Investigations of the Crystallinity of Polyamide-6 Fibers by Two X-Ray Diffraction Methods

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SYNOPSIS

The methods of Hindeleh and Johnson and of Ruland and Vonk were employed for determination of the crystallinity in polamide-6 fibers. The values given by the methods were found to be relatively close to one another. However, using the method of Hindeleh and Johnson, the manner of the amorphous background approximation must be changed. © 1992 John Wiley & Sons, Inc.

1. INTRODUCTION

The crystallinity is defined as the weight fraction of the crystalline portion of a polymer. The physical and mechanical properties of polymers are considerably dependent on that parameter.

Wide-angle X-ray diffraction is most frequently used to measure crystallinity in polymers. The method is based on the assumption that it is possible to separate the intensity contributions arising from crystalline and amorphous regions. There are several various procedures to derive the degree of crystallinity from an X-ray diffraction pattern. However, the numerical results of calculations given by various procedures may differ considerably.

The differences may be caused by the fact that in most X-ray procedures for crystallinity determination the separation of crystalline peaks and amorphous background is carried out in an arbitrary manner. As a result, the overlap of adjacent crystalline peaks is simply neglected. The background scatter is due both to the amorphous regions in a sample as well as to the imperfections in the crystal lattice of real polymers. Two kinds of distortions give rise to both the broadening of the peaks and the decrease in their height. Drawing a line between the minima in a diffraction curve gives a background that incorporates a part arising from peaks overlapping, i.e., a part to imperfections in lattice order.

The analysis of the differences and investigation of the correlations between the results of measurements are very important tasks from the point of view of the methodology of crystallinity determination. In this work, we compare the crystallinity values calculated with two procedures. The first procedure was elaborated by Hindeleh and Johnson[1] and the second was presented by Ruland,[2] and later modified by Vonk.[3] Both methods derive the degree of crystallinity based upon the ratio of the integrated intensity under the crystalline peaks to the integrated intensity under the complete X-ray diffraction trace. The measurements were performed for polyamide-6 fibers with various elongation ratios.

2. THE PROCEDURE OF HINDELEH AND JOHNSON

In this method, a corrected and normalized diffraction pattern is resolved into individual peaks and a polynomial background. An experimental X-ray diffraction pattern is approximated by the theoretical function Y_c of the form

$$Y_c = \sum_{i=1}^{n} Q_i + B \qquad (1)$$

where n is the number of crystalline peaks.

Each peak is represented by a "peak" function Q_i that is a combination of Gaussian and Cauchy profiles:

$$Q_i = f_i \cdot A_i \cdot \exp\left\{ -\ln 2 \cdot \left[\frac{2(x - P_i)}{w_i} \right]^2 \right\}$$
$$+ \frac{A_i \cdot (1 - f_i)}{1 + [2(x - P_i)/w_i]^2} \quad (2)$$

The peaks are defined by the following four parameters: the profile function parameter f_i, peak height A_i, peak width at half-height W_i, and peak position P_i. x is the scattering angle 2ϑ.

The profile function parameter is $f_i = 0$ for a Cauchy function and $f_i = 1$ for a Gaussian function and can be any fraction for combined functions. A background has a polynomial form:

$$B = ax^3 + bx^2 + cx + d \quad (3)$$

The background comprises all the scattering intensity that cannot be fitted to the crystalline peaks.

All the parameters of the "peak" functions Q_i and background function B are found by minimization of the sum of squares:

$$S = \sum_{i=1}^{n} (Y_{ci} - Y_{ei})^2 \quad (4)$$

where Y_{ei} are the experimental x-ray scattering intensities and Y_{ci} are the calculated ones and n is the number of intensity data.

The crystallinity is calculated as the ratio of the total area under the resolved crystalline peaks to the total area under the unresolved normalized X-ray scattering curve. The area under the background line is assigned to the amorphous component of the polymer. The calculations are performed between two arbitrarily chosen scattering angles.[4] Hindeleh and Johnson applied their method to cellulosic materials[5-7] as well as to polyamide-6 and PET.[4]

Hindeleh and Johnson consider that their method, thanks to the resolution of overlapping peaks and a background, gives a reliable measure of actual crystallinity. The values found for annealed polyamide-6 and PET samples were nearly 100% and about 85%, respectively.[4] The values are considerably larger than those of Ruland[8] and of other authors.[9,10]

3. RULAND'S METHOD MODIFIED BY VONK

Ruland's method is based on the paracrystal theory.[2,8] The method gives the distortion factor as well as an estimate of the crystallinity.

The intensity of the coherent x-rays scattered over all space by a specimen is equal to

$$\int_0^\infty I(s) \cdot dv_s = 4\pi \cdot \int_0^\infty s^2 \cdot I(s) \cdot ds$$
$$= 4\pi \cdot \int_0^\infty s^2 \cdot \overline{f^2} \, ds \quad (5)$$

$$\overline{f^2} = \frac{\sum_i n_i \cdot f_i^2}{\sum_i n_i} \quad (6)$$

where f_i is the scattering factor of the atom i, n_i is the number of atoms of type i in the stoichiometric formula, and, therefore, f^2 is the weighted mean-square atomic scattering factor of the investigated polymer. s is the reciprocal-lattice vector $s = 2 \cdot \sin\vartheta / \lambda$.

The part of the intensity that is concentrated in the crystalline peaks is equal to

$$\int_0^\infty I_c(s) \, dv_s = 4\pi \cdot \int_0^\infty s^2 I_c(s) \cdot ds$$
$$= x \cdot 4\pi \cdot \int_0^\infty s^2 \cdot f^2 \cdot D \cdot ds \quad (7)$$

where x is the degree of crystallinity and D is a distortion factor that includes distortions of both the first and second kinds. This factor expresses the loss of intensity due to deviations of the atoms from their ideal positions.

From eqs. (6) and (8), we obtain

$$x = \frac{\int_0^\infty s^2 \cdot I_c \cdot ds \cdot \int_0^\infty s^2 \cdot \overline{f^2} \cdot ds}{\int_0^\infty s^2 \cdot I \cdot ds \cdot \int_0^\infty s^2 \cdot \overline{f^2} \cdot D \cdot ds} \quad (8)$$

This equation is valid even if the limits of integration are not 0 and ∞ provided that the range is sufficiently wide. We can therefore write

$$x = x' \cdot K \quad (9)$$

where

$$x' = \frac{\int_{s_1}^{s_2} s^2 \cdot I_c(s) \cdot ds}{\int_{s_1}^{s_2} s^2 \cdot I(s) \cdot ds)} \tag{10}$$

$$K = \frac{\int_{s_1}^{s_2} s^2 \cdot f^2 \cdot ds}{\int_{s_1}^{s_2} s^2 \cdot f^2 \cdot D \cdot ds} \tag{11}$$

s_1 and s_2 are limits of integration.

However, the crystallinity x must not be dependent on the limits of integration. Therefore, x' is found from eq. (10) for various ranges $(s_1 - s_2)$ and K must be adjusted so that x is independent of the limits of integration. The value of x found in this way is a true measure of crystallinity.

Using the scattering factors for $(CH_2)_n$ and assuming D to obey the relation,

$$D(s) = \exp(-k \cdot s^2) \tag{12}$$

Ruland showed that K can be approximated by

$$K = 1 + (k/2) \cdot (s_2)^2 \tag{13}$$

Vonk[3] noticed that using eqs. (9) and (13) we can write

$$\frac{1}{x'} = y = \frac{1}{x} + \left(\frac{k}{2x}\right) \cdot (s_2)^2 \tag{14}$$

It results from eq. (14) that a plot of y vs. $(s_2)^2$ should be close to a straight line. Such a plot is used for determining x and k in Vonk's modification of the method of Ruland. Vonk elaborated a computer program for calculation of the degree of crystallinity.[3] He indicated that in many cases the plots of y vs. $(s_2)^2$ may be better approximated by curves of upward curvature, which are the cases in which the position of the background in the X-ray intensity distribution is estimated at too high a level. It results in an increase of y at high $(s_2)^2$ values.

This is why a second-degree curve is fitted to the y curve in the full version of the program, i.e., when the scattering curve is taken up to $(s_2)^2 \approx 1.56$ (corresponding to $2\vartheta \approx 150°$ for CuKα radiation).

The crystallinity is calculated from the intercept at $(s_2)^2 = 0$ and k from $k = 2x \cdot y'(0)$. Aiming at the normalization of the observed data, the intensity is integrated over the whole reciprocal space. Then, the integrated total theoretical intensity is calculated using f^2 and the average of the incoherent intensities for the atoms present in the polymer considered. Next, the ratio T of the observed integral intensity to the theoretical one is determined. The plot of T vs. s_2 (the upper limit of integration) tends to a constant level R for large s_2 values. The mean of the ratio T between $s = 0.8$ and $s = 1.2$ is used for scaling of the observed integral intensity to the level of the absolute integrated intensity. Then, the incoherent scattering is subtracted. Vonk noticed that a well-estimated value of R can be obtained even at lower values of s_2; $s_2 \approx 0.6$ ($2\vartheta = 55.5°$). For this reason, a reduced version of the procedure was prepared, where the scattering curve is registered only up to $s = 0.6$ and R is taken as T at $s = 0.6$. In such a narrow range of s_2, a plot of y vs. $(s_2)^2$ may be approximated by a straight line. Vonk found that the crystallinities obtained with the reduced version differ less than 0.03 from the values given by the full procedure. The separation of the crystalline peaks from the background is made using the diffraction curve of the amorphous fraction, which must be known for each investigated polymer.

In the method proposed by Vonk, all of the registration range $2\vartheta_1 - 2\vartheta_2$ of the investigated sample is divided into two groups. The first group contains the 2ϑ intervals in which no crystalline peaks are considered to be present (amorphous intervals). The second group contains the intervals where both the crystalline peaks and the amorphous background are present (mixed intervals). Using the pattern of the amorphous fraction, the background curve in the mixed intervals is determined according to the relation

$$I_B = I_A \cdot C \tag{15}$$

where I_B is the background intensity of the investigated sample, I_A, the intensity of the amorphous fraction; and C, the factor varying lineary between two values c_1 and c_2 that are calculated at the beginning and the end of the considered mixed interval:

$$C_1 = I_1/I_{A1}; \quad C_2 = I_2/I_{A2}$$

I_1, I_2, and I_{A1}, I_{A2} are the values of the observed intensities and the intensities of the amorphous fraction, respectively, at those two points.

4. EXPERIMENTAL

The crystallinity was determined for four types of polyamide-6 fibers with the elongation ratio varying from 0% to 300%. The fibers were formed with a Brabender extruder using a five-hole extrusion die with diameter of 0.2 mm. The fibers were cooled in air.

The X-ray investigations were performed for powdered fibers. WAXS measurements were made by a TUR diffractometer. The symmetrical reflection method of registration was used. A copper target X-ray tube, operated at 30 kV and 30 mA, was used as the source of radiation. Monochromatization was carried out by the Ross double-filter method. The scattering curves were taken in two overlapping intervals: 5°–35° and 30°–100° using the step-scanning mode with the step of 0.1° and 0.2°, respectively. The WAXS patterns for three investigated samples are presented in Figure 1.

To employ the method of Hindeleh and Johnson, two computer procedures were elaborated. The first was used for

- subtraction of the intensity data registered with the cobalt filter from those taken with the nickel filter;
- scaling of the intensity data from both the intervals and combining them to a resulting intensity distribution in the whole range of registration;
- correction for the polarization factor;
- normalization of the integrated experimental intensities by comparison with the integrated theoretical (coherent + incoherent intensities; and
- subtraction of the incoherent scattering.

The program creates the plots of the normalized diffraction curve in the absolute scale as well as the plots of incoherent scattering and the mean-square atomic-scattering factor of the polymer concerned. Exemplary plots for the sample PAO2 are presented in Figure 2(a). Figure 2(b) presents the diffraction curve for the same sample before and after subtraction of the incoherent scattering. The resulting corrected and normalized intensity data are used by
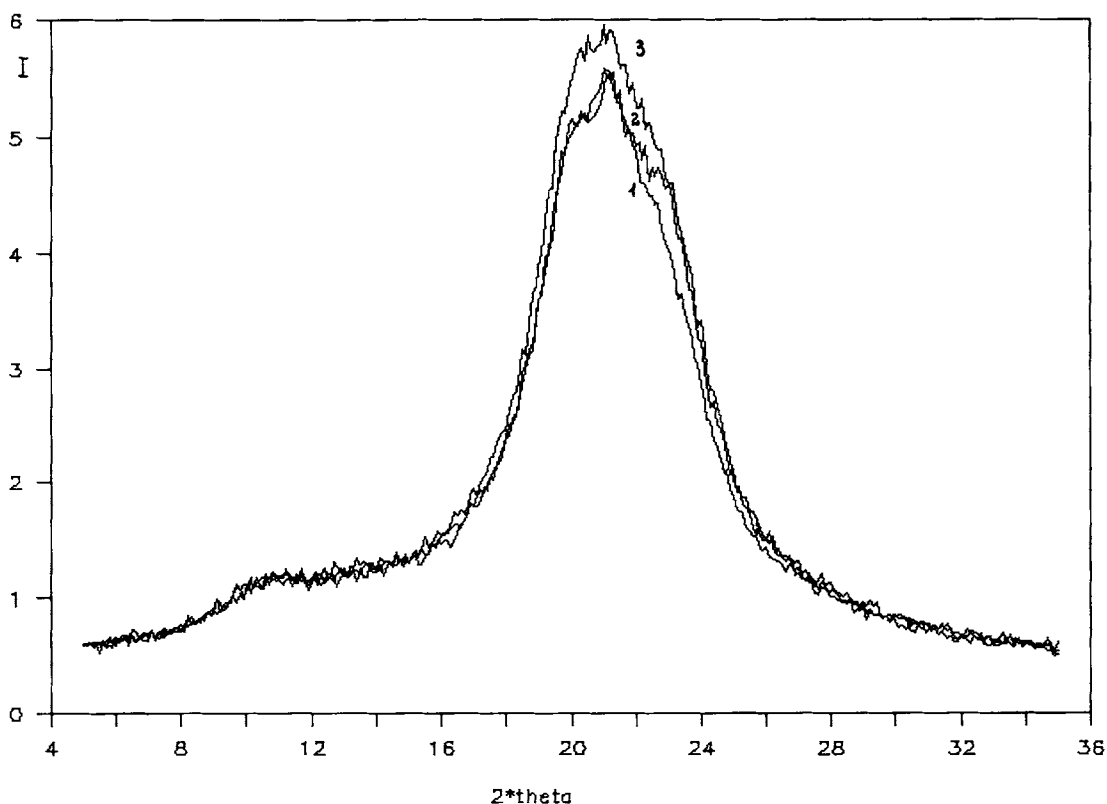

Figure 1   X-ray diffraction curve for three investigated samples. The scattering intensity *I* is given in relative units: (1) PA00 sample; (2) PA02 sample; (3) PA03 sample.
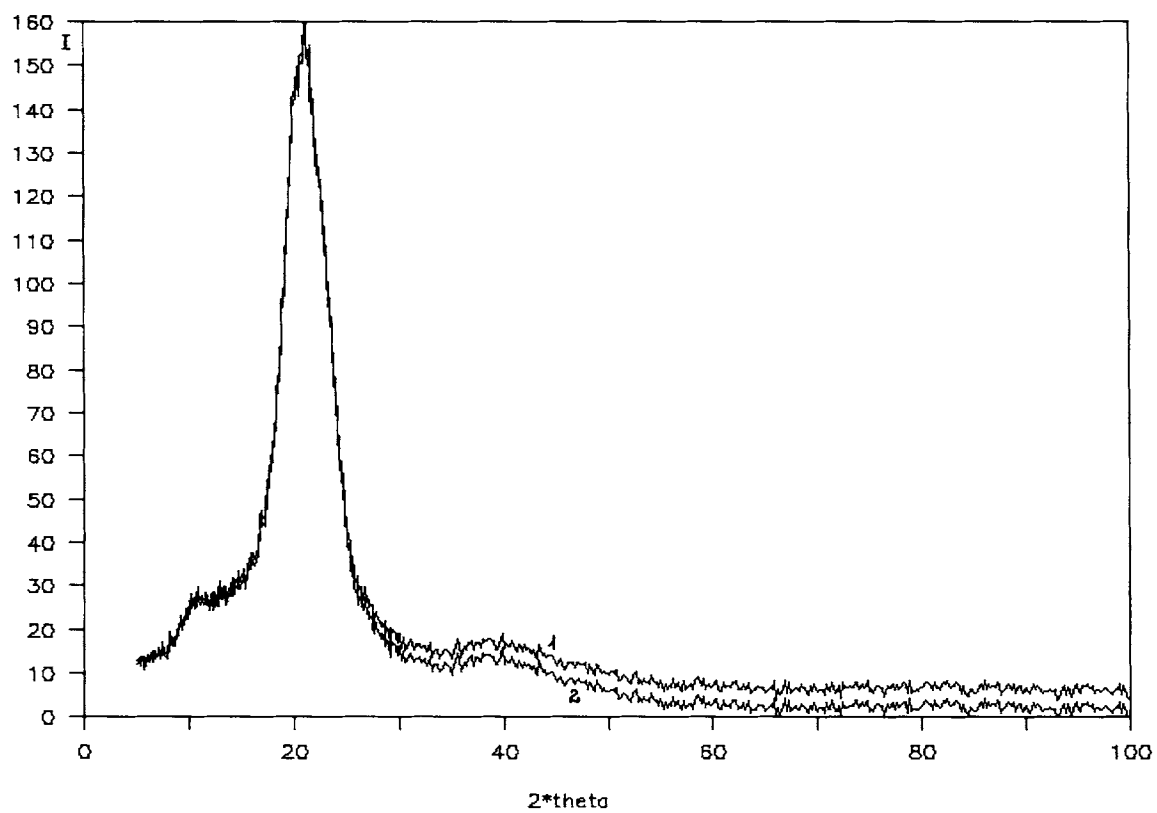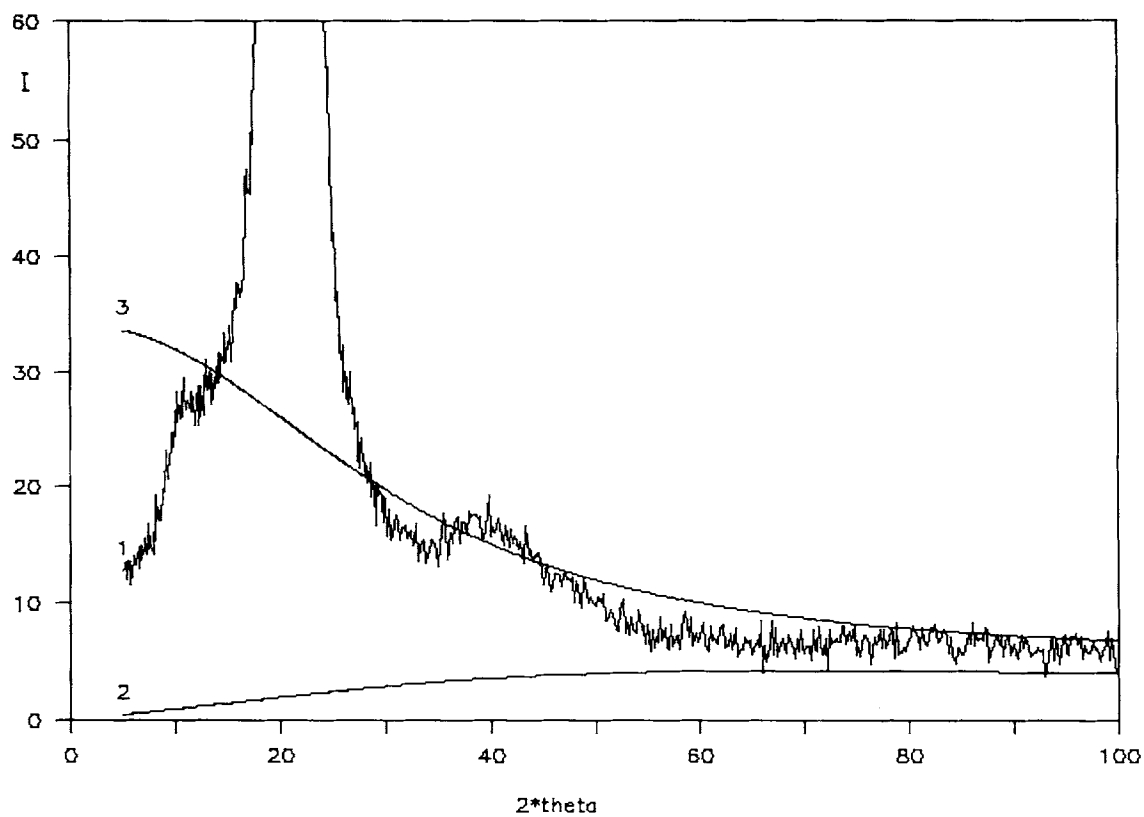
Figure 2 (a) The WAXS plots for the PA02 sample: (1) normalized diffraction curve; (2) incoherent scattering; (3) the mean-square atomic scattering factor for polyamide-6. (b) X-ray diffraction curve for the PA02 sample (1) before and (2) after subtraction of the incoherent scattering.
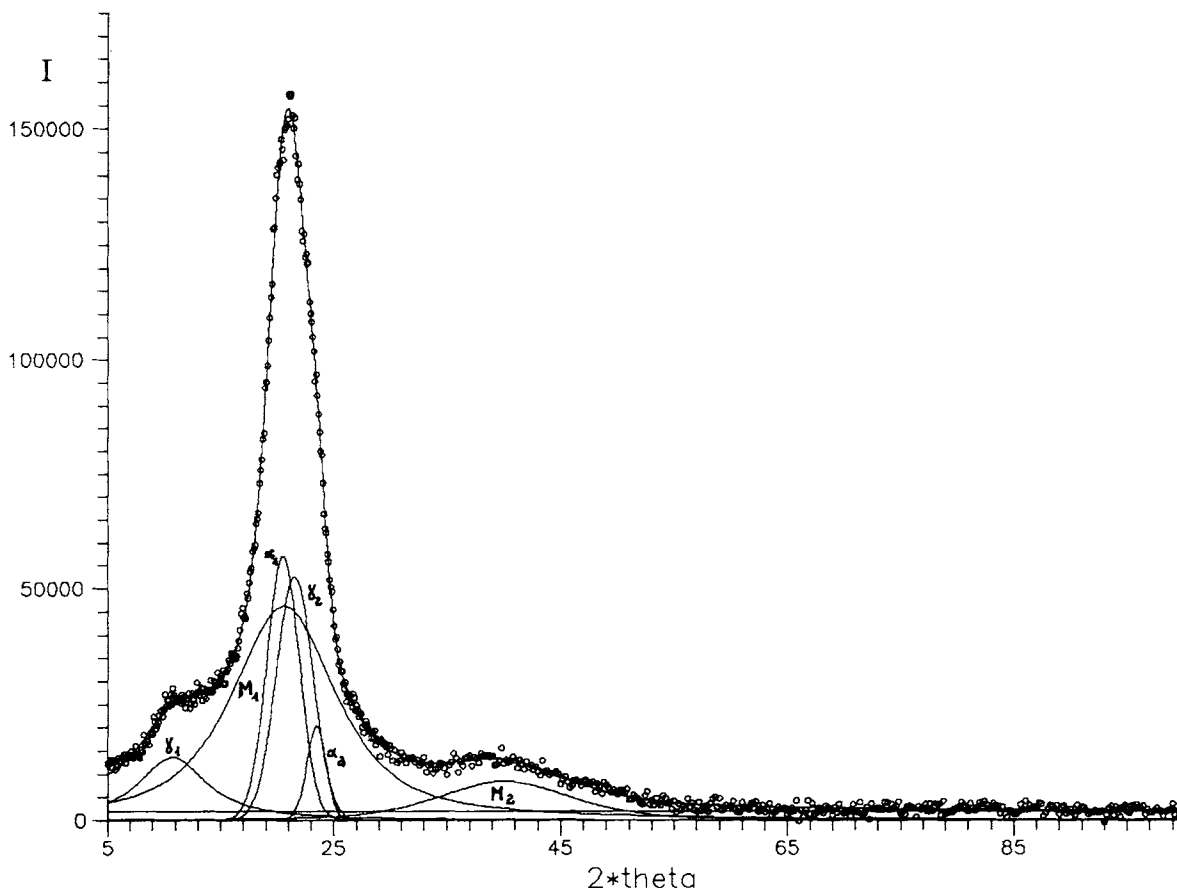
Figure 3   X-ray diffraction curve for the PA02 sample resolved into parts: (circles) the experimental intensity values; (solid line) the approximating function that originates as a composition of all the component peaks and amorphous background. The strongest peaks are shown.

the main program that determines the parameters of the crystalline peaks and amorphous halo by minimization of the sum of squares S [eq. (4)].

The minimization is realized by means of the Rosenbrock's method.[11] The main program creates the plots of peaks, demonstrates the degree of fitting of the theoretical function to the experimental one, and calculates the relative errors of the fitting.

The second way for determination of the crystallinity was the method of Ruland modificated by Vonk. In this case, we used a computer program FFCRYST elaborated by Vonk. The diffraction curve of the amorphous fractions for polyamide-6 was given as data. This curve was used for separation of the crystalline peaks from the amorphous background. The program was adapted to work with an IBM AT personal computer and was provided with new graphical utilities and additional options for the analysis of the output data.

5. RESULTS AND DISCUSSION

Hindeleh and Johnson, investigating the cellulosic materials as well as polyamide and PET obtained very high crystallinity values compared with the results obtained by other authors.[8–10] For some polyamide samples, the authors obtained the crystalinity of about 100%. It seems that such high crystallinity values result from the method of the amorphous background approximation employed by the authors. Considering the diffraction curves within a rather narrow angular interval, 10°–34°, they assumed a third-order polynomial for the amorphous background line. The shapes of diffraction curves for the majority of polymers in the amorphous state are much more complicated than is the shape of a third-order polynomial. Therefore, it is difficult to find the reason why the amorphous background line of partially crystalline polymers should have such a
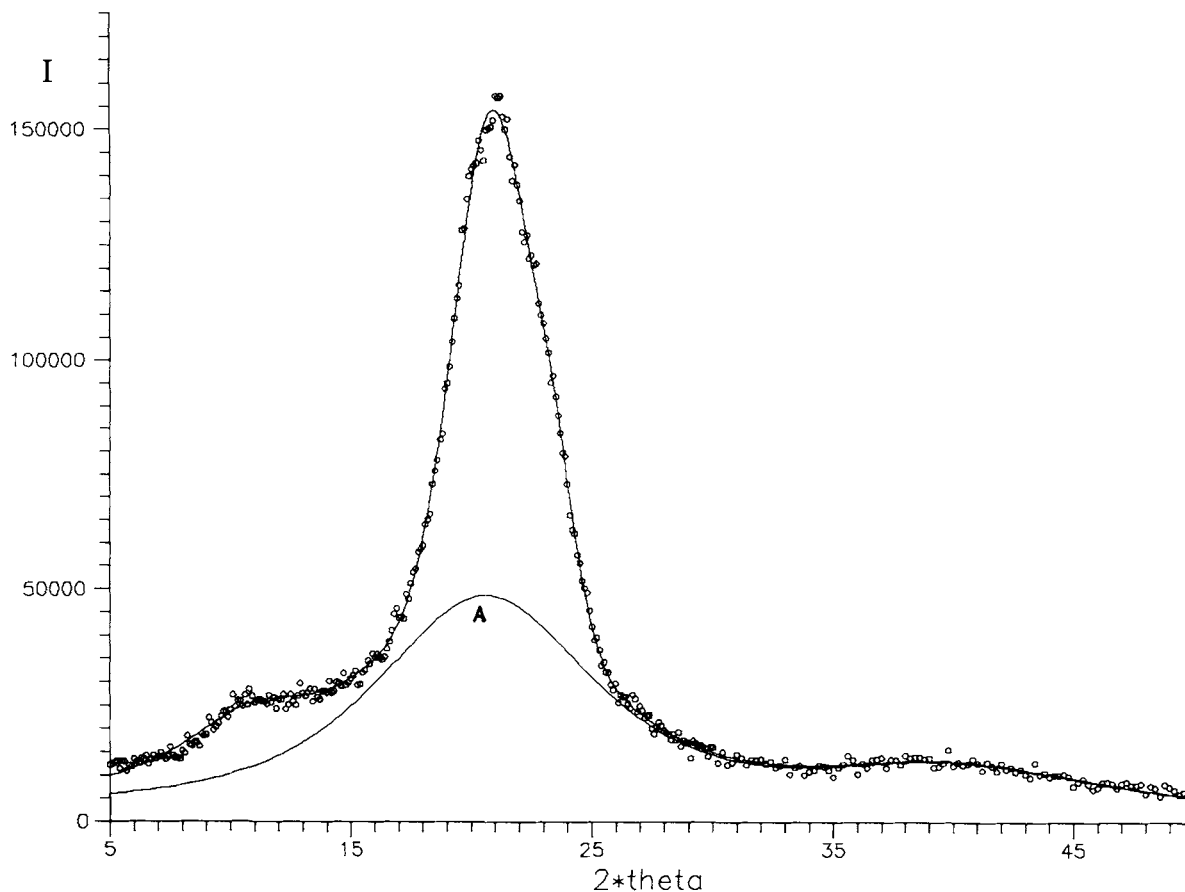
Figure 4   X-ray diffraction curve for (circles) the PA02 sample and (solid line) the amorphous background.

form. The analysis of the diffraction curves for several semicrystalline polymers shows that their background cannot be described by any third-order polynomial. This is particularly clear when one examines the WAXS patterns for polymer samples of low crystallinity registrated within a sufficiently large angular interval. Some examples for polyethylene, polypropylene, and poly(ethylene terephthalate) are presented in our paper.[12] In the case of partially crystalline polyamide-6 fibers, a polynomial cannot be used for the amorphous background approximation either. The most intense

crystalline peaks for the α and γ crystalline phases take place at the following angles 2ϑ (Refs. 13–15):

α phase: $\alpha_1 = 20.33°$ (200), $\alpha_2 = 24.07°$ (002, 202)

γ phase: $\gamma_1 = 10.48°$ (020), $\gamma_2 = 21.33°$ (201, 011)

(Miller indices are given in the parentheses).

The amorphous background line comprises two broad maxima: the larger M_1 situated at $2\vartheta = 20.2°$ and the smaller M_2 at $2\vartheta = 39°$. At larger angles, the intensity decreases continuously and reaches a

Table I

Peak	α_1	α_2	γ_1	γ_2	M_1	M_2
hkl	(200)	(002), (202)	(002)	(201), (011)	Amorphous	Amorhpous
2ϑ	20.50°	23.46°	21.51°	10.76°	20.59°	40.04°

hkl, Miller's index.

Table II

| Sample | λ (%) | Method of Hindeleh–Johnson Range of Calculations | | | Method of Ruland–Vonk | |
		5°–30°	5°–50°	5°–100°	x	k
PA00	0	48.2	41.0	37.7	34.1	3.6
PA01	100	49.9	42.5	39.2	35.1	3.6
PA02	200	51.0	43.8	40.5	36.3	3.9
PA03	300	55.2	48.7	45.4	38.9	3.2

λ, elongation ratio. The crystallinity is given in %.

constant level at $2\vartheta > 60°$. It is clear that such a curve cannot be approximated by a third-order polynomial. In this work, a combination of three functions was used to this aim: two so-called peak functions and a third-order polynomial. The polynomial approximates the shape of the background line at large angles and the "peak" functions approximate the maxima M_1 and M_2. The "peak" functions are the linear combinations of Gauss and Cauchy functions.

The experimental diffraction curves were resolved into four crystalline peaks and the amorphous background using the computer program MINIMAL. Figure 3 shows the diffraction curve for the PA02 sample resolved into parts. The circles stand for the experimental intensity values, and the solid line is
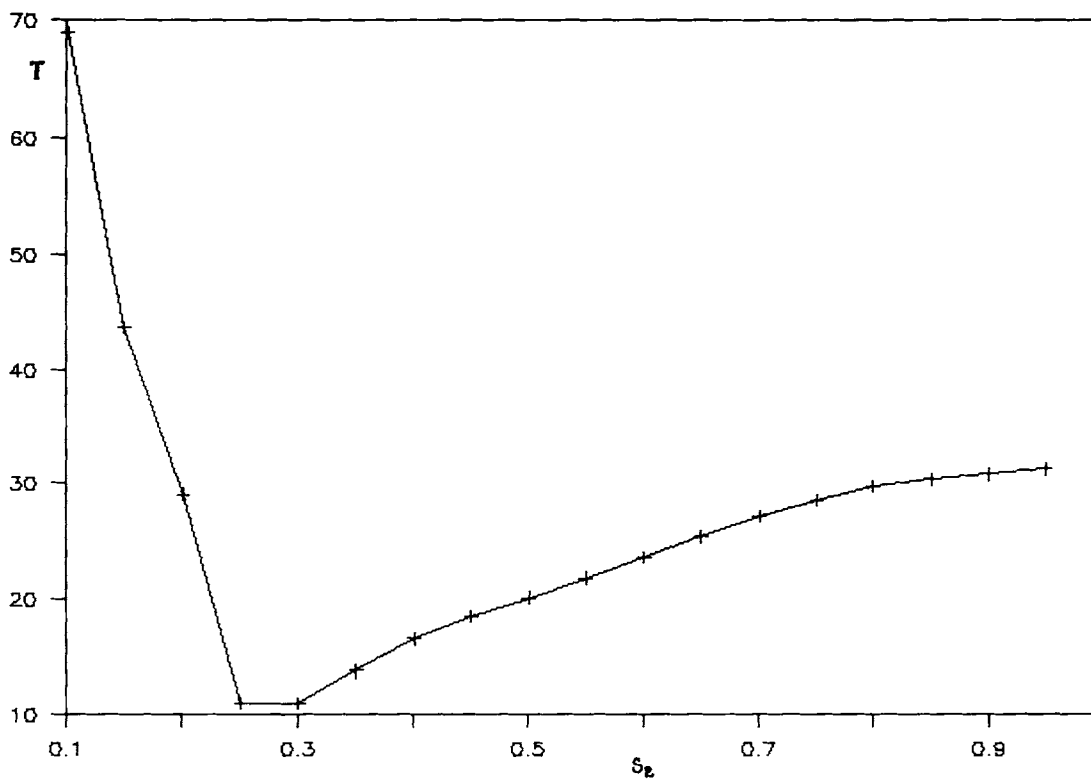

Figure 5   The plot of the function T vs. the upper limit of integration s_2 for the sample PA02.
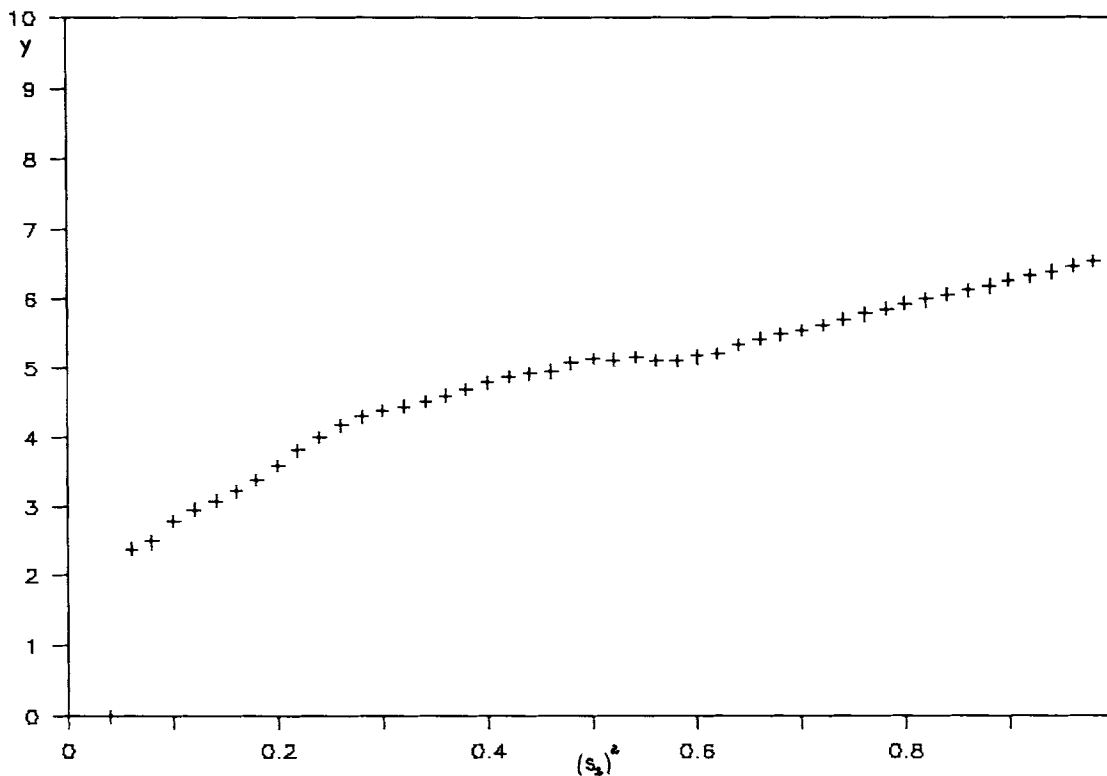
Figure 6   Plot of y vs. $(s_2)^2$ for the PAO2 sample, used for the crystallinity calculation.

for the approximating function that originates as a composition of all the component parts. In Figure 4, the amorphous background is presented for the same sample. The angular positions determined by the program MINIMAL for all the crystalline peaks and amorphous maxima are presented in Table I.

The degree of crystallinity was calculated as the ratio of the total area under the resolved crystalline peaks to the total area under the unresolved diffraction curve. The results of calculations for all the samples are presented in Table II. The calculations were performed for three arbitrarily chosen intervals of integration. The intervals were chosen in this way so that the first interval comprises only the strongest crystalline peak and the main amorphous "halo," the second includes all the peaks, and the third equals to the whole range of registration.

Calculations of the degree of crystallinity with Ruland and Vonk's method were made using the computer program FFCRYST elaborated by Vonk. Normalization of the experimental intensity values was performed in the way described in Section 3. Figure 5 presents the plot of T vs. the upper limit of integration s_2 for the sample PAO2. At large an-

gles, s_2 T tends to a constant value. This value is used for scaling of the experimental integral intensity to the level of the absolute integral intensity. Calculations of the crystallinity were performed using a linear approximation of y vs. the $(s_2)^2$ function [eq. (14)]. The plot of that function for sample PAO2 is presented in Figure 6. The results of calculations are presented in Table II. As one can see, the results obtained with both methods are close to one another. The calculated values are considerably smaller than those determined by Hindeleh and Johnson for PET, polyamide,[7] and cellulosic materials. It is evident that such high crystallinity values obtained by Hindeleh and Johnson were directly connected to the assummed manner of the amorphous background approximation.

Summarizing, the results of calculations obtained in this work with both methods confirm that the way of the amorphous background approximation employed so far in Hindeleh and Johnson's method should be modified. In this work, the assemblage of polynomial and a Gauss and Cauchy "peak" function was used to this aim. However, it seems that other component functions are possible.

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