A New Method to Determine the Exact Values of the Fiber Identity Period of Polyamides

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Abstract
A method to determine the exact fiber identity periods (FIP) of polyamides from the X-ray meridional reflections has been found, which is essential especially for the γ forms of polyamides with large values of the FIP. The basic concept of this method is that the γ form has two kinds of reflections, the peak positions of which are shifted from the corresponding reciprocal-lattice points to the wide- and small-angle directions, so that the true FIP is between the maximum and minimum values calculated from the former and latter kinds of reflections, respectively. For an example, this method was applied to poly(lauryllactam) (nylon 12) and a value of 31.92 ± 0.02 Å was obtained as a more precise FIP.

1. Introduction
The values of the fiber identity period (FIP) of a polyamide calculated from the observed peak positions of various orders of X-ray meridional reflections do not agree with one another. This phenomenon was first noted for poly(e-caprolactam) (nylon 6) and interpreted by Wallner (1948a, b) on the basis of a concept that the peak position of a reflection shifts from its corresponding reciprocal-lattice point when the crystallite size is very small and the structure factor changes steeply within the main maximum of the Laue lattice factor. According to this concept, Kaji & Sakurada (1974) calculated such shift amounts for meridional reflections of nylon 6, and found that, in the case of the α form, the true FIP could be obtained from the maximum position of the 0,14,0 reflection. For the γ form, however, there are no meridional reflections which give the true FIP. In the present paper, therefore, an experimental method to determine the true FIP of the γ form of polyamides is reported.

Nylon 12 usually assumes the γ form, which shows many orders of X-ray meridional reflections. The accurate value of the FIP, however, has not yet been obtained because of the above phenomenon. The reported values of the FIP are different from author to author: 31 Å by Northolt, Tabor & van Aartsen (1972), 31.9 Å by Cojazzi, Fichera, Garbuglio, Malta & Zannetti (1973) and 32.2 Å by Inoue & Hoshino (1973). Thus, nylon 12 is a good material to demonstrate how to determine the accurate value of the FIP.

2. Experimental
Uniaxially oriented monofilaments of nylon 12 (Toray Co. Ltd, XF 5000) were used in this study. Each monofilament was 180 µm in diameter. The annealing was carried out in a silicon oil bath at 403 or 443 K at constant length. The profiles of X-ray meridional reflections were obtained with a diffractometer with a scintillation counter and pulse-height analyser by the symmetrical transmission technique. As the X-ray source, Ni-filtered Cu Kα radiation was used, produced by a rotating-anode generator (Rigaku-Denki Rotaflex RU-100) at 50 kV and 80 mA. The scanning speed was 0.125° min⁻¹. The correction of reflection angles was carried out with LiF powder as a standard sample, but such a correction was negligibly small.

3. Experimental results
Fig. 1 shows the observed values of the FIP of nylon 12, which were calculated from the maximum positions of X-ray meridional reflections. As seen from the figure the values of the FIP do not agree with one another, but depend on the order of reflection and the annealing temperature of the sample. As described in the
Introduction, such a phenomenon is caused by both the smallness of the crystallite size and the special structure factor. The crystallite size increases with increasing annealing temperature, so that the change of the FIP with annealing temperature is due to the change of the crystallite size. Since the shift amount of the peak position of a reflection decreases with increasing crystallite size, the observed values of the FIP for the sample annealed at a higher temperature are nearer to the true FIP.

The value of the FIP for the 020 reflection is extraordinarily small compared with those for the other orders of reflection, which may be due to the anomalous shape of this reflection. As seen in Fig. 2, the 020 reflection is very much deformed and the peak position is not at the center of the reflection. The causes of such a deformation were discussed by Kaji, Yamagishi, Horii & Kitamaru (1979) and will be published elsewhere. The observed values of the FIP for the 040 to 0.24,0 reflections are on a curve with the maximum value at the 0.16,0 or 0.18,0 reflection. On the other hand, the values of the FIP for the 0.26,0 and 0.28,0 reflections are not on this curve but are somewhat larger than those for the lower orders of reflection. A method to obtain the true value of the FIP from these observed values will be described below.

4. Determination of the exact value of the FIP

4.1. Basic concept

The basic concept to determine the exact FIP is as follows. The X-ray diffraction intensity is proportional to the intensity function $I$, defined as

$$I = |F|^2 G^2,$$

where $|F|^2$ is the structure factor and $G^2$ is the Laue lattice factor. When the crystal is sufficiently large, the maximum positions of the reflections agree with those of the principal peak of $G^2$ or the reciprocal-lattice points. For small crystals, however, the function $G^2$ has a large extension at the reciprocal-lattice points, so that the peak positions of reflections shift from the corresponding reciprocal-lattice points, depending on the gradients of $|F|^2$ within the main peaks of $G^2$. The shift direction depends on the sign of the slope of $|F|^2$ around the reciprocal-lattice point as schematically shown in Fig. 3. The peak position of reflection shifts to the wide- or low-angle direction according to the positive or negative slope, and does not shift when the slope is zero.

The calculation of $|F|^2$ for the γ form of nylon 6 showed that the slopes of $|F|^2$ for the 020 to 0.12,0 reflections were positive, whereas that for the 0.14,0 reflection was negative (Kaji & Sakurada, 1974). Therefore, the true FIP is between values calculated from the former reflections and the latter one. Further, the positive slopes of $|F|^2$ decrease with the order of reflection to assume the minimum at the 080 or 0.10,0 reflection, and then increase again, so that the shift amount $\Delta \eta$ in reciprocal-lattice coordinates is a minimum at the 080 or 0.10.0 reflection. Here it must be noted that the deviation $\Delta P$ of the FIP is calculated from the $\Delta \eta$ of the nth-order reflection by the following equation:

$$\Delta P = -\frac{\Delta \eta}{n} P,$$

where $P$ is the FIP. Therefore, the minimum value of $\Delta P$ does not necessarily correspond to that of $|\Delta \eta|$.

However, it is true that, in the case of reflections with positive slopes of $|F|^2$, the maximum value of the FIP's calculated from them is the nearest to the true FIP, and that in the case of reflections with negative slopes the minimum value is the nearest to it. Thus, the true FIP is between the above maximum and minimum values. This is the principle to determine a more exact value of the FIP.

4.2. Calculation of $|F|^2$ on the meridian for nylon 12

The crystal structure of polylauryllactam (nylon 12)

![Graph showing the relationship between the gradient of the structure factor $|F|^2$ and the shift direction of the maximum position of the intensity function $H = |F|^2 G^2$. $G^2$ is the Laue lattice factor, and $\eta$ is the reciprocal-lattice coordinate.](image-url)
has been investigated by several authors (Monobe & Fujiwara, 1967; Northolt et al., 1972; Inoue & Hoshino, 1973; Cojazzi et al., 1973; Ishikawa & Nagai, 1977). Monobe & Fujiwara (1967) succeeded in making single crystals of nylon 12 with \( \alpha \) and \( \gamma \) forms from water-formic acid and triethylene glycol solutions, respectively. The single crystals with \( \alpha \) and \( \gamma \) forms were parallelogrammic and ribbon-like, and their selected-area electron diffraction patterns were very similar to those of the \( \alpha \) and \( \gamma \) forms of nylon 6, respectively. The diffraction pattern for the \( \gamma \) form showed the six innermost spots, of which four had a spacing of 4.0 Å and two a spacing of 4.1 Å. The unit cell of the \( \gamma \) form, therefore, cannot be represented by a hexagonal shape in spite of some proposals in the literature (Northolt et al., 1972; Cojazzi et al., 1973; Ishikawa & Nagai, 1977).

Inoue & Hoshino (1973) also confirmed, from the end-view X-ray diffraction pattern of doubly oriented monofilament, that the crystal system of the \( \gamma \) form is not hexagonal but monoclinic. However, with respect to the crystal structure of the molecular chain of the \( \gamma \) form, the model by Cojazzi et al. (1973) was found to be the most reliable during our study on the anomalous shape of the 020 meridional reflection of nylon 12 (Kaji et al., 1979). For calculation of \(|F|^2\) on the meridian, therefore, Cojazzi's model was used. The calculation was carried out not only for the reciprocal-lattice points but also for all coordinates on the meridian from zero to 32-0. The result is shown in Fig. 4; the profile is very similar to that of the \( \gamma \) form of nylon 6. The reflections from 020 to 0,24,0 have positive slopes in \(|F|^2\), whereas those from 0,26,0 to 0,30,0 have negative ones. The reflection with the minimum positive slope is 0,20,0 and the maximum value of the FIP corresponds to the value calculated from this reflection, even if (2) is considered. As seen from Fig. 1, the reflection which shows the maximum value is 0,16,0 or 0,18,0; the small discrepancy may be due to the same causes as those which deform the 020 reflection (Kaji et al., 1979).

The true value of the FIP is determined from Fig. 1 as 31.92 ± 0.02 Å, since it must be between the maximum value in the FIP's from the 020 to 0,24,0 and the minimum value in those from the 0,26,0 and 0,28,0 reflections. This value agrees well with the value of 31.9 Å reported by Cojazzi et al. (1973), within experimental error.

Fig. 4. Calculated structure factor \(|F|^2\) on the meridian for nylon 12 using the structure model by Cojazzi et al. (1973).

References