

# ***X-Ray Diffraction Pole Figure Measurements on a Poly(Vinyl Fluoride) Film***

## **INTRODUCTION**

Although the general molecular dimensions of poly(vinyl fluoride) (PVF) are not dissimilar to those of branched polyethylene, which has been the subject of a number of structural studies, very little x-ray diffraction work has been reported on PVF. Typically, the polymer is substantially crystalline, thus permitting basic structural studies. Golike<sup>1</sup> proposed a hexagonal unit cell, whereas Natta and co-workers<sup>2</sup> preferred an orthorhombic system; it is clear that the experimental results are sensibly interpretable on either basis. There is agreement that the chain repeat distance contains one monomer unit and that the conformation of the chain is planar zig zag. Furthermore, infrared spectroscopic studies by Zerbi and Cortili<sup>3</sup> have shown that the placement of the fluorine atoms is such as to give a substantially syndiotactic structure.

This note reports the results of pole figure measurements on a commercial PVF film. They show that the technique is readily applicable and that a high degree of orientation is present. Furthermore, a detailed interpretation of the pole figures favors the orthorhombic unit cell for the sample examined.

## **EXPERIMENTAL**

The film examined was 25  $\mu\text{m}$  thick DuPont "Tedlar" 100SM30PC, which is understood to be prepared by casting followed by biaxial drawing. The diffraction intensities from a film of this thickness proved to be too low and the method of stacking aligned discs punched from the sheet, which proved very satisfactory in the case of blown polyethylene films,<sup>4</sup> was followed. Pole figure measurements were made with a Schulz texture goniometer, using computer interpretation of the data to give a resolution of one to two degrees in latitude and longitude.<sup>5,6</sup> The experimental technique was similar to that already reported in the case of the blown polyethylene films.<sup>4</sup> Flat-plate photographic measurements were made with a Philips PW1030 flat-plate camera.

## **RESULTS AND DISCUSSION**

A conventional powder diffractometer scan showed three principal reflections, the  $d$  spacings and alternative assignments of which are summarised in Table I; the 4.28  $\text{\AA}$  reflection is particularly intense. Pole figures were obtained for both the 4.28 and 2.53  $\text{\AA}$  reflections, the latter being resolved from the 2.47  $\text{\AA}$  reflection by very careful adjustment of the Schulz texture goniometer. They are shown in Figures 1(a) and 1(b), respectively.

Since the assignment of 2.53  $\text{\AA}$  reflection is (001) for both a hexagonal and an orthorhombic unit cell, Figure 1(b) indicates a very high degree of orientation of the  $c$  axis in the transverse direction. This observation is fully consistent with a final biaxial drawing stage, with a high draw ratio along the transverse direction, during the manufacture of the film.

Regardless of the particular assignment of the 4.28  $\text{\AA}$  reflection Figure 1(a) indicates clearly that the  $b$  axis lies predominantly along the machine direction. In this case for a hexagonal system, where the assignment of the reflection would be (100), one would expect three equally intense and well defined maxima, separated from each other by 60° in the sheet normal-machine direction plane. As is evident from Figure 1(a), there are three maxima which satisfy the above angular requirement. They do not, however, satisfy the intensity requirement as the outer maxima are much less pronounced than the central one. This behavior is much more consistent with an orthorhombic unit cell, in which case the central maximum corresponds to the intense (200) reflection and the outer maxima to the coincident but much weaker (110) reflection.

The above conclusions are fully supported by the flat-plate camera measurements on the same PVF film. These show that there is a predominant orientation of the  $a$  and  $b$  axes of the orthorhombic system in the sheet normal-machine direction plane and a corresponding predominant

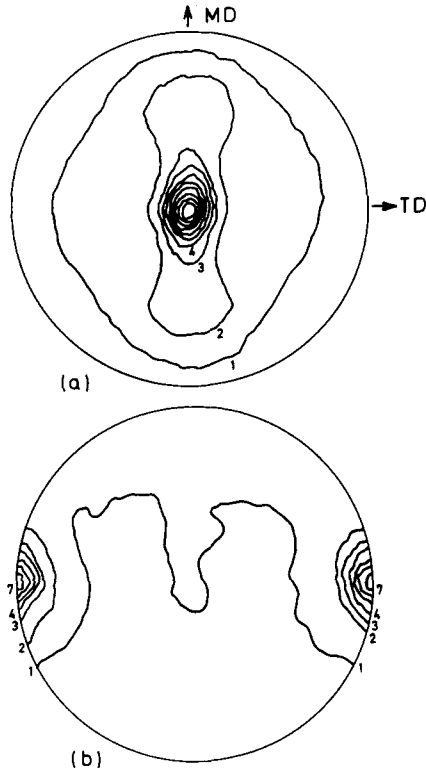


Fig. 1. Pole figures for the 4.28 Å reflection (a) and the 2.53 Å reflection (b) of DuPont "Tedlar" 100SM30PC poly(vinyl fluoride) film.

orientation of the  $c$  axis in the transverse direction. A thicker ( $100\ \mu\text{m}$ ) sheet of PVF was examined by the same flat plate method but was found to show no preferred orientation. It was presumably produced by a different method.

The high degree of orientation of the thinner film is very reminiscent of that found with high-density polyethylene films blown under very high-stress conditions, although the disposition of the  $c$  axis is very different. In the absence of a precise knowledge of the processing conditions of the "Tedlar" film it is difficult to make an exact comparison with blown polyethylene films. However, a rather lower degree of orientation might have been anticipated on the grounds that PVF will probably resemble somewhat branched polyethylene rather than the linear polymer so far as chain perfection and packing are concerned. Nevertheless, in the absence of pole figure measurements on films prepared under known conditions it is clearly speculative to attempt a further comparison with the well-documented studies on rolled<sup>7-9</sup> and blown<sup>4,10,11</sup> polyethylene.

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TABLE I  
Measured  $d$  Spacings and Assignments of the Principal Reflections in the Powder X-Ray  
Diffraction Pattern of PVF

Measured $d$ spacing (Å)	Assignment	
	Hexagonal	Orthorhombic
4.28	(100)	(200), (110)
2.53	(001)	(001)
2.47	(110)	(020), (310)

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