Polymer Bulletin 24, 233–240 (1990)

Polymer Bulletin

Orientation factors and orientation distribution function of anisotropic polymer glasses determined by X-ray scattering: A comparison of different evaluation methods

Gyula J. Vancso

University of Toronto, Department of Chemistry, 80 St. George Street, Toronto, Ont. M5S, 1A1, Canada

Abstract

This paper presents a critical analysis of the available evaluation methods to calculate the chain orientation distribution function and the orientation factors of uniaxially oriented polymer glasses from wide angle X-ray scattering data. Experimental results obtained on a stretched atactic polystyrene sample are used for the calculations.

Introduction

It was discovered long ago [1] that the azimuthal intensity of crystalline reflections observed in wide angle X-ray scattering (WAXS) patterns of semicrystalline materials could be used to characterize anisotropy. The reason for this is that the scattered intensity, at a given angle to the meridian, is related to the number of crystallites inclined at the same angle to the orientation direction. This result can be used to quantify orientation of the crystallites, in terms of statistical averages of the orientation distribution function (ODF). In polymer materials science this approach was first applied for semicrystalline polymers [2,3] and was later extended to include the amorphous polymer phase [4, 5]. In this paper the results of the most frequently used mathematical methods, to calculate the orientation factors (OF) and the entire ODF, will be compared using WAXS data obtained on a drawn atactic polystyrene sample.

The ODF of a polycrystalline material is defined as the probability of the edges of the crystalline unit cell being aligned in a given spatial direction [2,6]. In the most general case ODF is a function of three independent variables, the three Euler angles, which specify the spatial position of the crystalline unit cell [6]. However, in order to describe anisotropy in amorphous polymers, in most cases only the main chain orientation must be characterized [2,4]. The ODF is then defined as the probability of having a polymer segment aligned in a given direction. For most applications, polymer segments can be regarded to have cylindrical symmetry. Therefore the corresponding ODF is related to the segment axis orientation, which can be specified using two angles only [2]. It must be mentioned that if rotatable side groups are attached to the main chain, their relative position may also change during orientation [7]. If so, both main chain and side group orientations must be described. This possibility will not be discussed further in this paper.

In the characterization of the orientation of polymers, further simplifications are possible in most situations due to symmetry properties of the orientation texture. For example, transverse isotropy holds for many important applications [2]. This means that there is no preferential orientation in a plane which is perpendicular to a single direction; for example, the stretching direction (if we deal with uniaxially drawn materials). In such cases ODF for glassy polymers is a function of one angle only, that angle is closed by the preferred orientation direction (POD) and the segmental direction [2]. This structural symmetry is usually called fiber symmetry. In this paper only this sample symmetry will be further considered.

The Chain Orientation Distribution Function and the Orientation Factors

The ODF, $h(\chi)$, for uniaxially oriented amorphous polymers with segments showing cylindrical symmetry, is related to the fractional number of segments, $dN(\chi)$, having the segmental axis lying at an angle between χ and $\chi+d\chi$ to the POD. According to the definition [2,4]:

$$dN(\chi) = h(\chi)\sin\chi\, d\chi \tag{1}$$

with the normalization condition

$$\int_0^{\pi} h(\chi)\sin\chi\, d\chi = 1 \tag{2}$$

It is not the entire ODF but rather its low order moments that are used to quantitatively characterize anisotropy [2,4]. In case of uniaxial symmetry, these moments are averages of $\cos^n\chi$ (for n=2k, k=0,1,2,...) and are defined as:

$$<\cos^n\chi> = \frac{\int_0^{\pi/2} H(\chi)\cos^n\chi\,\sin\chi\, d\chi}{\int_0^{\pi/2} H(\chi)\sin\chi\, d\chi} \tag{3}$$

where $H(\chi)$ is not necessarily normalized to unit integral, i.e. $H(\chi)=\text{const}\cdot h(\chi)$.

In expressions describing anisotropy of physical properties, well defined functions of the above moments are used. These are often called orientation factors (OF) [2,4]. The n-th order expressions for OF correspond to Legendre polynomials of n-th order, $P_n(\cos\chi)$ [2,4]. For example, the second order OF (f_2) which is needed e.g. to describe optical anisotropy, is written as:

$$f_2 = <P_2(\cos\chi)> = \frac{1}{2}(3<\cos^2\chi> - 1) \tag{4}$$

where < ... > corresponds to an ensemble average over $h(\chi)$. The value of f_2 is 1 for perfect parallel, and - 0.5 for perfect perpendicular, chain orientation. For isotropic samples f equals zero which corresponds to an average orientation angle of 54.7° (1/3 direction cosines, i.e. equal weights to all the three spatial directions). If the polymer shows uniaxial symmetry, then the next two non-vanishing OF's, which are needed e.g. to describe mechanical anisotropy [2], have the following form:

$$f_4 = \langle P_4(\cos\chi)\rangle = \frac{1}{8}(35\langle\cos^4\chi\rangle - 30\langle\cos^2\chi\rangle + 3) \tag{5}$$

$$f_6 = \langle P_6(\cos\chi)\rangle = \frac{1}{16}(231\langle\cos^6\chi\rangle - 315\langle\cos^4\chi\rangle + 105\langle\cos^2\chi\rangle - 5) \tag{6}$$

The Method of the Azimuthal Breadth [8]

The interrelation between the WAXS azimuthal intensity and the ODF can be used to obtain a simple, empirical measure of the orientation. This can be obtained either from the azimuthal breadths [3] or from the normalized maximum to minimum height of the measured WAXS azimuthal intensity $I(\chi)$ [8]. However, this approach can be applied to a rough estimation of the second order OF only. One possible way to calculate f_2 with this method was discussed by May [8] who used the following expression:

$$f_2 \approx 1 - \frac{\bar{I}}{I_{max}} \tag{7}$$

where $\bar{I}$ is the average, and I_{max} is the maximum azimuthal intensity. The use of the expression (7) is further restricted to equatorial reflections.

The Legendre Polynomials Method (LPM) [10]

The first analysis of a WAXS azimuthal profile at constant diffraction angle in terms of Legendre polynomials was carried out by Deas [9]. His method was later generalized to obtain the values of OF's of any order from an arbitrary reflection [10]. For example, for equatorial reflections, the even order moments are written as:

$$f_{2n} = \langle P_{2n}(\cos\chi)\rangle = C_{corr}\frac{(-1)^n 2^{2n}(n!)^2}{(2n)!}\;\frac{\int_0^{\pi/2} I(\chi)\,P_{2n}(\cos\chi)\,\sin\chi\,d\chi}{\int_0^{\pi/2} I(\chi)\,\sin\chi\,d\chi} \tag{8}$$

$$(n=1, 2,...)$$

where C_{corr} refers to a correction factor which takes into account the intrinsic azimuthal linewidth [4] (in this paper we assume further $C_{corr} = 1$ since its value equally affects all calculated OF data, independently of the applied calculation procedure), and the fraction following C_{corr} in Eq. (8) {i.e. $(-1)^n 2^{2n}(n!)^2/(2n)!$} depends on the nature of the X-ray reflection. In case of sharp molecular scattering the entire form of h(χ) can also be estimated using a series expansion with Legendre polynomials [10]. The number of terms that must be included in the series depends on the sharpness of h(χ). For equatorial WAXS reflections, the series expansion with the first four non-vanishing terms has the form:

$$h(\chi) = \frac{1}{2\pi}\left[1 - 10\langle P_2\rangle_I P_2(\cos\chi) + \frac{72}{3}\langle P_4\rangle_I P_4(\cos\chi) - \frac{208}{5}\langle P_6\rangle_I P_6(\cos\chi) + \ldots\right] \qquad (9)$$

where

$$\langle P_{2n}\rangle_I = \int_0^{\pi/2} I(\chi)\, P_{2n}(\cos\chi)\, \sin\chi\, d\chi \Big/ \int_0^{\pi/2} I(\chi)\, \sin\chi\, d\chi \qquad (10)$$

$$(n=1,2,\ldots)$$

A similar equation holds for meridional reflections [10] with different proportionality constants.

The Biangardi Method (BM) [11]

This technique enables the calculation of the entire ODF and thus the values of the OF's by inverting Kratky's expression [12] which relates the WAXS azimuthal profile to the ODF. The measured azimuthal profile is first expanded in a Fourier series:

$$I(\tilde{\chi}) = \sum_{j=0}^{N} A_j \cos(j\tilde{\chi}) \qquad (11)$$

where $\tilde{\chi}=(\pi/2) - \chi$.

The ODF is then written using the A_j Fourier coefficients in the following form:

$$h(\chi) = \frac{2}{\pi}\left[\, I(\tilde{\chi}=0^{o}) - \sum_{j=0}^{N} A_j j \int_0^{\frac{\pi}{2}-\chi} \frac{\sin(j\tilde{\chi})d\tilde{\chi}}{(1 - \sin^2\tilde{\chi}/\cos^2\chi)^{1/2}}\right] \qquad (12)$$

The OF values can be subsequently calculated from equation (3) using the numerical values for h(χ) obtained with Eq. (12). This method is applicable for equatorial reflections, since it is assumed that the corresponding WAXS reflection is caused by intermolecular distances which are perpendicular to the direction of the polymer segments [11].

Computer Programs

The ODF and OF calculations were carried out using an AST Premium/386 microcomputer and the IBM Professional Fortran programming language. A computer program for the calculation of Legendre polynomials method was developed using some subroutines of the IMSL-PC library [13]. The values of the

Legendre polynomials were calculated up to 16th order (n=8 in Eq. (10)) with hypergeometric functions F(-n, n+1/2; 1/2; $\cos^2\chi$) [14]:

$$P_{2n}(\cos \chi) = (-1)^n \frac{(2n-1)!!}{2^n n!} F(-n,\ n+\frac{1}{2};\ \frac{1}{2};\ \cos^2\chi) \qquad (13)$$

where the hypergeometric functions were expanded in the following series (which terminates if a or b is equal to a negative integer or zero) [14]:

$$F(a,b;c;z) = 1 + \frac{ab}{c} z + \frac{1}{2!}\frac{a(a+1)b(b+1)}{c(c+1)} z^2 + \dots \qquad (14)$$

The program to evaluate the Biangardi method was kindly supplied by H. J. Biangardi [15].

Experimental

A typical WAXS pattern, obtained on a uniaxially stretched atactic polystyrene (PS) sample, was used for the reported calculations. Orientation was performed in a tensile test machine at 108.5 ^{o}C. The elongation was stopped at a given strain, and the force was kept constant while the sample was quenched by applying a cooled air stream. WAXS patterns were obtained on the quenched sample using a Siemens D 500 diffraction system equipped with a Huber texture goniometer. The azimuthal intensity profile $I(\chi)$ was determined at $2\Theta = 9.9^o$ diffraction angle which corresponds to an equatorial reflection. To obtain a true $I(\chi)$ function without influence of overlapping higher order haloes, the WAXS pattern was measured between $2^o \le 2\Theta \le 50^o$ diffraction angles and at 8 different azimuthal directions between $0^o \le \chi \le 90^o$; and subsequently resolved into three peaks. The intensity of the first resolved peak was then plotted against the azimuth angle. The obtained profile was subsequently fitted by the following formula:

$$I(\chi) = [\alpha \sin^{2\beta}\chi + I(\chi = 0^o)] \backslash I(\chi = 0^o) \qquad (15)$$

Other details of the experiments and the profile fitting procedure are published elsewhere [7] and are subject of a forthcoming publication [16].

Results and Discussion

The ODF and OF values were calculated using the analytical $I(\chi)$ function defined by Eq. (15) with α=1.428 and β=1.380. The values for the α and β parameters were obtained from the measured azimuthal profile of the considered equatorial reflection of the stretched PS sample by performing a non-linear least squares fit analysis.

Figure 1 shows two calculated $H(\chi)$ orientation distribution functions normalized to 1 at the maximum amplitude (at $\chi=0^o$). The solid line in Figure 1 corresponds to ODF calculated from Legendre polynomials (Eq. (9); with max{2n}=16),; while the dashed line represents the result of the Biangardi method (Eq. (12), with max{N} = 20). The functions are plotted only between $\chi=0^o$ (corresponding to the POD) and

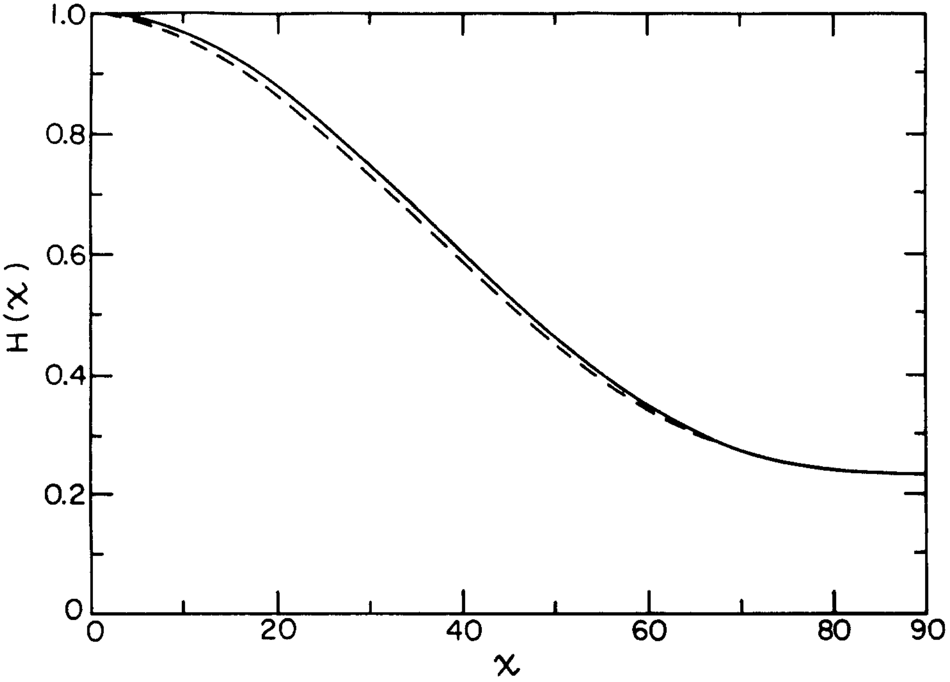

Figure 1

Chain orientation distribution functions for a uniaxially stretched atactic PS sample calculated with Legendre polynomials (solid line) and by the Biangardi method (dashed line).

Table 1

Calculated orientation factors for a uniaxially stretched atactic PS sample

Method		$<P_2(\cos\chi)>$	$<P_4(\cos\chi)>$	$<P_6(\cos\chi)>$
May		0.295	n.a.	n.a.
Legendre polyn.	LPM	0.222	0.0218	- 0.00276
Biangardi	BM	0.219	0.0239	- 0.00217
(LPM-BM)/LPM	[%]	1.4	- 9.6	21.4

$\chi=90^o$ (corresponding to the perpendicular direction), since due to the axial texture, ODF is symmetrical to both the $\chi=0^o$ and $\chi=90^o$ lines. (The maximum at 0^o means that polymer segments show most likely to the POD.)

(corresponding to the POD) and $\chi=90^o$ (corresponding to the perpendicular direction), since due to the axial texture, ODF is symmetrical to both the $\chi=0^o$ and $\chi=90^o$ lines. (The maximum at 0^o means that polymer segments show most likely to the POD.)

Table 1 shows the first three calculated even order orientation factors obtained with the May method (Eq. (7)); using Legendre polynomials (Eq. (8)) and from the ODF which was calculated by the Biangardi method (see dashed curve in Figure 1). The last row in Table 1 shows the relative differences between the data obtained by the Legendre polynomial and the Biangardi methods.

The method of May yields for $<P_2(\cos\chi)>$ a numerical value which is significantly different from the results obtained by the two other techniques. The reason of the poor agreement is that this method does not take into account the shape of the ODF. The use of this technique is therefore not recommended for any quantitative estimation of OF values. The numerical values of the second and fourth order orientation factors calculated by LPM and BM agree reasonably well. The agreement is less good for the sixth order OF. Nevertheless the shapes of the two calculated ODF by LPM and BM match very well (see Figure 1). This means that even a slight change in the shape of the ODF has a significant effect on the values of the high order OF's.

The basic difference between the LPM and BM procedures is that for LPM the values of the OF's are calculated first and with them the ODF calculated afterwards; while for BM the ODF is first determined and the OF's are calculated subsequently. Although at this stage of our work we do not have any objective comparison to say which OF values are more correct, but we believe that due to the mentioned differences in the two procedures the LPM might yield better OF values while the BM a better ODF. It must be mentioned that even with the simple $I(\chi)$ profile used, numerical problems arose in the OF values calculated by the LPM if $2n \geq 16$. On the other hand, the more moments that are known (i.e. the more terms that are taken into account in Eq. (9)) the better the calculated ODF approaches the reality. In this respect the Fourier series used by the BM "behaved" in our case numerically better and more stable. The use of the Biangardi technique is nevertheless restricted to equatorial reflections, while the Legendre polynomial method is applicable to any kind of reflection.

Acknowledgement

Financial support by the Ontario Centre for Materials Research is greatfully acknowledged. The author is indebted to Dr. H. J. Biangardi for the supplement of his computer program and for the stimulating discussions, to Mr. D. Snétivy for performing the X-ray measurements and to Mr. G. Bruce for his comments concerning the manuscript.

References

1. W.A. Sisson and G. L. Clark, *Chem. Eng. News, Anal. Ed.* **5**, 296 (1933)
2. I. M. Ward, ed., "Structure and Properties of Oriented Polymers", Applied Science Publishers, London, 1975.
3. L. E. Alexander, "X-Ray Diffraction Methods in Polymer Science", Wiley, New York, p. 198, 1969.
4. A. H. Windle, in "Developments in Oriented Polymers - 1", I. M. Ward, ed., Applied Science Publishers, London, Chapter 1, 1982.
5. Z. W. Wilchinsky, *J. Polym. Sci. Polym. Phys. Ed.* **6**, 281 (1968)
6. H. J. Bunge, "Texture Analysis in Materials Science: Mathematical Methods", Butterworths, London, 1982.
7. G. J. Vancso, D. Snétivy and I. Tomka, *Polym. Comm.* in press; *J. Appl. Polym. Sci.*, submitted.
8. M. May, *J. Polym. Sci. Polym. Symp.* **58**, 23 (1977)
9. H. D. Deas, *Acta Cryst.* **5**, 542 (1952)
10. R. Lovell and G. R. Mitchell, *Acta Cryst.* **A37**, 135 (1981)
11. H. J. Biangardi, *J. Polym. Sci. Polym. Phys. Ed.* **18**, 903 (1980)
12. O. Kratky, *Kolloid Z.* **64**, 213 (1933)
13. IMSL-MATH/PC and STAT/PC Program Libraries for IBM Professional FORTRAN Compiler, January 31, 1985.
14. I.S. Gradshteyn, I.M. Ryzhik, "Table of Integrals, Series, and Products", Academic Press, New York, 1965.
15. H. J. Biangardi, A FORTRAN program to calculate the orientation distribution function and its moments for oriented polymers, private communication.
16. G. J. Vancso, D. Snétivy, *Eur. Polym. J.*, to be published.

Accepted May 22, 1990 K