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Crystal orientation function of poly(trimethylene terephthalate) by wide-angle x-ray diffraction

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Summary

A wide-angle X-ray diffraction method for measuring poly(trimethylene terephthalate) (PTT) crystal orientation function was described. It was based on Wilchinsky's treatment of uniaxial orientation. Although PTT has a low symmetry triclinic cell only one equatorial reflection is needed for the measurement because the unit cell ß-angle happened to be 90°, and there is a strong *010* reflection. The choice of unit cell parameters from the conflicting literature data and the reduction of Wilchinsky's equation into a simple form allowing the measurement of only one reflection were presented. The discrepancies between literature wide-angle X-ray and electron diffraction unit cell volumes and crystal densities were also discussed.

Introduction

Poly(trimethylene terephthalate) (PTT) is an aromatic polyester with three methylene units in its chemical structure. Compared to the familiar poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) with two and four methylene units respectively, there have been very few studies on PTT because the polymer was not readily available until recently [1]. Early work by Ward *et al*, [2,3] showed PTT to have some unusual mechanical properties. For examples, PTT fiber has a tensile elastic recovery of >90%, much better than those of PET and PBT; and it has a very low modulus of 25 MPa. PTT's crystal modulus measured from wide-angle X-ray diffraction stress-strain experiment was only 2.59 GPa [4] compared to 107 GPa of PET [5]. The excellent elastic recovery and low fiber modulus were attributed to PTT's three methylene units arranged in highly contracted, helically coiled *gauche-gauche* conformation [3] compared to the *trans* conformation of PET. Both properties were utilized in the polymer's commercial debut for making resilient carpets, soft-, stretchable-textile fabrics for sports active wears, and for clothing with soft sensory touch [6,7]. Other applications under development include non-woven, monofilament, film and engineering thermoplastic.

With increasing interest in PTT as a new fiber material, orientation characterization is an important tool for studying the polymer's structural development in fiber spinning and drawing. This communication reports the method used in our laboratory over the last ten years during the course of PTT commercial development [8]. It was based on

Wilchinsky's treatment of uniaxial orientation [9]. Through fortuitous symmetry conditions of PTT crystal unit cell, only one wide-angle X-ray reflection is needed to measure crystal orientation function despite the polymer's low symmetry triclinic cell. It is therefore a simple method.

Experimental

PTT (M_n,=17,300, M_w,=35,200, Shell Chemical Company) was compression molded at 250°C into 30-mil thick film. It was quenched in water, die-cut into dog-bone shape samples and was drawn at 50°C and 75°C in an Instron tensile machine (Model 1122), equipped with a circulating hot air chamber at an extension rate of 2.54 cm/min. Draw ratios were measured from the change in the lengths of spacings marked at 1 cm interval. *010* reflection was azimuthally scanned at $2\theta = 15.4°$ from 90 to 0° using a Rigaku Denkki wide-angle X-ray diffractomer equipped with a goniometer. 90° corresponds to the transverse and 0° corresponds to the draw directions of the sample. Monochromatic Cu K_α, beam was generated with a nickel filter at 40 kV and 35 mA. Azimuthal intensities were also scanned at the tails of the *010* peak at $2\theta = 13.8$ and 17.6° for background correction. The background intensity at 15.4° was obtained by interpolating the data of these two azimuthal scans. $\langle\cos^2\phi_{010,\,Z}\rangle$ was calculated from the corrected azimuthal intensities, $I(\phi)$ from

$$\langle\cos^2\phi_{010,Z}\rangle = \frac{\int_0^{\pi/2} I(\phi)\sin\phi\cos^2\phi\, d\phi}{\int_0^{\pi/2} I(\phi)\sin\phi\, d\phi} \tag{1}$$

Results and Discussion

The degree of uniaxial orientation of a polymer's chain axis is described by the Herman-Stein orientation function:

$$f_c = \frac{3\langle\cos^2\phi_{c,Z}\rangle - 1}{2} \tag{2}$$

where $\langle\cos^2\phi_{c,Z}\rangle$ is the average cosine square angle the polymer's *c*-chain axis made with the draw direction, Z. For an isotropic material, $f_c = 0$. For a fully oriented chain, $f_c = 1$, and $f_c = -0.5$ when the chain is oriented perpendicular to the draw direction. Several methods such as wide-angle X-ray diffraction (WAXD), IR dichroism, solid-state nuclear magnetic resonance can be used to measure $\langle\cos^2\phi_{c,Z}\rangle$.

Wilchinsky's treatment is perhaps the most commonly used method to measure $\langle\cos^2\phi_{c,Z}\rangle$ by WAXD. The unit cell *a, b* and *c*-axis are superimposed on an orthogonal co-ordinates, X,Y,Z with Z as the draw direction, Figure 1; *e, f, g* and $\cos\phi_{X,Z}$, $\cos\phi_{Y,Z}$, $\cos\phi_{c,Z}$ as the respective set of director cosines. $\langle\cos^2\phi_{c,Z}\rangle$ is given by the dot product of the two unit vectors in the Z and in the direction of the normal,

N(*hkl*), to the selected (*hkl*) plane:

$$\begin{aligned}\langle\cos^2\phi_{hkl,Z}\rangle = {} & e^2\langle\cos^2\phi_{X,Z}\rangle + f^2\langle\cos^2\phi_{Y,Z}\rangle + g^2\langle\cos^2\phi_{c,Z}\rangle \\ & + 2ef\langle\cos\phi_{X,Z}\cos\phi_{Y,Z}\rangle + 2fg\langle\cos\phi_{Y,Z}\cos\phi_{c,Z}\rangle \\ & + 2eg\langle\cos\phi_{c,Z}\cos\phi_{X,Z}\rangle \end{aligned} \qquad (3)$$

For polymers with low symmetry such as a triclinic crystal structure, up to six WAXD reflections [10] may be needed to measure $\langle\cos^2\phi_{c,Z}\rangle$ according to equation (3). When too many reflections are needed they often discourage WAXD f_c measurement, however, the number can be reduced by applying appropriate symmetry conditions [9] or using suitable strong *00l* reflection. For example, three reflections, *100*, $\bar{1}10$ and *010* were used for the triclinic PET [11]. The measurement is, however, often simplified by using just one off-meridian $\bar{1}50$ as a substitute for *00l* reflection with good results [12].

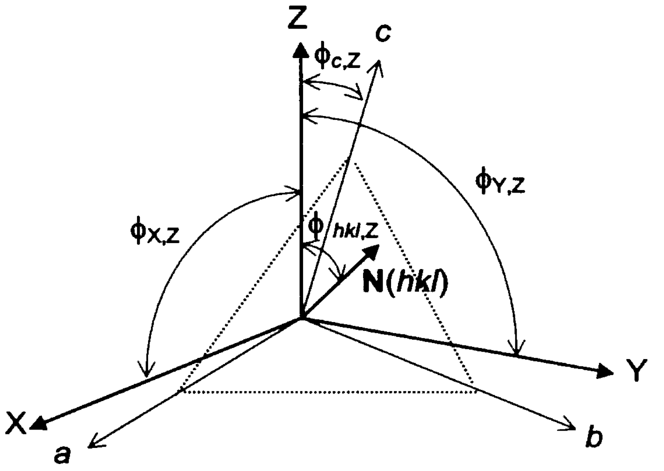

Figure 1: Wilchinsky's generalized co-ordinate systems for specifying crystal orientation. Unit cell *a,b* and *c* axis superimposed on an orthogonal X,Y,Z coordinates. N(*hkl*) is the normal of the (*hkl*) plane. (After Alexander [10]).

Although PTT has a *002* reflection, the intensity is weak and it is not a true meridional reflection. It is offset from the meridian by about 3°. The offset reflections are so close that they overlap each other and appear as one meridional reflection [13]. Unlike PET's $\bar{1}50$ reflection, the overlapped PTT *002* reflection could not be separated easily even at high orientation. We therefore chose the more intense *010* equatorial reflection for orientation measurements. The use of only one *010* reflection for orientation measurement based on Wilchinsky's method warrants discussion on how to reduce equation (2) with six unknowns into a simple form.

PTT crystallizes into triclinic cell with two repeating units in the *c*-axis fiber period. The methylene units are arranged in *gauche-gauche* conformations, and the chains are helical-like at the methylene units when viewed in the *bc* plane. Table 1 shows the unit cell parameters determined from WAXD and electron diffractions (ED) [13-16], and Figure 2 shows the WAXD pattern and reflection indices. Although the unit cell dimensions appeared to be quite close to each other the calculated unit cell volume and crystal densities showed they were divided into two distinct groups. Cell

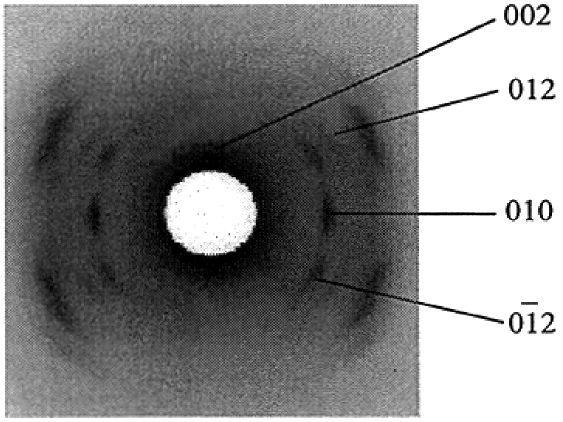

Figure 2: PTT WAXD pattern and reflection indices.

parameters obtained by WAXD have a higher density of about 1.43 compared to 1.38 g/cm^3 by ED. By plotting densities of 19 PTT samples with crystallinities between 14-35 wt. % determined by differential scanning calorimetry, Ziabicki [17] extrapolated a crystal density of 1.441 g/cm^3 (R^2=0.984, standard deviation = 0.002) in good agreement with those obtained by WAXD. Since ED measurements focused on very small area of selected crystalline regions while WAXD measurements were over a larger macroscopic area where crystal defects, amorphous scattering, size of crystallites etc. could contribute to reflection broadening, it is surprising WAXD gave higher density and agreed better with experimental value. The reason for such distinct grouping of WAXD and ED data is not clear and needs to be addressed in the future. One should therefore be cautious in using the published densities to measure crystallinity by density method

Table 1: Unit Cell Parameters and Densities of PTT Crystal

Method:	Desborough *et al.* [13] WAXD	Chatani *et al.* [15] WAXD	Poulin-Dandurand *et al.* [14] ED*	Moss and Dorset [16] ED
Cell Parameters:				
a (Å)	4.5(9)	4.58	4.637	4.64
b (Å)	6.2(1)	6.22	6.226	6.27
c (Å)	18.3(1)	18.12	18.64	18.64
α (°)	98.(0)	97	98.4	98
β (°)	90.(0)	89	93.0	93
γ (°)	111.(7)	111	111.1	111
Volume (Å^3)	479.2	478.1	493.5	498.3
Density (g/cm^3)	1.432	1.429	1.387	1.374

*Supplemented with WAXD data.

Because of the density discrepancy, we calculated PTT bond distances from the ED and WAXD atomic fractional coordinates given by Poulin-Durandand *et al.* [14] and Desborough *et al.* [13], and found the former gave some bond lengths much higher than the standard lengths, notably the C-O bonds. Anomaly in calculated bond lengths could be due to least-squares refinement of the crystal structure. Wanocott [18] showed least-squares refinement of PET atomic fractional coordinates could give unreasonable bond lengths despite a lower R-factor than using constraint least-squares method supplemented with reliable bond lengths and bond angle. Bond distance calculations using Desborough *et al*. fractional coordinates were quite consistent with those considered standard. Based on the agreement between WAXD and experimental crystal densities, and the consistent bond lengths with standard Desborough *et al*.'s crystal structure data were used for WAXD orientation study. Future studies may provide better data to resolve the crystal density discrepancies.

The following conditions were applied to simplify Wilchinsky's equation [9]: (1) for *hk0* reflection the director cosine g is 0, (2) in uniaxial orientation, $\langle\cos^2\phi_{X,Z}\rangle = \langle\cos^2\phi_{Y,Z}\rangle$ since they are equally distributed around the *c*-axis, and (3) using the orthogonal relationships between the two sets of director cosines e, *f* and *g*, and $\langle\cos^2\phi_{X,Z}\rangle$, $\langle\cos^2\phi_{Y,Z}\rangle$ and $\langle\cos^2\phi_{c,Z}\rangle$, equation (3) is reduced to

$$\langle\cos^2\phi_{hk0,Z}\rangle = 1 - \langle\cos^2\phi_{c,Z}\rangle + 2ef\langle\cos\phi_{X,Z}\cos\phi_{Y,Z}\rangle \tag{4}$$

with three unknowns. Fortuitously, PTT unit cell ß-angle is 90° [13]. Therefore the normal of (*010*) plane, **N**(*010*), is perpendicular to both *a*- and *c*-axes, thus $\langle\cos\phi_{Y,Z}\rangle = 0$. Equation (4) is simplified as

$$\langle\cos^2\phi_{c,Z}\rangle = 1 - 2\langle\cos^2\phi_{010,Z}\rangle \tag{5}$$

The Herman-Stein orientation function is thus obtained by measuring $\langle\cos^2\phi_{010,\ Z}\rangle$ from the azimuthal scan of *010* reflection, and is given by:

$$f_c = 1 - 3\langle\cos^2\phi_{010,Z}\rangle \tag{6}$$

Equation (5) would become an approximation if ß is significantly different from 90°. Despite the discrepancies found in WAXD and ED crystal densities, ED ß-angle is about 3° off from being orthogonal to the *c*-axis. Chatani et al.'s [15] WAXD ß-angle is 89°, and is quite close to Desborough *et al*. Further argument for the orthogonality between *a*-axis and *bc* plane is Desborough *et al*. could have chosen a monoclinic crystal structure with *a*- as the unique axis. They chose a triclinic cell to be consistent to and for convenience in comparing crystal structures of other aromatic triclinic polyesters [13]. The projection of PTT crystal structure down the *c*-axis is also pseudo-hexagonal. It is therefore reasonable to accept the fortuitous *a*-, *c*-axis orthogonality in simplifying $\langle\cos^2\phi_{c,Z}\rangle$ measurement until a better structure determination proved otherwise.

To simplify PET orientation measurement, Kunugi *et al*. [19] had also derived the following equation using a single *010* reflection:

$$\langle \cos^2\phi_{c,z}\rangle = \frac{1 - g^2 - 2\langle \cos^2\phi_{010,z}\rangle}{1 - 3g^2} \qquad (7)$$

When $g = 0$, it reduces to equation (6) of PTT. However, PET ß-angle varies from 98.5 to 101° [20], therefore equation (7) did not offer advantages over method by Dumbleton and Bolwes [12].

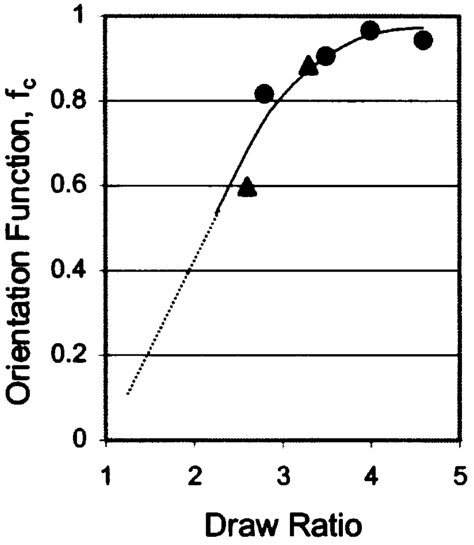

Figure 3: Development of PTT crystal orientation function as a function of draw ratio. Drawing temperatures: 50°C (●) and 75°C (▲).

It is interesting to note that equation (5) could also be obtained as an approximate equation by using Polyani's relationship between the angle $\langle\cos\phi_{010,\,Z}\rangle$ of the normal of (*010*) plane made with the fiber axis, and the azimuthal spread of $\langle\cos\phi_{Y,Z}\rangle$ [10]. For small Bragg 2θ angle, they are related as follow:

$$\langle\cos\phi_{010,Z}\rangle = \frac{\langle\cos\phi_{Y,Z}\rangle}{\cos\theta} \qquad (8)$$

Since 2θ = 15.4° for (*010*) plane, $\cos\theta \cong 1$. The Polyani relationship would give equation (5) as a good approximation without invoking ß-angle = 90° as long as $\cos\theta \cong 1$.

Figure 3 shows the development of PTT crystal orientation function drawn at 50 and 75°C, just above the glass transition temperature of 45°C. At a draw ratio of 2.6, f_c was already 0.6 with the polymer chains making an average angle of 39° to the draw direction. At higher draw ratios, f_c reached a plateau at about 0.96. The trend of PTT crystal orientation development appeared to be similar to that of PET [21]. The use of a single *010* reflection for WAXD crystalline orientation measurement is therefore simple and informative for studying PTT's structural development in fiber spinning and drawing. In addition to f_c, the *010* azimuthal scan also gave *b*-axis orientation, f_b, and *a*-axis orientation could be obtained from $f_a + f_b + f_c = 1$ relationship. Our study of

PTT structure development in tensile drawing by WAXD, IR dichroism, birefringence, shrinkage, including angles of the transition moments of the IR vibration modes will be reported in a separate publication.

Conclusion

A simplified Wilchinsky's equation for PTT crystal orientation function measurement was derived. There were discrepancies in literature WAXD and ED unit cell parameters and crystal densities. Based on the close agreement with experimental crystal density and results of bond length calculations from fractional atomic co-ordinates, WAXD unit cell parameters were selected. The fortuitous coincidence of WAXD determined ß-angle of 90° and uniaxial orientation symmetry reduced Wilchinsky's equation to only one unknown, and involved the azimuthal scanning of a single WAXD *010* equatorial reflection. The consequence of ß-angle deviating from 90° was discussed. Based on Polyani's relationship, the derived Wilchinsky's equation would still be valid as a good approximation should future crystallography work gave more accurate ß-angle different but close to 90° because of small the *010* Bragg 2θ angle. The method was illustrated with examples of f_c measurements of PTT drawn at 50 and 75°C. Crystal orientation increased rapidly with draw and saturated at $f_c \cong 0.96$, similar to tensile drawing of PET.

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