

## **A Preliminary X-Ray Study on Ferroelectric Phase Transition of Poly(Vinylidene Fluoride) Crystal Form I**

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### Summary

Ferroelectric phase transition of poly(vinylidene fluoride) crystal form I has been investigated by X-ray diffraction measurements. The X-ray reflections of form I decrease in intensity steeply in the vicinity of 172°C and new reflections of the high-temperature phase, the conformation of which is essentially equivalent to that of form III ( $T_3GT_3\bar{G}$ ), begin to appear, maximize in intensity at about 183°C, and disappear above 190°C. These phenomena are consistent with the previously reported infrared spectral data. The X-ray reflections observed for the high-temperature phase contain the (100), (120), etc. forbidden for polar form III, suggesting a possibility of another crystal structure of anti-polar or non-polar form III.

### Introduction

In the previous paper (1) we reported a thermally-induced phase transition of poly(vinylidene fluoride) [PVDF] form I, which was found to occur at about 172°C, immediately below the melting point, by means of infrared spectroscopy and DSC measurement: in this temperature region the infrared bands characteristic of  $T_3G$  and  $TG$  rotational isomers increase in intensity and simultaneously the trans bands of form I decrease as shown in Figure 1. This conformational transition point fits well to the curve of the phase transition temperature vs VDF molar content for vinylidene fluoride-trifluoroethylene (VDF-TrFE) copolymer, which has been clarified by many kinds of measurements to exhibit ferroelectric phase transition between ferroelectric phase of all-trans conformation and paraelectric phase of gauche-typed conformation (2-6). From the essential equivalency in transitional behavior between PVDF form I and VDF-TrFE copolymers, we proposed a possibility of "ferroelectric" phase transition between polar form I ( $TT$ ) and non-polar or anti-polar form III ( $T_3GT_3\bar{G}$ ) for PVDF form I sample (1). Thereafter we measured the temperature dependence of X-ray diffraction of form I, the result of which supports our proposition and will be reported in this paper.

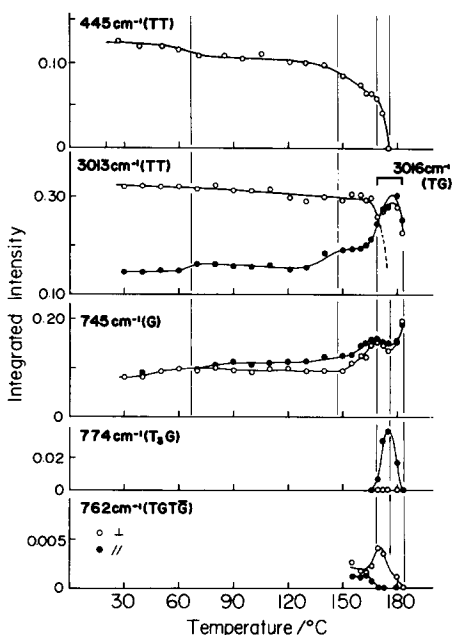


Figure 1. Temperature dependence of infrared absorbances of poled PVDF form I: o, incident electric vector perpendicular to the draw direction; ●, incident electric vector parallel to the draw direction. Quoted from ref (1).

## Experimental

PVDF samples used were KF 1000 (Kureha Chemical Industry Co. Ltd.). Films of form I with a thickness of ca. 40 $\mu$ m were prepared by stretching the melt-quenched film to about four times the original length at 60°C followed by annealing at 130 ~ 170°C for 100 min under tension. These films were subjected to the poling treatment by corona charging (from a point 1 cm distant from the surface of the film; a voltage of about 10 kV: at room temperature) because the phase transition of PVDF form I has been found to be detected more explicitly for a poled sample (1). For X-ray diffraction measurements a few sheets of strip cut out of the poled thin film were stacked together and packed into a glass capillary, which was then set into a heating cell equipped with a temperature controller. A temperature dependence of X-ray diffraction was measured by a photographic method and also by utilizing a PSPC (position sensitive proportional counter) system with a sample-to-detector distance of 10 cm.

## Results and Discussion

In Figure 2 is shown the temperature dependence of X-ray diffraction of PVDF form I measured by PSPC system. The X-ray intensity of (200, 110) reflection of form I decreases largely as a rise of temperature but there appears no new reflection until 172°C, where some reflections begin to appear along with a steep decreasing of form I reflections. The

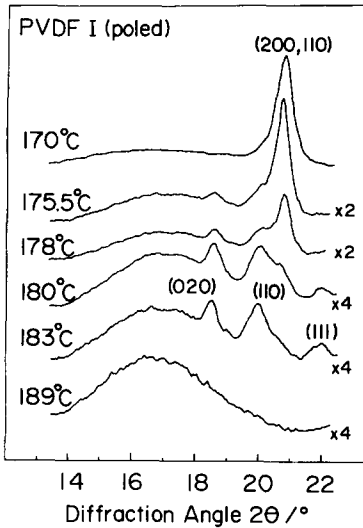


Figure 2. Temperature dependence of X-ray diffraction pattern of PVDF form I. The equatorial reflections were measured by a PSCP system.

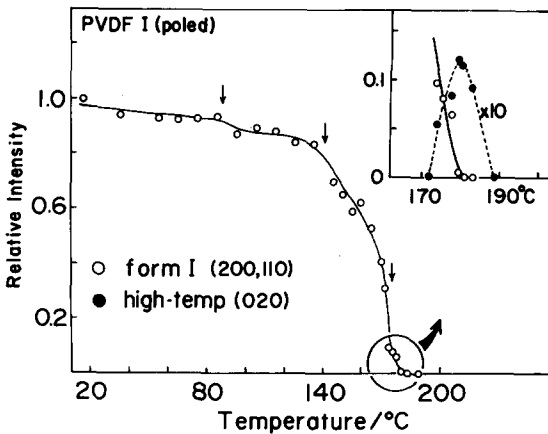


Figure 3. Temperature dependence of X-ray diffraction intensity for PVDF form I and the high-temperature phase.

newly observed reflections of the high-temperature phase can be indexed based on the cell parameters of PVDF form III (7,8): in Figure 2 the reflections of (020), (110), and (111) could be detected. Figure 3 shows a temperature dependence of relative intensity for the (200, 110) reflection of form I and the (020) reflection of the high-temperature phase. The reflection intensity of the high-temperature phase begins to increase in the vicinity of 172°C, maximizes at about 183°C, and disappears at about 190°C. Above 190°C only a broad amorphous halo remains as shown in Figure 2. These X-ray behaviors are quite consistent with the infrared data shown in Figure 1. The reflection intensity of form I decreases also in the other temperature regions as indicated by arrows in Figure 3. These X-ray intensity changes are parallel to the infrared intensity change of the  $445\text{ cm}^{-1}$  trans band (Figure 1) and may be interpreted qualitatively by the structural changes occurring within the form I crystallites as reported in the

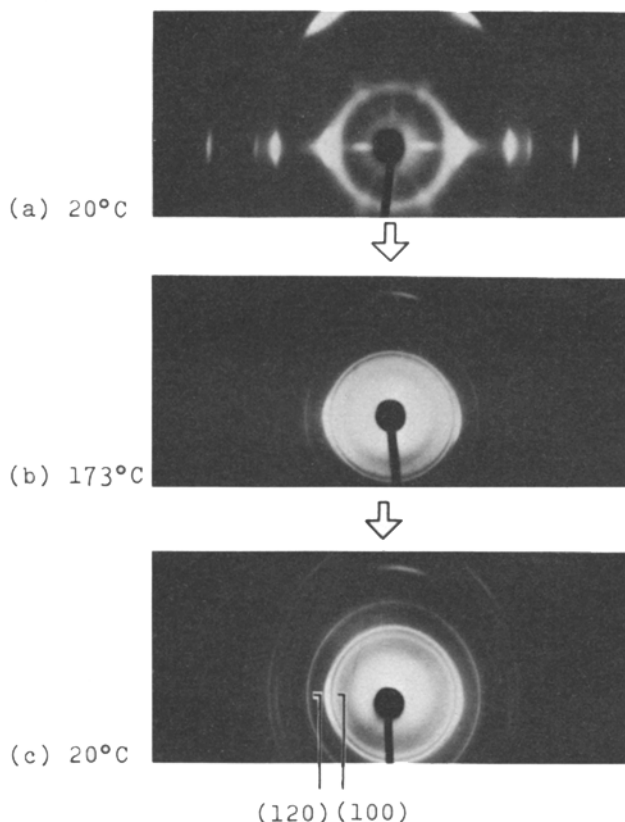


Figure 4.  
X-ray fiber diagrams  
for PVDF form I  
sample taken at the  
various temperatures  
successively.

previous paper (1).

In Figure 4 are shown the X-ray fiber diagrams of PVDF form I sample taken at the various temperatures successively. Although the degree of orientation is very low, a new reflection pattern is observed at about 173°C, which is irreversibly retained even after cooling down to the room temperature just likely the case of infrared measurements (1). All the observed reflections can be indexed by the unit cell of form III as already stated in Figure 2. But, in addition to the reflections of (020), (110), and (111) observed in Figure 2, the reflections of (100), (120), etc., which could not be observed clearly in that figure because of their weak intensity, are detected in Figure 4 (b) and (c). These reflections should be forbidden from the space group symmetry for the polar structure of form III (Space group  $Cc-C_2^2$ ) (8). They might be observed also for non-polar form II (Space group  $P2_1/c-C_2^2$ ) (9). But the sample of Figure 4 (c) consists mostly of form III-type conformational chains, with a slight residue of form I, as understood from the Fourier-transform infrared spectra of Figure 5 (10), where the characteristic bands of T<sub>3</sub>G rotational isomer are predominant and those of form II (e.g., 795, 766 cm<sup>-1</sup>) are not practically detected. Therefore the possibility of form II reflections will be excluded.

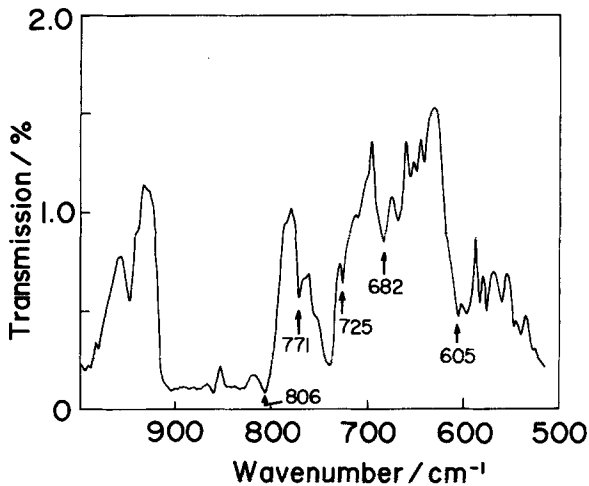


Figure 5. Fourier-transform infrared spectrum of PVDF sample used in Figure 4 (c). The wavenumbers indicated are characteristic of form III conformation (10).

Thus the observation of X-ray reflections (100), (120), etc. in Figure 4 (b) and (c) suggests a possibility of another way of chain packing for form III obtained here; for example, a favorable packing of "anti-polar" or "non-polar" structure. Here the anti-polar structure means an anti-parallel arrangement of dipoles of  $T_3GT_3\bar{G}$  chains along the a axis of the unit cell as described by Lovinger (11) and the non-polar structure corresponds to the statistically disordered packing of these chains. Then the ferroelectric phase transition of polar form I might be described as follows as one possible model.

$$T_c \sim 172^\circ\text{C}$$

polar form I  $\longrightarrow$  anti-polar or non-polar form III

This transitional scheme is consistent with that derived for VDF-TrFE copolymers (5,6). As discussed in the previous paper (6), the molecular chains of the high-temperature phase of VDF-TrFE copolymers experience an appreciable thermal motion and so the X-ray diffraction pattern has been interpreted by the statistical conformational model of  $T_3G$ ,  $TG$ ,  $T_3\bar{G}$ , and  $T\bar{G}$  isomers cylindrically averaged around the chain axis. Although the high-temperature phase of PVDF form I might be in the same situation as the case of VDF-TrFE copolymers, the X-ray reflections are relatively sharp even at the high temperature, suggesting an appreciably high degree of ordering within the crystal.

Since the transition in PVDF form I occurs in the temperature region quite close to the melting point, the degree of chain orientation is very low as seen in the X-ray photograph of Figure 4, making it difficult for us to study the more detailed structural investigation at the present stage.

### Acknowledgement

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