicts the Debye-Scherrer powder photographs for the three polymorphic phases of PVF₂ as originally presented by Doll and Lando [3]. As can be seen in Fig. 1, if photographic techniques alone are used, the phase III Debye-Scherrer photograph resembles neither phase I nor II. Any attempts to orient phase III resulted in a polymorphic transition to a phase having an X-ray fiber pattern very similar to that of PVF₂ phase I. In general, however, the sam-

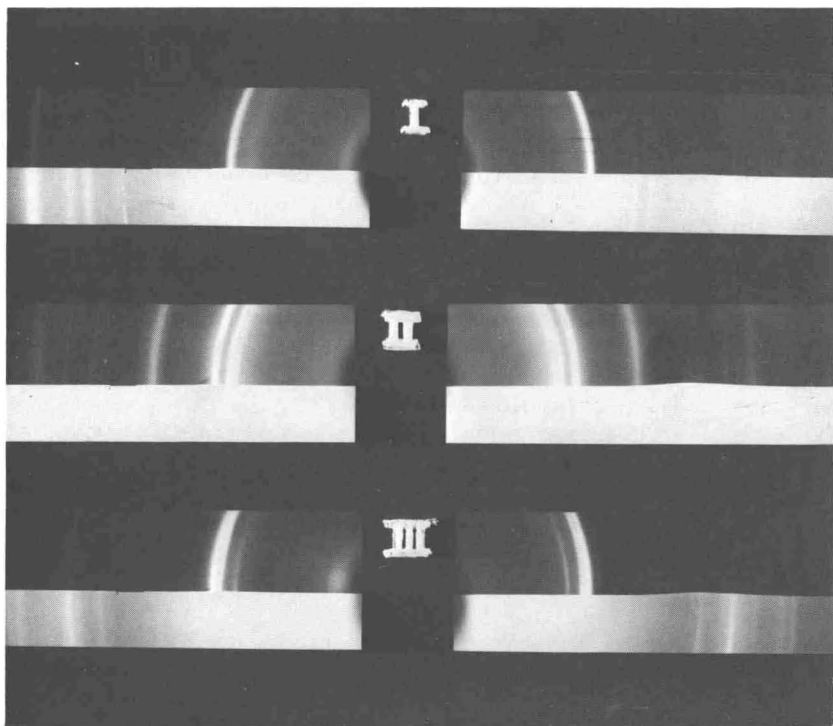


FIG. 1. Debye-Scherrer powder photographs of phases I and II and the high-pressure-crystallized form of PVF₂.

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

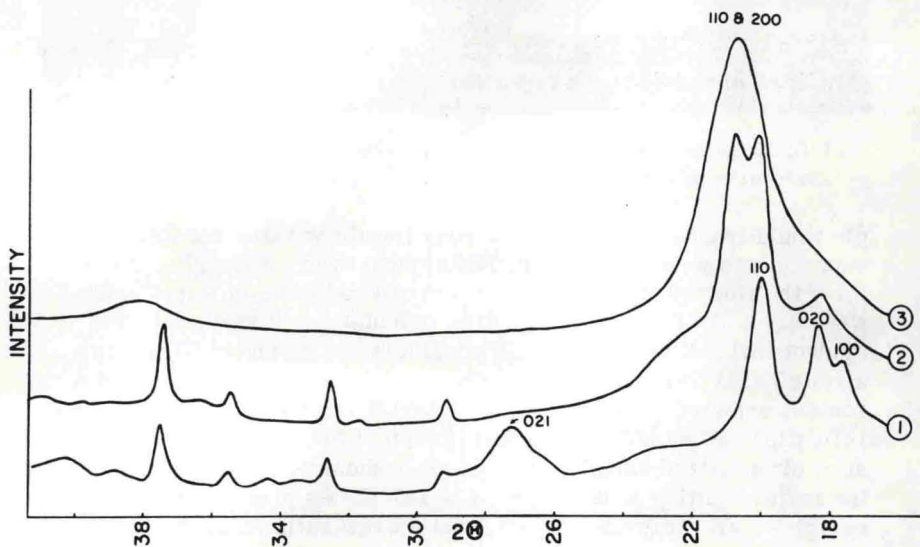


FIG. 2. X-ray diffractometer scans of phases I and II and the high-pressure-crystallized form of PVF_2 . (See note in text concerning relative intensities.) (1) Phase II, (2) high-pressure-crystallized PVF_2 , (3) phase I.

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 PVF₂ 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^a

Crystallization temperature (°C)	Degree of Supercooling (°C)	Intensity of peaks occurring near the following d spacings (Å) ^b :				
		5.00	4.81	4.45	4.27	3.34
—	Low-pressure- crystallized PVF ₂ 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

^aAll samples were crystallized at 5000 atm.

^bA = 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.

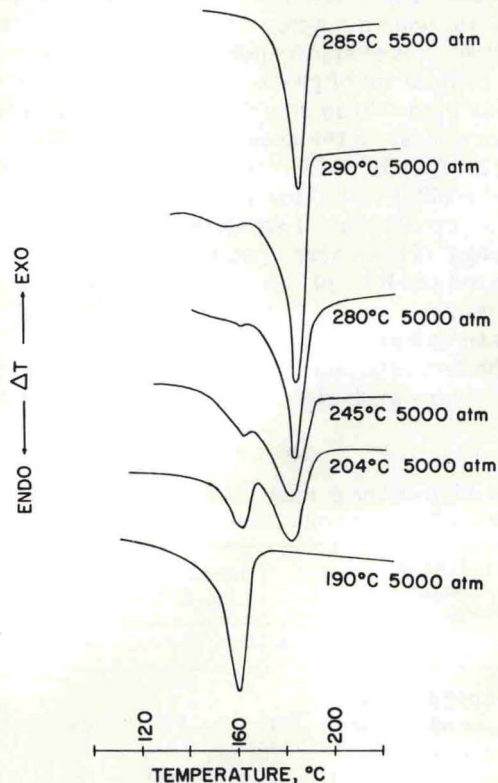


FIG. 3. DTA thermograms as a function of crystallization temperature for PVF_2 samples crystallized at 5000 atm.

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 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

sample heated to 285°C and pressure-crystallized at 5500 atm is very similar to that of a PVF₂ 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 PVF₂ 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 PVF₂ [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/cm³), 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 PVF₂. However, electron microscopy of fracture surfaces of high-pressure crystallized PVF₂ 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 PVF₂ 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 PVF₂, 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 PVF₂.

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 PVF₂ homopolymer.

REFERENCES

- [1] J. B. Lando, H. G. Olf, and A. Peterlin, *J. Polymer Sci.*, (A-1)4, 941 (1966).
- [2] W. W. Doll and J. B. Lando, *J. Macromol. Sci.*, B4, 309 (1970).
- [3] W. W. Doll and J. B. Lando, *J. Macromol. Sci.*, B2, 219 (1968).
- [4] J. L. Kardos and E. Baer, *J. Polymer Sci.*, A3, 2827 (1965).
- [5] T. Davidson and B. Wunderlich, *J. Polymer Sci.*, (A-2)7, 377 (1969).

Received by editor February 26, 1970

Submitted for publication April 29, 1970