Microfibril Dimensions from Small-Angle X-ray Scattering

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Abstract

Model calculations based on parallel cylindrical fibrils with a distribution of radii are used to derive fibrillar radii obtained from the transverse intensity profile of the small-angle X-ray scattering (SAXS) peaks. The results are expressed in terms of moments of the distribution function of the radii. The transverse integral breadth of the peak leads to \(\langle R^4/R^3 \rangle\), the initial slope gives \(\langle R^2 \rangle\), and the analysis of the characteristic function gives \(\langle R^2/R^1 \rangle\). The first two methods are applied to the SAXS patterns of well oriented samples of nylon 6, for which it is found that \(\langle R^4/R^3 \rangle \approx 1.2\). This result is consistent with a positively skewed distribution of fibrillar radii. The relation between these analyses of uniaxially oriented systems and other SAXS and wide-angle diffraction methods is considered.

Introduction

The basic morphology of uniaxially oriented semicrystalline polymers is fibrillar. Drawn fibers and films display rotational symmetry about the deformation direction; this symmetry is imparted by the presence of parallel, semicrystalline microfibrils (hereafter termed fibrils) with diameters of tens or hundreds of ångströms. In recent years, there has been a growing body of evidence that the transverse dimensions of these fibrils are correlated with mechanical and other properties of oriented polymers (Peterlin, 1975; Pervorsek, Harget, Sharma & Reimschuessel, 1973). Fibrillar diameters have been estimated from electron microscopy and from peak widths of X-ray diffraction patterns. Previous analyses of fibrillar widths from wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) will be reviewed briefly.

Wide-angle diffraction

Perhaps the most frequently employed technique for estimating fibrillar diameters is application of the Scherrer equation to the equatorial WAXD peaks (Alexander, 1969). While the result is expressed as a single dimension, it should be recalled that the integral breadth \(\Delta(2\theta)\) of the hkl peak is related to the dimension of the perfect crystals in directions perpendicular to the (hkl) planes according to (International Tables for X-ray Crystallography, 1962):

\[
\frac{M^2}{M^1} = \frac{\lambda}{\Delta(2\theta) \cos \theta_0}.
\]

Implicit in (1) are the assumptions that the diffraction peak is symmetric about the angle 2\(\theta_0\) and that the intensity profile is free of instrumental or strain broadening. The averages are taken over \(g(M)\), the probability density function describing the distribution of crystal dimensions perpendicular to the (hkl) planes. Any particular moment of this distribution can be written as

\[
\overline{M^n} = \int_0^\infty M^n g(M) dM.
\]

Thus the Scherrer equation yields the ratio of the second and first moments of \(g(M)\). As \(g(M)\) depends on the shape of the crystals as well as the size distribution of crystals within the sample, so does the result of the Scherrer equation.

In practice, the integral-breadth analysis is complicated by the presence of other broadening mechanisms which affect the shape of the diffraction peak. Some efforts have been made to resolve the various components of the WAXD line-widths in polymers by considering the dependence of integral breadth on reflection order; see for example the papers of Buchanan & Miller (1966), Glenz, Peterlin & Wilke (1971), Hosemann (1972) and Wilke & Martin (1974). The analysis of Fourier coefficients has been applied by Buchanan & Miller (1966) and by Wecker, Cohen & Davidson (1974) to eliminate effects of microstrain on the size determination. This latter technique yields \(M^1\), the first moment of the size distribution function.

In concluding this section, it should be repeated that the majority of published size analyses from polymer WAXD patterns have used the observed line-width (corrected for instrumental broadening) together with equation (1) or the equivalent expression for full width at half maximum. While the 'effective crystal size' obtained by such a method is obviously a lower bound, more detailed studies indicate that the integral breadths of the lowest-order peaks are determined almost exclusively by size broadening. Examples of this can be found in the work of Buchanan & Miller (1966), Hosemann (1972) and Fakirov, Fischer, Hoffmann & Schmidt (1977).
Small-angle scattering

Oriented semicrystalline polymers typically have SAXS patterns with a single rather broad maximum along the meridian. It is the transverse or lateral width of this diffraction spot which is of interest here. We will adopt the derivation of Bear & Bolduan (1950) for the diffraction of a single smooth cylindrical fibril of radius \( R \) possessing an alternating structure along the fibril axis. For the condition of normal incidence of the X-ray beam, the scattering vector \( s \) is separated into its axial \( (s_1) \) and radial \( (s_2) \) components. This situation is sketched in Fig. 1. The scattered intensity for this model can be written as

\[
I(s_1, s_2) = I_\infty(s_1) \pi^2 R^4 \left[ \frac{J_1(2\pi R s_2)}{\pi R s_2} \right]^2.
\]  

(3)

The leading factor \( I_\infty(s_1) \) is the scattering per unit cross-sectional area of an infinitely wide fibril. This factor includes the incident intensity and the nature of the axial density fluctuations which define the one-dimensional 'macrolattice' within the fibril; the relation between this axial structure and \( I_\infty(s_1) \) has been discussed for example by Hosemann & Bagchi (1962), Crist (1973) and Ruland (1977).

Note that in equation (3) the lateral width of the SAXS pattern is independent of \( s_1 \), depending only on the transverse dimension of the fibril. Implicit in this statement is the assumption that the interphase boundaries demarking the electron-density fluctuations along the fibril axis are smooth in the radial direction. Roughness of these boundaries will cause additional transverse broadening which has a strong \( s_1 \) dependence, as discussed by Bear & Bolduan (1950) and by Bonart (1964). This effect will be ignored in this treatment, as we are unaware of a case in which phase-boundary roughness or 'waviness' affects the width of the first-order SAXS peak of polymer fibers. A recent two-dimensional analysis by Beumer & Hosemann (1978) showed 'waviness' effects on the second-order maximum, but none on the first-order peak.

Bolduan & Bear (1951) proposed two related methods for evaluating \( R \) from the experimental dependence of the intensity on \( s_2 \), one involving the width at half maximum and the other the 'persistence of intensity with tilt'. As the integral breadth is more easily developed for complex systems, it will be considered rather than the width at half maximum. The transverse integral breadth of a peak with meridional displacement \( s_1 \) is defined according to

\[
\beta_2 = \sqrt{\frac{\int_{-\infty}^{\infty} I(s_1, s_2) ds_2}{I(s_1, 0)}}.
\]  

(4)

In order to integrate the intensity expression in (3) as required by (4), the numerical result

\[
\int_{-\infty}^{\infty} \left[ \frac{J_1(2\pi R s_2)}{\pi R s_2} \right]^2 ds_2 = 0.93 \frac{1}{\pi^{1/2} R}
\]  

(5)

is required. Further, with the substitution \( \beta_2 = \Delta(2\theta_2)/\lambda \), (4) is rearranged to yield

\[
R = \frac{0.52\lambda}{\Delta(2\theta_2)},
\]  

(6)

in which \( 2\theta_2 \) is the transverse scattering angle measured from the meridian.

The 'persistence of intensity with tilt' involves measuring the transverse intensity distribution of a peak or 'layer line' for rather small values of \( s_2 \). One first assumes that the intensity for a particular reflection has a disk-like locus in reciprocal space. This condition is certainly met for a single fibril or a parallel assembly of identical fibrils. With the 'tilt' method, the meridional intensity \( (s_2 = 0) \) of the peak maximum is measured as the fiber axis is tilted toward the primary beam in the plane defined by \( S_0 \) and \( X_0 \) in Fig. 1. By this technique, the intensity profile is measured along a radial vector which is perpendicular to \( s_2 \) as defined in Fig. 1. Since the intensity has cylindrical symmetry, a series of 'tilt' measurements (with suitable geometric and absorption corrections) can be used to generate a transverse intensity profile identical to that obtained from a more conventional \( s_2 \) scan with normal incidence.

While the preceding description may imply that the 'tilt' method is a complicated technique to acquire information which is more readily available by another method, Bolduan & Bear (1951) showed that the 'tilt' method can be interpreted with an infinite slit-like beam perpendicular to the fiber axis, thereby permitting a radial or transverse analysis of quite weak reflections. It should be emphasized that the preceding is the only inherent advantage of the 'tilt' method over normal-incidence geometry. While the 'tilt' method has been used with pin-hole collimation (Gezalov, Kuksenko & Slutsker, 1971; Prevorsek, Harget, Sharma & Reimschuessel, 1973), under these conditions the 'tilt' method has absolutely no advantages such as freedom from diffuse (void) scattering, accuracy, etc.

What is of interest in the present discussion is the radial or transverse intensity analysis suggested by Bolduan & Bear (1951). To consider the decrease in
intensity as one first moves away from the meridian, the factor \( J_1(2u)/u \) in (3) is approximated by \( \exp(-u^2) \). This substitution is valid for \( u = \pi R s_2 < 0.4 \), leading immediately to

\[
\ln \left[ \frac{I(s_1, s_2)}{I(s_1, 0)} \right] = - (\pi R s_2)^2 .
\] (7)

Thus a semilogarithmic plot of intensity vs \( s_2^2 \) should be linear [for \( s_2 < (3R)^{-1} \)] with a slope of \(- (\pi R)^2 \). For our model of a single fibril (or a collection of identical fibrils), the integral breadth analysis (equation 6) should yield the same result as the initial slope (equation 7). The effects of a distribution of fibril diameters will now be considered.

**Distribution of radii**

The preceding analyses will now be extended to the case of an assembly of parallel fibrils having a distribution of radii. It is assumed that the packing of these fibrils is otherwise random, i.e. there are no longitudinal or transverse interference effects. If the number fraction of fibrils with radius \( R_k \) is \( N_k \), the intensity scattered by each fibril is added to give

\[
I(s_1, s_2) = I(\alpha)(s_1) \pi^2 \sum_k N_k R_k^4 \left[ \frac{J_1(2\pi R_k s_2)}{\pi R_k s_2} \right]^2 .
\] (8)

In this expression, it is assumed that there is no correlation between the radius and the internal structure of a fibril. This allows for separate averaging over the factors involving \( s_1 \) and \( s_2 \); \( I(\alpha)(s_1) \) is thus \( I(\alpha)(s_1) \) suitably averaged over the ensemble.

This discussion has been confined to the consideration of cylindrical fibrils. While scattering equations similar to (3) can be written for fibrils with any cross-sectional shape – see for example Gezalov, Kuksenko & Slutsker (1971) for square cross-sectioned fibrils – we are aware of no strong evidence for any particular shape. Furthermore, it is obvious that the SAXS intensity of a macroscopic fiber has rotational symmetry about the fiber axis. Therefore, it seems logical to consider cylindrical fibrils, thereby avoiding the unrewarding complications involved in establishing rotational symmetry with less symmetric models.

**Initial slope**

For the analysis of the transverse peak shape near the meridian, the Bessel functions in (8) are expanded, retaining only terms through \( (\pi R_k s_2)^2 \), which leads to

\[
I(s_1, s_2) = I(\alpha)(s_1) \pi^2 \sum_k N_k R_k^4 \left[ \frac{\pi^2 s_2^2 R_k^4}{\sum_k N_k R_k^4} \right] .
\] (9)

This expression is valid for \( (\pi R_k s_2) \leq 0.4 \), which is, of course, most stringent for the thickest fibrils in the distribution. For systems containing large numbers of fibrils, the sums over \( N_k \) may be replaced by integrals over the continuous probability density function \( g(R) \) of the type

\[
\bar{R}^6 = \int_0^\infty R^6 g(R) dR .
\]

Defining the resulting ratio \( (R^6/R^4) = \langle R^2 \rangle \) and using the standard exponential approximation, one obtains the final expression:

\[
I(s_1, s_2) = I(\alpha)(s_1) \pi^2 R_k^4 \exp \left[ - (\pi^2 \langle R^2 \rangle s_2^2) \right] .
\] (10)

Thus, for a collection of parallel microfibrils, the initial \( s_2 \) dependence of the intensity yields a 'mean square' radius \( \langle R^2 \rangle \) which is the ratio of the sixth and fourth moments of the distribution function \( g(R) \). It should be noted that the derivation and interpretation of equation (10) bears a strong resemblance to analysis of Guinier & Fournet (1955) of the zero-order peak. The relation between equation (10) and Guinier's law will be treated below.

**Integral breadth**

To evaluate the transverse integral breadth in the presence of a distribution of radii, each term in the sum of equation (8) is integrated over \( s_2 \) and evaluated by equation (5). Subsequently replacing the sums over \( N_k R_k^4 \) by integrals as above, the transverse integral breadth of an interference maximum becomes

\[
\beta_2 = \frac{0.93}{\pi^{1/2}} \left( \frac{R^3}{R^4} \right) .
\] (11a)

This can be rearranged to give

\[
\langle R \rangle = \frac{0.52 \lambda}{\Delta(2\theta_2)} .
\] (11b)

In (11b) we have defined the average dimension obtained from the integral breadth, which is the quotient of the fourth and third moments of \( g(R) \), as \( \langle R \rangle \).

In concluding this section, a brief discussion of the significance of equations (10) and (11) is in order. It is apparent that the initial-slope and integral-breadth analyses need not give identical results; indeed one expects to find \( \langle R^2 \rangle^{1/2} > \langle R \rangle \) except for the case in which all radii are equal. In principle, the inequality between these results would enable one to estimate (at least in a qualitative sense) the width of the distribution function \( g(R) \). This suggestion has been put forth by Smith (1976) for crystal size distributions inferred from WAXD. In studies of GP zones in aluminum alloys Baur & Gerold (1964) and Harkness, Gould & Hren (1968) used the results of SAXS to confirm the nature of the size distribution function obtained from electron microscopy.

It is of some interest to compare equations (10) and (11) with other calculations. In an analysis of WAXD peaks, Smith (1976) showed that the initial-slope technique (equation 10) yields \( M^2/M^4 \). Guinier & Fournet (1955) demonstrated that the same analysis of an isotropic zero-order peak gives \( R^8/R^6 \). These results are consistent with one another if one considers...
the number of dimensions over which the averaging is being performed. In the WAXD analysis of an hkl reflection the magnitude of only one dimension of the crystal (that parallel to \( r_{\hkl} \)) is being considered. In the present study, a two-dimensional or 'area' averaging is being performed. In an analysis using Guinier's law the entire volume of each particle is being considered. For the initial-slope method, increasing the number of dimensions being averaged by one increases the rank of each moment of \( g(R) \) by two; a similar relation holds for the results of the integral-breadth expressions (compare equations 1 and 11).

Four-point SAXS patterns

Many highly oriented polymer fibers have SAXS patterns with a distinct quadrant or four-point nature. The most accepted model for this effect is the existence of slanted or sheared crystalline blocks within the fibrils, as sketched in Fig. 2. An alternative explanation involves either lamellar stacks with a periodic 'waviness' of the crystals, or the equivalent of parallel microfibrils with strong axial correlation (Bonart, 1964). Only the case of uncorrelated fibrils possessing obliquely shaped crystals will be treated here. With reference to Fig. 2, it is apparent that the intrafibrillar structure is defined along the interface normal \( n \). The size broadening of the pattern is still in the radial or \( s_2 \) direction, while the internal structure of the fibril is seen along \( s_1 = a s_1 + s_2 \). The inclination angle of the crystal surfaces is given by \( \tan \alpha = 1/a \).

In general, the transverse width of one of these SAXS peaks is affected by the macrolattice perfection, as the expression for the intrafibrillar scattering \( I_\alpha(s_\alpha) \) has a component in the \( s_2 \) direction. It should be noted, however, that in most four-point patterns from polymer fibers, the elliptical spots are distinctly elongated in the radial \( s_2 \) direction, not along \( s_\alpha \). In this case one may assume with some justification that the effects of the fibril structure are vanishingly small, and that equation (3) obtains with \( I_\alpha(s_1) \) replaced by \( I_\alpha(s_\alpha) \). In this simplifying limit the initial-slope and integral-breadth relations in equations (10) and (11) hold as well.

Experimental

Small-angle diffraction patterns were recorded photographically for four uniaxially oriented fibers of nylon 6. The fibers labelled \( A \) and \( B \) are monofilaments with macroscopic draw ratios of 3 and 4 respectively. Fiber \( C \) is a commercial high-strength fiber and fiber \( D \) was prepared by annealing \( C \) at 200°C with fixed ends. Further details of the fiber characteristics and diffraction measurements have been published elsewhere (Matyi & Crist, 1978).

Results and discussion

The SAXS patterns of each of the nylon 6 fibers indicated good axial orientation of the semicrystalline macrolattice; no arcing of the patterns was evident. The observed discrete pattern contained only one reflection order. This was of the conventional two-bar type for \( A \) and \( B \), and of the four-point type for \( C \) and \( D \). The transverse intensity profiles are shown in

![Fig. 2. Sketch of a fibril with internal structure along \( n \) which is not parallel to the fibril axis; a square cross section is depicted for easier visualization of the system. The four-point pattern results from rotationally averaging such structures about \( X_0 \).](image)

![Fig. 3. Transverse intensity profiles of nylon 6 fibres in which the traces have been vertically shifted for clarity. The arrows indicate the location of the maxima in the resolved components of the four-point patterns in \( C \) and \( D \); these maxima were shifted to \( s_2 = 0 \) for analysis with equations (10) and (11).](image)
Fig. 3: In each case the transverse scan was made along the position of the meridional maximum at $s_1 \approx 0.01$ Å$^{-1}$ (the axial periodicity in each of the fibers is similar). Note that in the traces for fibers C and D the four-point patterns have been decomposed empirically into symmetric components. This was accomplished by assuming that each component is centered about a point midway between the meridian ($s_2 = 0$) and that point on the wing of the curve having half the meridional intensity.

The observed intensity profiles of A and B and the resolved curves of C and D were analyzed according to equations (10) and (11). The results are summarized in Table 1. Note that the limiting-slope method gives a slightly larger result than the integral breadth, i.e. $\langle R^2 \rangle^{1/2} > \langle R \rangle$. As mentioned above, this effect is anticipated with a finite distribution of fibrillar radii. One question which can be asked is: what information is conveyed by these inequalities? The answer is very little, at least in the absence of supplementary information on the shape of the distribution function $g(R)$. It can nevertheless be concluded that $g(R)$ is quite probably not symmetric, but is positively skewed. This conclusion is reached by considering the moments of a Gaussian form of the radius distribution function with variance $\sigma$. With the largest permissible width $\sigma/R^1 = 0.3$ (larger values of $\sigma$ permit negative lengths), the calculated ratio $\langle R^2 \rangle^{1/2}/\langle R \rangle = 1.13$, which is somewhat less than most of the observed ratios for the nylon 6 fibers. In order to account for the results in Table 1, a positively skewed form of $g(R)$ must be assumed. In the absence of further information on the nature of this distribution function, it would be fruitless to make further model calculations. To conclude this section, it will be pointed out that Gezalov, Kuksenko & Slutsker (1970) report that the ratio $\langle R^2 \rangle^{1/2}/\langle R \rangle$ is as low as 0.9. In this case, the initial-slope analysis (equation 10) was made with the 'tilt' method. It is not known whether this result signifies experimental difficulties or genuine information on the nature of $g(R)$.

Table 1. Average radii of nylon 6 fibrils

<table>
<thead>
<tr>
<th>Fiber</th>
<th>$\langle R^2 \rangle^{1/2}$ (Å)</th>
<th>$\langle R \rangle$ (Å)</th>
<th>$\langle R^2 \rangle^{1/2}/\langle R \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>47</td>
<td>39</td>
<td>1.20</td>
</tr>
<tr>
<td>B</td>
<td>31</td>
<td>30</td>
<td>1.03</td>
</tr>
<tr>
<td>C</td>
<td>34</td>
<td>29</td>
<td>1.16</td>
</tr>
<tr>
<td>D</td>
<td>45</td>
<td>36</td>
<td>1.23</td>
</tr>
</tbody>
</table>

**Additional moments of g(R)**

In principle, additional information on the shape of the distribution function can be gained by other measurements of the SAXS pattern of a fiber. Consider first the information contained in the transverse tails of a particular diffraction maximum; this is analogous to Porod's (1951) law, which is frequently used in considering the zero-order peak in the small-angle region. The Bessel functions in (8) have damped oscillations as the argument $(2\pi R_s s_2)$ increases. Approximating the mean square value of the amplitude of these oscillations by $C$, one can write for large values of $s_2$

$$I(s_1, s_2) = I_\infty(s_1) C R^2 / s_2^2.$$

Thus a plot of $s_2^2 I(s_1, s_2)$ should reach a nearly constant value which is proportional to $R^2$. While this quantity has the same dimensions as the internal surface area obtained from Porod's law, in (12) the factor $R^2$ is in fact more closely related to the cross-sectional area of a typical fibril.

In order to analyze the transverse tails of the peak as written in (12), both $I_\infty(s_1)$ and $C$ must be known and absolute intensities must be measured. While $C \approx 0.04$, the factor $I_\infty(s_1)$ depends on the detailed composition of the fibril and is not readily calculated. To avoid this latter difficulty, it is a simple matter to divide both sides of (12) by the meridional peak intensity to obtain

$$I(s_1, s_2) / I(s_1, 0) = C (R^2 / R^4).$$

Provided the intensity distribution in the transverse tails of the peak is well enough defined, the results of (13) may be used to complement the initial-slope and integral-breadth analyses.

The final method to be considered involves the one-dimensional Fourier transform of the experimental peak profile. It is well established that the limiting slope of this function yields $M^1$ in the case of a WAXD peak in a powder pattern (Guinier, 1963) and $R^3 / R^2$ in the case of an isotropic zero-order peak (Guinier & Fournet, 1955). Turning to our system of oriented fibrils, one can show in a straightforward manner that the characteristic function $\gamma(t)$ can be written as

$$\gamma(t) = 1 - \left( \frac{2R_1}{\pi R^2} \right)^t + \ldots,$$

in which $t$ is measured in direct space perpendicular to the fibril axis. This analysis thus yields the ratio $R^2 / R^1$ for the collection of fibrils.

It should be recalled that the limiting value of $\gamma(t)$ is most strongly influenced by the shape of the diffraction peak at large $s_2$. Thus the use of equations (12)–(14) requires that accurate intensity measurements be made in the wings of the curve. As the film detection used in the current experiments is unsuitable for this, no such analyses have been made.

**WAXD linewidths**

Statton (1959) first noted that the apparent fibrillar diameters in polyethylene fibers obtained from SAXS are systematically larger than the comparable quantities from equatorial WAXD peaks. In that analysis, the integral breadth of the SAXS pattern yielded $D^2 / D^3$ values (fibril diameter $D = 2R$) which were typically 25% larger than the $M^2 / M^1$ results from the
WAXD peaks. Prevorsek, Harget, Sharma & Reimenschussel (1974) similarly reported that the result of the 'tilt' method of initial slopes, which has been shown to equal \((D^6/D^4)^{1/2}\), is nearly twice as large as the apparent crystal size from WAXD. These results are all consistent with the presence of a distribution of fibril diameters within the oriented polymers.

It is not the purpose of this paper to examine in detail the results of WAXD lineshape analysis with polymer fibers. We will repeat the conclusion of Buchanan & Miller (1966) that it is difficult to separate strain or paracrystallinity effects from size broadening in WAXD peaks of polymers. While Mignot & Rondot (1975) have demonstrated that it is possible to obtain \(M\) by suitable Fourier analysis of a single WAXD peak, this technique has not been applied to polymers. Furthermore, in order to equate coherence lengths from WAXD to fibril dimensions, one must be sure that there are no intracrystalline subgrain boundaries parallel to the fibril axis. Other complications may arise if oblique crystals are present within the microfibrils. In summary, it is believed that the integral-breadth estimate of fibril diameters from WAXD peaks will generally give a lower bound to the fibril diameter. The fact that WAXD and SAXS analyses give similar results which respond similarly to processing conditions strongly suggests that the basic morphological model of uncorrelated microfibrils is correct.

Conclusions

By considering the scattering equation for a system of parallel but otherwise correlated microfibrils, it has been demonstrated that different analyses of the transverse intensity profile of a SAXS peak may yield different numerical quantities if a distribution of radii is present. Specifically, it is shown that the transverse integral breadth gives \(R^3/R^1\), while the initial-slope method (analogous to Guinier's law for the isotropic zero-order peak) yields \((R^3/R^1)^{1/2}\). If accurate relative intensities are available in the wings of the peak, these may be used to obtain \((R^6/R^4)^{1/2}\) (analogous to Porod's law) or \(R^2/R^1\) from the initial slope of the characteristic function. While these results are based on cylindrical fibrils, the conclusions apply to a collection of fibrils with any arbitrary cross section, though quantitative interpretation of the average dimensions and thickness distribution will of course depend on the particular shape (e.g. square or elliptical) assumed. It should be noted that the results of equations (10)–(14) can in principle be applied to the anisotropic zero-order peak for the system of oriented fibrils. In practice, however, this scattering tends to be weak and is further obscured by beamstops, parasitic scattering, etc.

The SAXS patterns of well-oriented nylon 6 fibers were analyzed by the integral-breadth and initial-slope techniques. It was found that \((R^6/R^4)^{1/2} \approx 2(R^3/R^1)\), which is consistent with a positively skewed distribution of fibrillar radii. This result was obtained from SAXS patterns of both the two-bar and four-point type.

It should be emphasized that each of these analyses is subject to the initial assumption that the transverse intensity profile is determined solely by size effects. As resolvable four-point patterns are generally observed in polymer fibers after sufficient uniaxial drawing, one suspects that transverse broadening due to unresolved splitting of the pattern may be present at smaller draw ratios. In such a case the initial-slope method is more susceptible to errors. While the integral breadth would also lead to a smaller \(\langle R \rangle\) than is actually present, the estimate so obtained would nevertheless be more representative of the actual average radius.

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References


