polymer communications

Orientation distribution functions for biaxially oriented polymers

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The use of the 'most probable' distribution function previously introduced for the prediction of orientation distribution functions for uniaxially oriented polymers is extended to biaxial polymers. Isometric projections of plots of the functions for model distributions are given, together with the application to a set of experimental data.

Keywords Polymer; orientation; biaxial; poly(ethylene terephthalate); distribution; prediction

Introduction

It has recently been shown[1] that if the values of $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ can be determined for the chain axes in a uniaxially oriented polymer a reasonably reliable prediction of the general form of the whole distribution function $N(\theta)$ can often be made. $N(\theta)d\omega$ is the fraction of chain axes which lie within the small solid angle $d\omega$ at the angle θ to the draw or extrusion direction and $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ are the values of the second and fourth-order Legendre polynomials in $\cos\theta$ averaged over the distribution. The prediction is made by assuming that $N(\theta)$ may be approximated by the 'most probable' distribution function

$$N_{mp}(\theta)=\exp(a_2P_2(\cos\theta)+a_4P_4(\cos\theta)) \qquad (1)$$

where a_2 and a_4 are chosen to give the correct values of $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$. This distribution is the most random distribution which has the correct values for these two averages.

It was shown that this predicted distribution was likely to be quite close to the true distribution for fairly smooth distributions, so that a plot of it gives a better appreciation of the form of the distribution function than the simple knowledge of the values of $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$. These are often the only pieces of information about the distribution which are available directly, since most methods of characterizing molecular orientation cannot give the full distribution function. The X-ray method, which can give the full distribution function, is only readily applicable to the crystalline chains.

The most probable function may also be used as a predictor for biaxially oriented polymers and it is the purpose of this communication to show its usefulness for this purpose by applying it to the results of Jarvis *et al.*[2] for a biaxially oriented poly(ethylene terephthalate) (PET) sheet.

Orientation averages for a biaxially oriented polymer

Jarvis *et al.* have studied a sample of biaxially oriented poly(ethylene terephthalate) using Raman and infra-red spectroscopies and have determined seven parameters P^r_{200}, P^r_{202}, P^r_{220}, P^r_{222}, P^r_{400}, P^r_{420} and P^r_{440} which characterize the distribution of orientations of the *para*disubstituted benzene rings. Axes were chosen in the ring so that the direction parallel to the *para*disubstituted carbon atoms was the Ox_3 axis, with the Ox_1 axis lying in the plane of the ring, and axes were chosen in the sample so that OX_3 was the draw direction and OX_1 was in the plane of the film. The quantities P^r_{200} etc. then refer to the average values of a set of generalized spherical harmonics $P_{lmn}(\theta,\varphi,\psi)$, where the angles θ, φ and ψ relate the orientation of $Ox_1x_2x_3$ to $OX_1X_2X_3$. P^r_{200} and P^r_{400} correspond directly to $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ where θ is the angle between the Ox_3 axis and the OX_3 axis. The remaining angles are defined in ref 2, which also gives the full definitions of the $P_{lmn}(\theta,\varphi,\psi)$. It is only necessary to point out here that if there is no preferred orientation around the Ox_3 axis, $P^r_{lmn}=0$ unless $n=0$ and if there is no preferred orientation around OX_3, $P_{lmn}=0$ unless $m=0$. Although there was no reason to believe that P^r_{402}, P^r_{404}, P^r_{422}, P^r_{424}, P^r_{442}, P^r_{444} were zero, it was not possible to determine them experimentally.

In the discussion of the results in ref 2, greatest use was made of the values of P^r_{2mn}. They were used to calculate values of $\langle\cos^2(x_iX_j)\rangle$ which showed that, on average, the chain axes were more highly oriented towards the draw direction the closer they lay to the plane of the sheet, and that the planes of the benzene rings were preferentially oriented towards the plane of the sheet. From the values of the P^r_{4mO} it was only possible to conclude that there was a tendency for the projections of the Ox_3 directions on the OX_1X_2 plane to be near to $\pm45°$ to OX_1 or OX_2 rather than near to either OX_1 or OX_2.

The most probable distribution function

In order to make such descriptions more precise, we assume that the best prediction for any distribution function when some of the P_{lmn} are known is the 'most probable' function

$$N_{mp}(\theta,\varphi,\psi)=\exp(\Sigma\alpha_{lmn}P_{lmn}(\theta,\varphi,\psi)) \qquad (2)$$

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where the sum extends over all *lmn* for which the $\langle P_{lmn}(\theta,\varphi,\psi)\rangle$ are known, and the α_{lmn} must be chosen so that these values are given correctly. (We have dropped the superscript *r* on the P_{lmn}, since we are now generalizing to any set of axes fixed in a polymer chain.)

Computer programs have been written to calculate the values of α_{lmn} and to allow some aspects of the function N_{mp} to be displayed graphically for any set of values of *lmn* for $l=2$ or 4. The form of graphical presentation chosen was first to display the distribution of orientations of the Ox_3 axes as a function of θ and φ (integration being performed over all values of ψ for a given θ and φ if the value of any P_{lmn} for $n\neq 0$ is known) and secondly to display the distribution of the Ox_2 axes as functions of θ', φ', where θ' and φ' are polar and azimuthal angles with respect to axes $OX'_1X'_2X'_3$ with $OX'_1 \equiv OX_3$, $OX'_2 \equiv OX_1$ and $OX'_3 \equiv OX_2$ (integration being now performed over all ψ' if necessary). In terms of the axes defined in the benzene ring, these two displays correspond to a plot of the C_1–C_4 direction in the ring with the draw direction as reference axis and to a plot of the normal to the benzene ring with the normal to the plane of the sheet as reference axis.

The plots are displayed as isometric projections of the function $N(\theta,\varphi)$ or $N(\theta',\varphi')$ plotted as the *z* coordinate in a set of cylindrical polar coordinates z,θ,φ (or z,θ',φ'). The direction of the axes $OX_1X_2X_3$ are shown on each display. A vertical section through each plot represents a plot of $N(\theta.\varphi)$ against θ for fixed φ, and for a uniaxially oriented sample with no preferred orientation around Ox_3 any such section of the first plot would be identical to a plot of $N(\theta)$ against θ of the type shown in *Figures 3–6* of ref 1. Note that for convenience in plotting, all functions have been normalized so that their greatest values are the same.

To accustom the reader to these forms of display we first show in *Figure 1* the two isometric plots for the most probable distribution corresponding to the simplest type of uniaxial polymer for $P_{200}=0.5$, $P_{400}=0.4$, and all other $P_{lmn}=0$, values which correspond to curve (b) of *Figure 4* of ref 1. The Ox_3 axis is assumed parallel to the chain axis and the Ox_2 axis is any *specified* direction in the chain which is normal to it. Note that in *Figure 1a* the height of the surface above the OX_1X_2 plane at the 'edge' of the plot represents the value of the function at $\theta=\pi/2$, i.e. normal to the draw direction, and similar remarks apply to *Figure 1b*. The fact that the height of the surface in *Figure 1b* is constant in the OX_1X_2 plane is a direct reflection of the uniaxial nature of the distribution. The small peak near the Ox_3 axis in this plot is a consequence of the relatively large number of chains which point normal to OX_3 when all angles φ are considered. The values of α_{200} and α_{400} for these plots are 1.203 and 2.016, respectively.

Secondly we show, in *Figure 2*, the isometric plots for a biaxially oriented polymer assuming that the distribution of orientations is exactly that predicted on the basis of the pseudo-affine deformation scheme[3]. For this scheme the chains orient (but do not extend) exactly as would the end-to-end vectors of the chains in a rubber which deforms affinely, i.e. so that each component of the end-to-end vector is multiplied by the corresponding draw ratio on drawing, and the product of the three draw ratios λ_1, λ_2 and λ_3 is assumed to be equal to unity. The Ox_3 axis is again the chain axis and the Ox_2 axis any *specified*

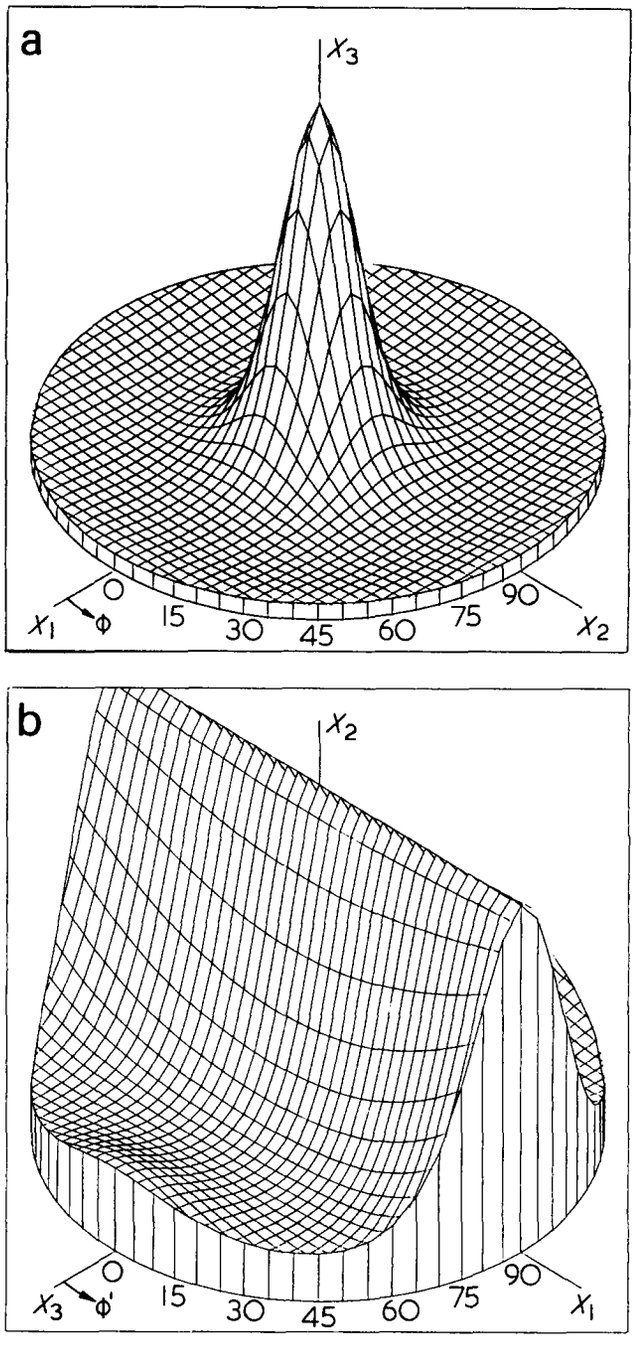

Figure 1 Uniaxial distribution. $P_{200}=0.5$, $P_{400}=0.4$, all remaining P_{lmn} = zero. Prediction of distribution function from equation (2). (a) Distribution of chain axes (b) distribution of specified normals to chain axes

direction in the chain which is normal to it. The draw ratios which correspond to *Figure 2* are $\lambda_1=1.0$, $\lambda_2=0.5$, $\lambda_3=2.0$ which are those for a sheet drawn to draw ratio 2.0 at constant width. *Figure 2b* illustrates the important fact that although there is no specific mechanism giving rise to preferred orientation of the Ox_2 axis with respect to the plane of the sheet, the probability that the Ox_2 axis is normal to the sheet (OX_2) is greater than the probability that it is parallel to the OX_1 direction. This latter probability is, as expected, greater than the probability that it lies in the OX_3 direction, i.e. parallel to the draw direction. It is, however, important to note that these statements would apply to *any* specified direction in the chain which lies normal to the chain axis.

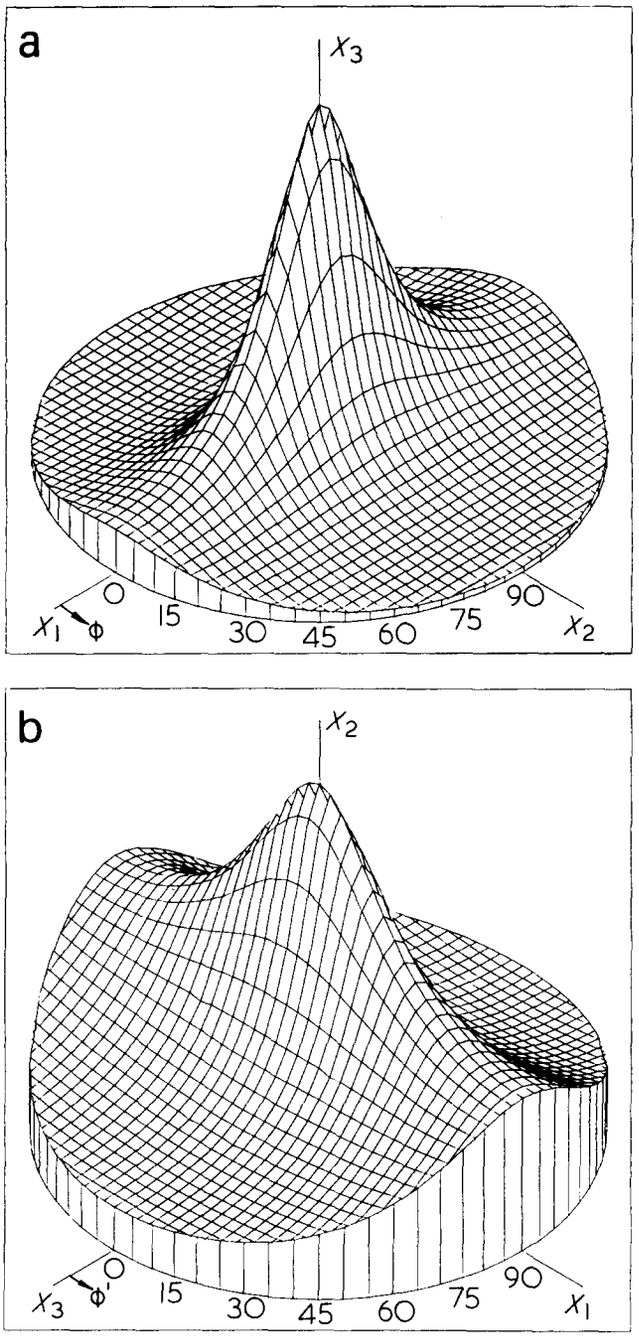

Figure 2 Pseudo-affine distribution. Exact function for biaxial orientation with draw ratios 1.0, 0.5, 2.0. (a) Distribution of chain axes (b) distribution of specified normals to chain axes

Figure 3 shows plots for the same pseudo-affine distribution according to the prediction of the most probable distribution, equation (2), truncated at $l=4$. The plots of *Figure 3* were made by first calculating the values of P_{200}, P_{220}, P_{400}, P_{420} and P_{440} from the exact distribution $N(\theta)$, e.g.

$$P_{200} = 2\pi \int_0^{\pi} P_{200}(\cos\theta) N(\theta) \sin\theta \, d\theta$$

$$= \pi \int_0^{\pi} (3\cos^2\theta - 1) N(\theta) \sin\theta \, d\theta \qquad (3)$$

It was assumed, as indicated in the previous paragraph, that no preferred orientation around Ox_3 arises in this model, so that $P_{lmn}=0$ for $n \neq 0$. Values of α_{200}, α_{220}, α_{400}, α_{420} and α_{440} were then calculated so that the function $N_{mp}(\theta,\varphi,\psi)$ given by equation (2), assuming only these values of α_{lmn} to be non-zero, gave the same values for P_{200}, P_{220}, P_{400}, P_{420} and P_{440} as did the exact distribution when used in equations of the type of equation (3). *Table 1* shows the values of P_{lm0} and the corresponding values of α_{lm0}. The fact that *Figures 2* and *3* are very similar shows that at least for this type of smooth distribution, equation (2) is a good predictor even when l extends only up to 4.

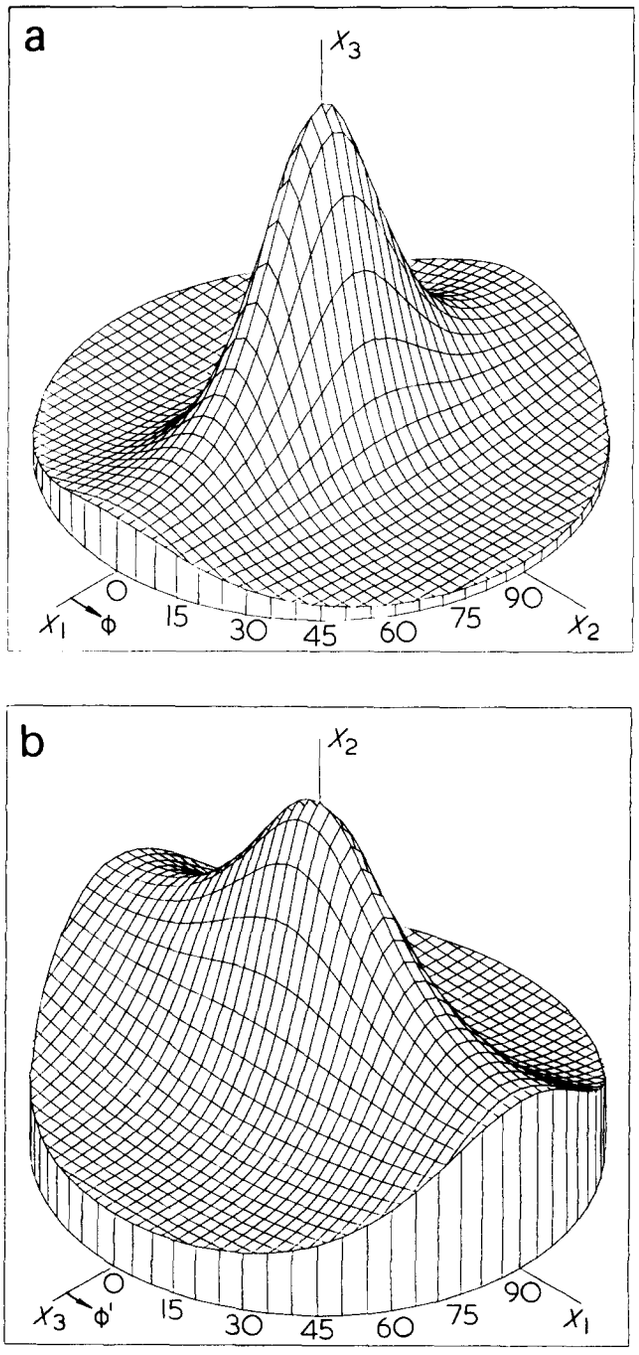

Figure 3 Pseudo-affine distribution. Prediction of distribution function from equation (2) given P_{lmn} values for $l=2$ and 4 calculated from the exact function shown in *Figure 2*. (a) Distribution of chain axes (b) distribution of specified normals to chain axis

Table 1 Calculated values of P_{lm0} and α_{lm0} for pseudo-affine model with $\lambda_1 = 1.0$, $\lambda_2 = 0.5$, $\lambda_3 = 2.0$

lm	P_{lm0}	α_{lm0}
20	0.404	1.616
22	0.043	4.828
40	0.189	0.807
42	0.007	8.854
44	0.003	3.452

Table 2 Experimental values of P_{lmn} for 3.5 : 1 one way drawn sheet[2]

lmn	P_{lmn}	α_{lmn}
200	0.25 ± 0.03	1.193
202	0.03 ± 0.01	3.052
220	−0.013 ± 0.006	−1.881
222	0.07 ± 0.02	1.212
400	0.10 ± 0.05	0.361
420	−0.003 ± 0.004	−4.753
440	−0.007 ± 0.003	−15.198

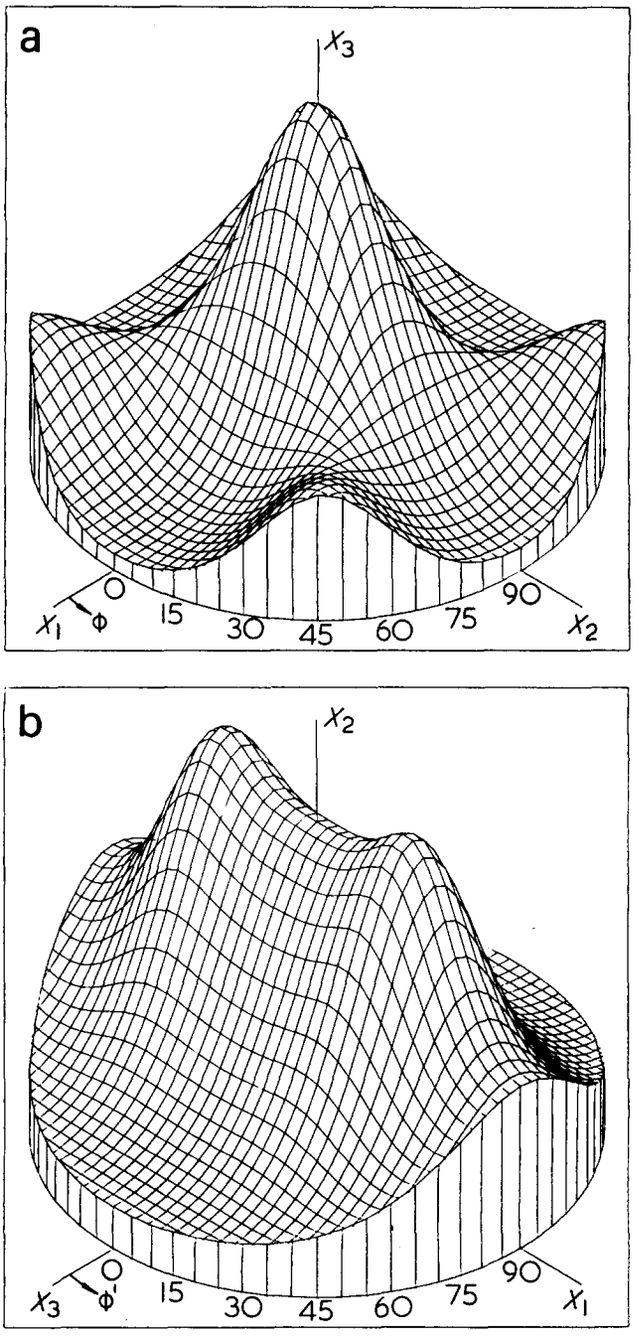

Figure 4 3.5 : 1 one-way drawn PET sheet. Prediction of distribution function from equation (2) and values of P^r_{lmn} given in *Table 1*. (a) Distribution of C_1–C_4 directions in *para*disubstituted benzene rings (b) distribution of ring normals

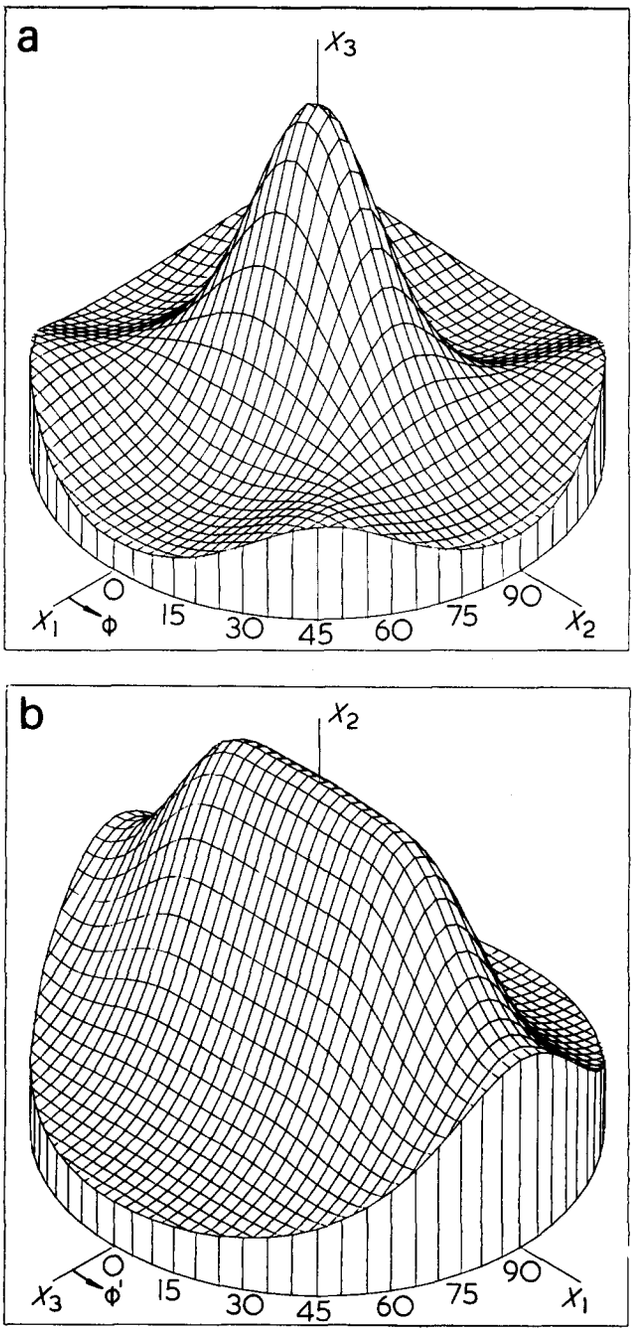

Figure 5 As *Figure 4* except that P_{440} was reduced to −0.004

Application to experimental data

Figure 4 shows plots for the benzene rings in the 3.5:1 one-way drawn sheet of Jarvis *et al.* calculated from the data shown in *Table 2*, which also shows the corresponding values of α_{lmn}. The small minimum in the OX_2 direction in *Figure 4b* is mainly a consequence of the large negative value of P_{440}. Reduction of this from −0.007 to −0.004, which is within the experimental uncertainty, leads to the plots shown in *Figure 5*, where the minimum has disappeared. The maxima near ±45° to OX_1 and OX_2 in *Figure 4a* have also been

substantially reduced in *Figure 5a*. *Figures 4a* or *5a* show that the Ox_3 direction is only slightly more likely to lie near the OX_3X_2 plane than the OX_3X_1 plane, with a greater probability of lying in planes nearly at 45° to these two planes.

Even the original 'best' values of the P_{lmn} clearly indicate preferential orientation of the benzene ring planes towards the plane of the sheet, as can be seen by comparing *Figure 6* with *Figure 4b*. *Figure 6* is plotted from the same data as *Figure 4b* with the exception that the signs of P_{202} and P_{222} have been reversed. This is equivalent to showing a polar plot of the distribution of Ox_2 axes (which lie in the planes of the rings). These axes are clearly oriented preferentially away from the normal to the sheet (OX_2) and preferentially towards OX_1 (normal to the draw direction) rather than OX_3, though this latter preference is not strong.

The data thus suggest that the biaxial nature of the orientation in the 3.5:1 sheet is most clearly shown by the tendency of the ring planes to lie in the plane of the sheet, rather than by the biaxial distribution of chain axes (which are nearly parallel to the Ox_3 directions).

The program which calculates the values of α_{lmn} also calculates those values of the P_{lmn} for $l=4$ which could not be determined experimentally. It is difficult to estimate the accuracies of these values, since they depend on both the accuracies of the experimental data and how accurately the most probable distribution agrees with the true distribution. It is hoped, however, that such data may contribute to an understanding of the mechanical compliances of a series of biaxially oriented sheets which are now being studied.

Conclusions

The most 'probable function' defined by equation (2) is useful in interpreting the values of the orientation parameters P_{lmn} which may be obtained by spectroscopic techniques for a biaxially oriented polymer. It also allows estimates to be made of some further orientation parameters which are so far difficult to determine directly.

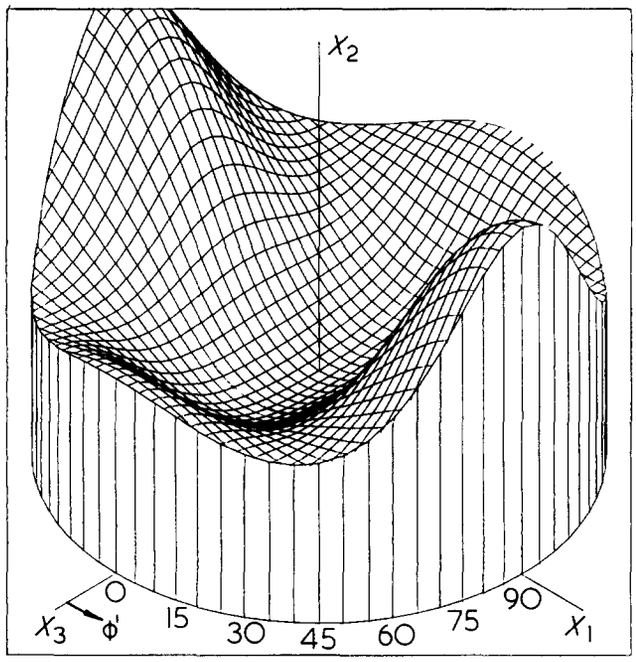

Figure 6 As *Figure 4b* except that the signs of P_{202} and P_{222} are reversed. This is equivalent to a plot of the distribution of the directions Ox_1 which lie in the ring plane normal to the C_1-C_4 direction

References

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