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On the calculation of $\langle P_n(\cos\chi)\rangle$ coefficients from X-ray diffraction measurements made on *hkl* reflections

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Wide-angle X-ray diffraction measurements of the orientation distribution of (*hkl*) crystal planes give values of some of the $\langle P_n(\cos\chi)\rangle_c$ coefficients, characterizing the orientation of the molecular chains, which disagree with those obtained from *hk*0 or 00*l* reflections. In this present article, a calculation method is proposed for obtaining reliable $\langle P_n(\cos\chi)\rangle_c$ values from any *hkl* reflection. This procedure involves an angular shift of the Legendre polynomial curves for the calculation of the coefficients relative to the (*hkl*) plane orientation, which is followed by a correction for this shift to yield the $\langle P_n(\cos\chi)\rangle_c$ coefficient. A comparison is made between results obtained by the regular and the angular shift procedures for oriented polypropylene sheets. It is shown that the calculation of the $\langle P_n(\cos\chi)\rangle_c$ coefficients from the 111,$\bar{1}$31/041 and 022/$\bar{1}$12 reflections, using the regular procedure, gives results which are, in some cases, outside the boundaries of the function, whereas results obtained by the angular shift procedure agree with those computed from the (110), (040) and (130) crystal planes. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Wide-angle X-ray diffraction (WAXD) is one of the most frequently used techniques for the investigation of molecular orientation in semicrystalline polymers[1,2]. It allows the measurement of the orientation distribution of different crystal planes, which can be used to calculate the orientation of molecular chains from the $\langle P_n(\cos\chi)\rangle$ coefficients characterizing the crystal plane orientation. Indeed, the $\langle P_n(\cos\chi)\rangle_c$ coefficients relative to the chain orientation can be obtained by a simple relationship in the case of cylindrical symmetry of the orientation distribution of the crystal planes about the reference direction[3,4].

Nevertheless, for X-ray reflections that are oriented neither parallel nor perpendicular to the molecular chain axis (the (*hkl*) crystal planes), the calculation of some of the $\langle P_n(\cos\chi)\rangle_c$ coefficients gives imprecise values which differ markedly from those calculated from (*hk*0) and (00*l*) crystal planes, and which are sometimes even outside the boundaries of the function[4,5]. For example, values of $\langle P_2(\cos\chi)\rangle_c$ above unity may be obtained for (*hkl*) planes oriented near the 'magic angle', namely $\chi = 54.7°$. In this present article, it will be shown that reliable values of the $\langle P_n(\cos\chi)\rangle_c$ coefficients can be calculated from such reflections by conducting the calculation after an angular shift of the Legendre polynomial curves and correcting afterwards for this shift. This procedure provides a simple method for gaining useful information from X-ray reflections that would otherwise be unsuitable for characterizing the molecular orientation.

THEORY

The complete characterization of crystalline orientation by wide-angle X-ray diffraction involves the measurement of pole figures, which give the orientation distribution $N(\chi,\phi)$ of the normal to the crystal planes. The angle χ defines the inclination between the plane normal and the reference direction, and ϕ defines the position of the projection of the plane normal in a plane perpendicular to the reference direction[1,2]. However, it can often be assumed that the orientation distribution of the crystal axes exhibit cylindrical symmetry with respect to the reference direction, as it is normally found in uniaxially deformed polymers, and the description of the orientation distribution then reduces to $N(\chi)$.

The molecular orientation distribution $N(\chi)$ is generally characterized by $\langle P_n(\cos\chi)\rangle$ coefficients (abbreviated as $\langle P_n\rangle$ in the rest of this paper), where the brackets indicate that the coefficients are averages taken over all orientations in the sample. These are the coefficients of a series expansion of the orientation distribution in terms of the Legendre polynomials $P_n(\cos\chi)$[1,6]:

$$N(\chi) = \sum (n + 1/2)\langle P_n\rangle P_n(\cos\chi) \qquad (1)$$

where the $(n + 1/2)$ term ensures the convergence of the series. Only the even n terms are calculated, with the odd terms being equal to zero for reasons of symmetry. All of

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the polynomials have their maximum value of $P_n(\cos\chi) = 1$ at $\chi = 0°$, and possess either a maximum or a minimum at $\chi = 90°$. For an isotropic sample, all of the $\langle P_n\rangle$ coefficients are equal to zero, except for $\langle P_0\rangle$, which is always equal to unity. For a perfect orientation parallel to the reference direction, which in oriented polymers is generally taken as the deformation axis, all of the $\langle P_n\rangle$ coefficients would be equal to unity. More generally, for a very narrow orientation distribution centred at an angle $\chi_{\max}$ with respect to the reference direction, the $\langle P_n\rangle$ coefficients take the value of their corresponding polynomial at that particular angle[4]. For example, the $\langle P_2\rangle$ coefficient measured for a highly oriented polymer with a reflection oriented around $\chi = 54.7°$ has a value close to zero, as would be obtained with an unoriented material, since $P_2(\cos\chi) = 0$ at this angle. Thus, X-ray reflections that appear near $\chi = 54.7°$ are generally considered as being unsuitable for the characterization of orientation[7], which for polymers deformed at low draw ratios is often expressed by the $\langle P_2\rangle$ coefficient only.

The $\langle P_n\rangle$ coefficients are calculated from WAXD measurements by using the following equation[1,6]:

$$\langle P_n\rangle = \int_0^{90} N(\chi)P_n(\cos\chi)\mathrm{d}\chi \qquad (2)$$

in which $N(\chi)$ is the normalized intensity distribution, defined as:

$$N(\chi) = \frac{I^*(\chi)\sin\chi}{\int_0^{90} I^*(\chi)\sin\chi\mathrm{d}\chi} \qquad (3)$$

where $I^*(\chi)$ represents the diffracted intensity after subtraction of the background. The sine function is introduced as a weighting term in order to take into account the fraction of crystal planes that contribute to diffraction at each point of measurement[8].

When the orientation distribution of (hkl) crystal planes exhibits cylindrical symmetry with respect to the reference direction, the $\langle P_n\rangle_c$ coefficients characterizing the molecular chain orientation can be obtained from the following [3,4]:

$$\langle P_n\rangle_c = \frac{\langle P_n\rangle_{hkl}}{P_n(\cos\phi_{hkl})} \qquad (4)$$

where ϕ_{hkl} is the angle between the normal to the (hkl) planes and the chain axis.

EXPERIMENTAL

Wide-angle X-ray diffraction measurements were made using a Rigaku rotating anode X-ray generator operating at 50 kV and 190 mA, using the Ni-filtered CuKα radiation ($\lambda = 1.5418$ Å). The collimation of the incident beam was achieved using a Soller slit and a 1.0 mm pinhole, and the detection of the diffracted intensity was made by a scintillation counter coupled to a pulse-height analyser mounted on a $\theta/2\theta$ goniometer. The orientation measurements were obtained by azimuthal (χ) rotation of the samples (about the normal to their surface), with a sampling interval of 0.5°, using slits of 1.0 and 0.5° for 2θ and χ resolution, respectively.

The isotactic polypropylene samples (iPP, α-form, monoclinic unit cell: $a = 6.67$, $b = 20.84$, $c = 6.495$ Å; $\beta = 99.33°$)[5,9,10] were prepared by roll-drawing in the laboratory of Professor R. Woodhams (University of Toronto, Canada). Details of the sample preparation[11,12] and the orientation measurements[5] can be found in previous publications.

RESULTS AND DISCUSSION

Figure 1 shows the curves involved in the calculation of the $\langle P_2\rangle$ coefficient for the distribution of the ($\bar{1}31$/041) crystal planes of an iPP sample drawn to $\lambda = 7.6$. The sine-weighted intensity curve, $N(\chi)$ (upper graph), has its maximum at $\chi_{\max} = 51.5°$, which indicates that the molecular chains are aligned in the rolling direction, since the normal to the ($\bar{1}31$) and (041) crystal planes is inclined at $\phi_{hkl} = 51.3°$ from the chain axis[5]. The product of the $N(\chi)$ distribution (upper graph) by the second-order Legendre polynomial (*Figure 1A*, middle graph) gives a sum of positive and negative areas, as presented in the bottom graph, and the integral of equation (3) therefore sums to a low value of 0.07. The $\langle P_2\rangle_c$ coefficient, which is then calculated using equation (4), is equal to 0.83, whereas measurements made using the (110), (040), and (130) crystal planes give an average value of $\langle P_2\rangle_c = 0.98$. It should be emphasized that, for reflections located near $\chi = 54.7°$, the $N(\chi)$ $P_2(\cos\chi)$ summation always leads to a low value, whatever the degree of orientation of the sample. For distributions centred around this angle, model calculations have shown that variations of the width or shape of the distributions always give a $\langle P_2\rangle$ value close to zero[13].

When $\langle P_n\rangle$ calculations are conducted on WAXD orientation distributions with high signal-to-noise ratios, the uncertainty on the coefficients is typically of the order of ± 0.02, as can be estimated by comparing results from several crystal planes[4,5,14], or from different characterization methods[15]. For an hkl reflection centred at a $\chi_{\max}$ angle where $P_n(\cos\chi) \sim 0$, the uncertainty is then comparable to the $\langle P_n\rangle_{hkl}$ value. Dividing this coefficient by $P_n(\cos\phi_{hkl})$ (equation (4)), which also has a value close to zero, then gives a $\langle P_n\rangle_c$ value bearing a high relative imprecision. To circumvent this problem, it is possible to conduct the $\langle P_n\rangle_{hkl}$ calculation on a curve generated by a function that fits the experimental orientation distribution. This method, which allows the calculation to be conducted on distributions devoid of any experimental noise, has been shown to give good results in studies of oriented polyethylene and polypropylene, with the $\langle P_n\rangle_c$ coefficients obtained from different (hkl) and $(hk0)$ crystal planes showing a good correlation[5,14].

An alternative method for obtaining reliable $\langle P_n\rangle_c$ coefficients from hkl reflections which are oriented neither parallel nor perpendicular to the reference direction in a sample (i.e. $\chi_{\max} \neq 0$ or 90°) is proposed here. This procedure, which is illustrated in *Figure 1B* for the calculation of the $\langle P_2\rangle$ coefficient, allows the calculation to be made directly with the experimental intensity curve rather than with a fitted curve. It involves a shift of the polynomial curve by an angle δ, in order to fit the polynomial extremum at $(\chi + \delta) = 90°$ with the position $\chi_{\max}$ of the maximum of the orientation distribution curve, $N(\chi)$. In the example given in the middle graph of *Figure 1B*, the second-order polynomial curve has been shifted by $\delta = 38.5°$, so that the

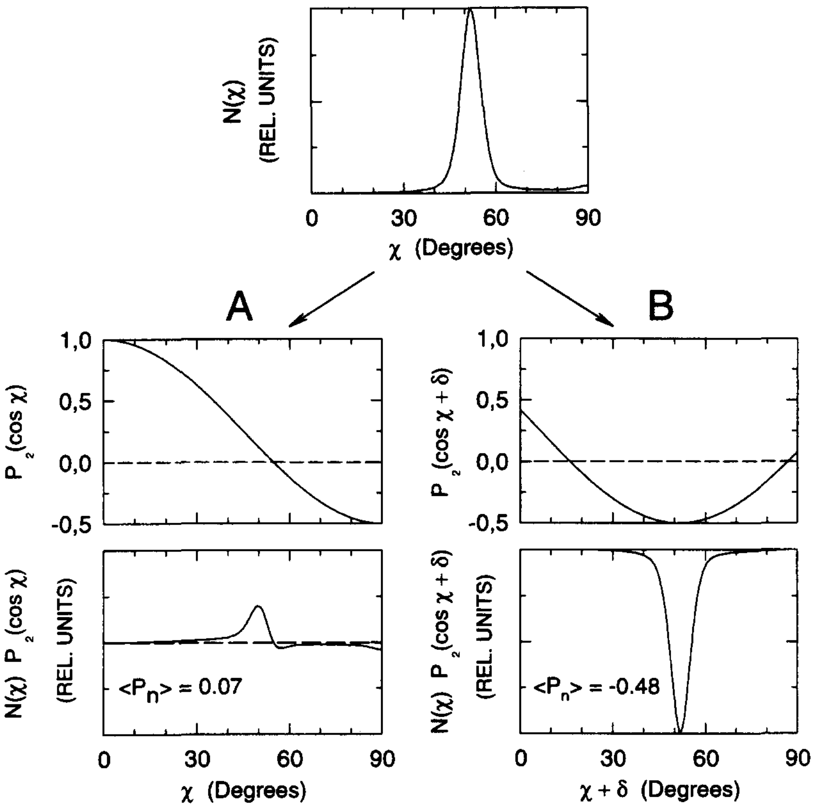

Figure 1 Calculation of the $\langle P_2\rangle$ coefficient for the $\bar{1}31/041$ reflection of $\lambda = 7.6$ roll-drawn isotactic polypropylene sample: (A) regular calculation with the $P_2(\cos\chi)$ polynomial, giving $\langle P_2\rangle = 0.07$ and $\langle P_2\rangle_c = 0.83$; (B) calculation with the shifted $P_2(\cos\chi + \delta)$ polynomial curve ($\delta = 38.5°$), giving $\langle P_2\rangle = -0.48$ and $\langle P_2\rangle_c = 0.96$

$P_2(\cos\chi + \delta)$ minimum coincides with the maximum of the $N(\chi)$ curve at $\chi_{\max} = 51.5°$. As can be observed in the bottom graph of *Figure 1B*, this procedure gives a negative area under the $N(\chi)$ $P_2(\cos\chi + \delta)$ curve, and a $\langle P_2\rangle$ value of -0.48 is then obtained. The correction for the angular shift is made by using $P_2(\cos 90°) = -0.50$ for the denominator of equation (4) ($\chi_{\max} + \delta = 90°$), instead of the value of $P_2(\cos\phi_{hkl})$ with $\phi_{hkl} = 51.3°$. This calculation gives a value of $\langle P_2\rangle_c = 0.96$, which agrees within experimental error with the average coefficient $\langle P_2\rangle_c = 0.98$ obtained from the *hk*0 planes for this sample.

Figure 2 compares the $\langle P_n\rangle_c$ coefficients calculated for *n* up to 40 by the regular (hollow symbols) and by the shifted polynomial (filled symbols) procedures, for the 111, $\bar{1}31/041$ and $022/\bar{1}12$ reflections of two different iPP samples, roll-drawn to $\lambda = 7.6$ and 15.8. It is observed that the coefficients obtained by the shifted polynomial method decrease smoothly with *n*, whereas the $\langle P_n\rangle_c$ values computed by the regular procedure are somewhat scattered on both sides of the former. The coefficients lying further away from the curves in *Figure 2* correspond to polynomials that change sign within a few degrees from the centre of the maximum of the X-ray reflection. For example, the $P_{16}(\cos\chi)$ function goes to zero at $\chi = 19.1°$, and the $\langle P_{16}\rangle_c$ coefficient for the $022/\bar{1}12$ reflection, centred at $\chi_{\max} = 19.5°$, is equal to -0.72 and 1.05 for the $\lambda = 7.6$ and 15.8 samples, respectively, values that are outside the boundaries of the polynomial. The calculation of the $\langle P_2\rangle_c$ and $\langle P_6\rangle_c$ coefficients from the 111 and $\bar{1}31/041$ reflections, centred at $\chi_{\max} = 50.0$ and 51.5°, respectively, similarly gives unreliable results (*Figure 2*), since the second- and sixth-order polynomials are respectively equal to zero at 54.7 and 48.6°.

This is further demonstrated in *Table 1*, which compares the $\langle P_2\rangle_c$ and $\langle P_6\rangle_c$ coefficients obtained from three intense *hk*0 reflections (110, 040 and 130), which are the most often used in orientation studies of iPP, to the coefficients calculated by the regular procedure and to those computed by the shifted polynomial method, for samples drawn to $\lambda = 6.6$ and 8.2. These results show, again, that for the 111 and $\bar{1}31/041$ reflections, the $\langle P_2\rangle_c$ coefficient calculated by

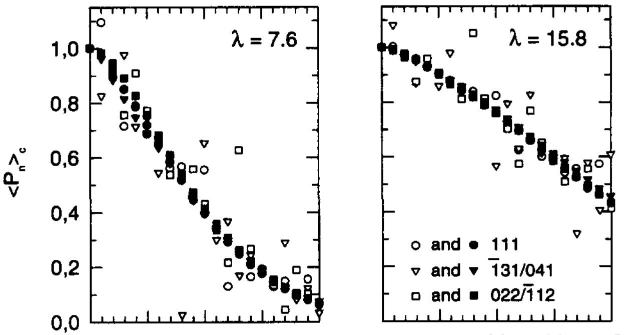

Figure 2 $\langle P_n\rangle_c$ coefficients obtained from the 111 (○ and ●), $\bar{1}31/041$ (▽ and ▼) and $022/\bar{1}12$ (□ and ■) reflections of isotactic polypropylene samples drawn to $\lambda = 7.6$ and 15.8; coefficients obtained by the usual calculation are represented by hollow symbols, while those calculated by the shifted polynomial method are displayed by filled symbols

Table 1 $\langle P_2\rangle_c$ and $\langle P_6\rangle_c$ coefficients calculated for the 111, $\bar{1}31/041$ and $022/\bar{1}12$ reflections, using the regular procedure (R) and the angular shift method (S), and average coefficients obtained from the 110, 040 and 130 reflections (*hk*0 average), for iPP samples drawn to draw ratios λ of 6.6 and 8.2

	$\langle P_2\rangle_c$		$\langle P_6\rangle_c$	
Reflection	6.6	8.2	6.6	8.2
111 (R)	1.42	1.14	0.39	0.75
111 (S)	0.91	0.97	0.61	0.85
$\bar{1}31/041$ (R)	1.15	1.07	0.59	0.78
$\bar{1}31/041$ (S)	0.93	0.97	0.63	0.84
$022/\bar{1}12$ (R)	0.91	0.96	0.34	0.67
$022/\bar{1}12$ (S)	0.93	0.97	0.61	0.84
*hk*0, average	0.90	0.97	0.63	0.85

the regular method do not agree with the average value obtained from the (*hk*0) crystal planes and from the $022/\bar{1}12$ reflection ($\chi_{\max} = 19.5°$). Furthermore, the $\langle P_6\rangle_c$ coefficient computed by the regular procedure for the 111, $\bar{1}31/041$ and $022/\bar{1}12$ reflections are all different from the average value given by the three *hk*0 reflections, since the sixth-order polynomial changes sign near the maximum of these three *hkl* reflections ($P_6(\cos\chi) = 0$ for $\chi = 21.2$, 48.6 and 76.2°).

In contrast, *Table 1* demonstrates that the coefficients calculated for the 111, $\bar{1}31/041$ and $022/\bar{1}12$ crystal planes by the shifted polynomial method are close to the average values obtained from the 110, 040 and 130 reflections. A similar agreement is obtained, within an experimental error of ± 0.02, for the $\langle P_n\rangle_c$ coefficients with $n = 2$ to 40, of eight different iPP samples drawn to values of λ between 6.6 and 15.8 (results not shown). A good correlation was also found for two high-density polyethylene samples ($\lambda = 6$ and 12), by comparing the $\langle P_n\rangle_c$ coefficients obtained from shifted polynomial calculations for the 011 and 211 reflections with the results obtained from the (110), (200), (020) and (002) crystal planes.

These results demonstrate that the angular shift method is applicable to any (*hkl*) crystal planes, for the polynomials that change sign near the $\chi_{\max}$ position of the *hkl* orientation distribution. Since the width and shape of orientation distributions may vary greatly, it is not possible to define an angular interval around the $\chi_{\max}$ position where the regular calculation method fails. Nevertheless, whenever the orientation distribution measured by X-ray diffraction indicates a significant molecular orientation when the $\langle P_n\rangle$ value (equation (2)) is close to zero, it is suggested that the angular shift method be used.

Despite the success of the angular shift method, as indicated above, shifting the polynomial curves by a negative δ value instead of a positive one, in such a manner that the maximum intensity of the orientation distribution $N(\chi)$ coincides with the maximum of the polynomials at $(\chi + \delta) = 0°$, gives coefficients that are higher than those obtained from (*hk*0) planes or from other characterization techniques. This discrepancy is related to the shape of the sine-weighted distribution $N(\chi)$ (equation (3)), which has to show a value of zero at $\chi = 0°$. On the other hand, using a negative δ value, the $P_n(\cos\chi + \delta)$ curves would multiply the maximum value of the $N(\chi)$ distributions at $\chi + \delta = 0°$, which leads to an overestimation of the $\langle P_n\rangle_c$ coefficients.

CONCLUSIONS

When *hkl* crystal reflections are measured by wide-angle X-ray diffraction, it is observed that the calculation of some of the $\langle P_n\rangle_c$ coefficients, which characterize the molecular chain orientation, gives results which disagree with those obtained from *hk*0 reflections. In this present article, it was shown that an agreement between the two sets of values can be reached by shifting angularly the $P_n(\cos\chi)$ polynomial curves for the calculation. Using five different *hkl* reflections of iPP and PE samples drawn to draw ratios between 6 and 16, it was demonstrated that the polynomial shift method gives reliable $\langle P_n\rangle_c$ coefficients for any *hkl* reflection. In particular, this simple calculation procedure allows the use of reflections oriented around the 'magic angle', i.e. $\chi = 54.7°$, to determine the $\langle P_2\rangle_c$ coefficient.

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