The determination of molecular orientation in uniaxially compressed PMMA by X-ray scattering

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(Received 7 *May* 1982; *revised* 5 *July* 1982*)*

A procedure is presented for obtaining full molecular orientation information from wide angle X-ray scattering patterns of deformed non-crystalline polymers. The method is based on the analysis of experimental and calculated scattering patterns into their spherical harmonics. The results obtained for PMMA are compared with values predicted by the pseudo affine and affine deformation schemes.

Keywords Molecular orientation; X-ray scattering; poly(methyl methacrylate); orientation models; orientation distribution function; orientation measurement

INTRODUCTION

Preferred orientation of the molecular segments in a polymer has a marked influence on mechanical properties, and thus on the utility of the material. The degree of preferred orientation (generally referred to simply as 'orientation') is largely determined by processing history. Its measurement is important not only to the understanding of materials' properties, but also in studies of the deformation process itself where plots of the degree of orientation against mechanical strain can give some indication of the type of mechanisms which operate. Not surprisingly considerable effort has been devoted to the development of physical techniques to measure orientation[1-6].

Where interest is centred on the orientations of polymer crystallites, X-ray diffraction is an appropriate method, supported as necessary by various spectroscopic techniques. Wide-angle X-ray scattering can give, in principle, full information about the distribution of molecular axes within the crystalline component, whereas small angle diffraction provides some indication of preferred orientation in the shape and local arrangement of the crystallites themselves. In the case of polymer glasses or rubbers, the interpretation of X-ray scattering, which is much more diffuse, is rather more complicated. Thus techniques such as birefringence, nuclear magnetic resonance, infra-red and Raman spectroscopy have been developed and widely applied despite their intrinsic limitation that they give only the second harmonic component of the orientation distribution although both n.m.r. and Raman spectroscopy may provide the fourth harmonic.

In a recent paper[6] the orientation introduced in atactic poly(methylmethacrylate) (PMMA) by deformation has been analysed by its effect on the wide angle X-ray scattering pattern, and the derived molecular orientation compared with spectroscopic measurements made the same specimen. The agreement was encouraging despite approximations made in both the X-ray and spectroscopic methods. However, the application of spherical harmonic analysis to the diffraction pattern, using relations derived by Deas[7] and developed by Ruland and Tompa[8] and Mitchell and Lovell[9] has enabled the X-ray method to be refined to the point where its accuracy and reliability are comparable with and perhaps surpass the spectroscopic techniques, while its intrinsic advantages are maintained. These are seen as the fact that higher harmonics are in principle accessible, and that one can be certain that the orienting unit which is being measured is a reasonably representative segment of the molecular chain itself, and not for example a highly polar pendant group.

The method described in this paper is illustrated in its application to the measurement of orientation in a-PMMA uniaxially compressed at 20°C. It is, of course, generally applicable.

HARMONIC COMPONENTS OF THE ORIENTATION FUNCTIONS

The polymer is seen as containing 'orienting units' to each of which is assigned a unique set of axes or directors. For uniaxial orientation of non-crystalline materials only one director is necessary and this is implicitly related to the chain axis. Such an approach is the basis of the aggregate model discussed by Ward[10]. The probability distribution of the orientation of the directors in space can be described in polar coordinates and viewed as a surface with uniaxial and inversion symmetry. The probability distribution (or the shape of the solid of revolution) can be described as a series of harmonic functions which are orthogonal. They are expressed in terms of $\cos\alpha$ where α is the angle between the director of the orienting unit and the unique axis of the specimen.

The form of the harmonic components is given in *Table 1*. If the magnitude of the components $\langle P_{2n}(\cos\alpha)\rangle$ is known, for instance from experiment, the full orientation distribution $D(\alpha)$ may be reconstituted by a weighted summation:

0032—3861/83/030285–06$03.00

Table 1 Form of the harmonic components

n	$P_{2n}(\cos\alpha)$
0	$P_0(\cos\alpha) = 1$
1	$P_2(\cos\alpha) = (3\cos^2\alpha - 1)/2$
2	$P_4(\cos\alpha) = (35\cos^4\alpha - 30\cos^2\alpha + 3)/8$
3	$P_6(\cos\alpha = (231\cos^6\alpha - 315\cos^4\alpha + 105\cos^2\alpha - 5)/16$

$$D(\alpha) = \sum_{n=0}^{\infty} (4n+1)\langle P_{2n}(\cos\alpha)\rangle P_{2n}(\cos\alpha) \qquad (1)$$

Correspondingly, the full distribution can be analysed into its harmonics by applying the relationship for the amplitude of the harmonics

$$\langle P_{2n}(\cos\alpha)\rangle = \int_0^{\pi/2} D(\alpha)P_{2n}(\cos\alpha)\sin\alpha\,d\alpha \qquad (2)$$

The use of harmonic components to describe the orientation of polymers is well established and dates from the work of McBrierty and Ward[11].

DEVELOPMENT

Application of convolution theorem

We have seen that the orientation distribution of molecular axes, or in general some molecularly defined director, can be defined in terms of spherical harmonics which are in the form of Legendre polynomials. Deas[7] recognized that the diffraction pattern of an oriented material could be similarly expressed in terms of spherical harmonics. For a particular magnitude of the scattering vector $s\,(s = 4\pi\sin\theta/\lambda)$ that is at a fixed Bragg angle, the variation of scattering intensity with orientation of the sample $I(\alpha)$ will be described by spherical harmonics given by an equation similar to (2). However in this case normalization is necessary following from the definition of $D(\alpha)$ as $\int_0^{\pi/2} D(\alpha)\sin\alpha\,d\alpha = 1/2\pi$. Hence the spherical harmonics are given by:

$$\langle P_{2n}(\cos\alpha)\rangle_I = \frac{\int_0^{\pi/2} I(\alpha)P_2(\cos\alpha)\sin\alpha\,d\alpha}{\int_0^{\pi/2} I(\alpha)\sin\alpha\,d\alpha} \qquad (3)$$

The fact that only even order harmonics are necessary is a consequence of the cylindrical and inversion symmetry of $D(\alpha)$ and $I(\alpha)$ when they are generated as a result of uniaxial deformation.

The orientation in the X-ray pattern $I(\alpha)$, which is the experimentally measurable function, can be considered to be the consequences of smearing or convoluting the scattering which would be associated with a single orienting unit with the orientation function $D(\alpha)$. If the single unit scattering is designated $I_u(\alpha)$ then:

$$I(\alpha) = I_u(\alpha) * D(\alpha) \qquad (4)$$

If these three orientation functions are expressed in terms of their spherical harmonics, then by the convolution theorem the coefficients of the harmonics are related by[7,12]:

$$\langle P_{2n}(\cos\alpha)\rangle_I = \langle P_{2n}(\cos\alpha)\rangle_{Iu} \cdot \langle P_{2n}(\cos\alpha)\rangle_D$$

Thus, if the scattering from a single oriented unit is known, the harmonic coefficients of the orientation function $D(\alpha)$ follow as a series of quotients. The full orientation function $D(\alpha)$ can thus, in principle, be synthesized from its harmonics using equation (1).

Scattering from an orienting unit

If it were possible to obtain completely oriented samples of the polymer, then the scattering from such could serve as the source of $I_u(\alpha)$ and the consequent harmonic coefficients. However for non-crystalline polymers it does not seem possible to even approach complete uniaxial orientation, no matter how extreme the extension. The only practicable route is to find the local molecular conformation and calculate the scattering from it. The conformation of a-PMMA has recently been determined by analysis of wide-angle X-ray scattering from unoriented samples[13,14]. The method employed qualitative information from oriented samples, and the resultant conformation was consistent with that predicted from conformational energy calculations and small-angle neutron scattering. A structural model which does not include interchain packing can of course only generate part of the scattering pattern, however with most non-crystalline polymers it seems that the intermolecular (packing) information is confined to scattering vectors at values of $s < 1.5\,\text{Å}^{-1}$. Hence a single chain model is able to generate a satisfactory pattern at higher scattering vectors.

The degree to which the coefficients of the spherical harmonics of $D(\alpha)$ remain independent of s, is itself a sensitive test of the correctness of this aspect of the conformational model used, and harmonics have been recently exploited as a means of model refinement for i-PMMA[15].

It is not the intention to discuss here the application of such procedures to a-PMMA, and the model used for the conformation of a-PMMA is based largely on scattering information from unoriented samples[13,14]. However, preliminary calculations suggest, using the refinement techniques referred to above, that an all-*trans* chain may be preferred to the near all-*trans* chain derived in references 13 and 14. Thus we shall take as our model an all-*trans* sequence with valence angles of 110°, 128°. It is appropriate to note that the values of $\langle P_{2n}(\cos\alpha)\rangle_{Iu}$ obtained for conformations at or close to the all-*trans* sequences are similar, and that since these 'correction factors' are independent of strain the shape of the orientation *versus* strain curves will be unchanged by such minor variations in these factors.

RESULTS FOR PMMA

The harmonic description of the calculated scattering from an oriented unit

The scattering calculated from a single chain model in the established conformation is presented as a two-

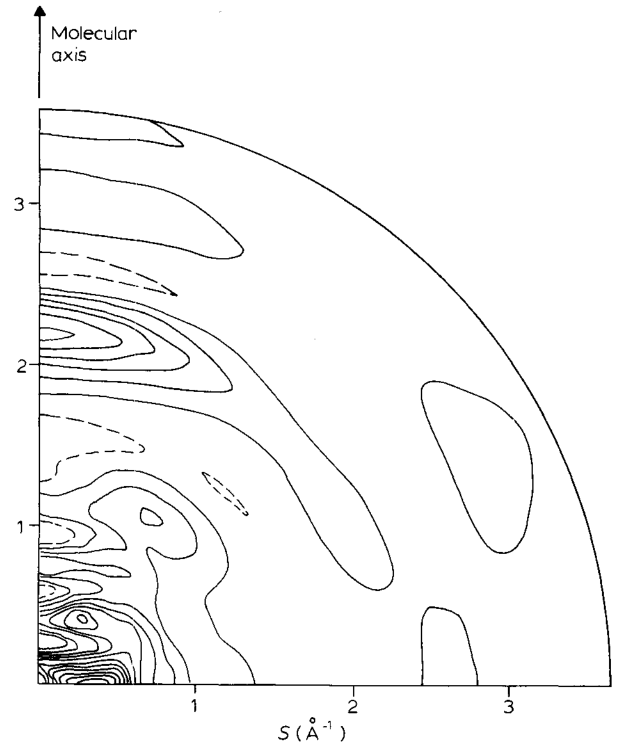

Figure 1 Scattering expressed as an s weighted reduced intensity function $si(s, \alpha)$ calculated from a single chain model (10 repeat units) of s-PMMA in the conformation of 0°, 0°, 0°, 0° (skeletal bond rotation angles) and 110°, 128° (skeletal bond valence angles). The molecular axis is set vertical. Broken contours represent negative values

dimensional reduced intensity function in *Figure 1*. It was generated using the procedures described in ref. 15. The intensity increase close to the origin results from the finite size of the model, but since we only consider scattering vectors >1.5 Å^{-1} it need not concern us. The calculation has been made for the syndiotactic molecule, however it has been pointed out[15] that the WAXS patterns from PMMA glasses are only slightly affected by tacticity across the range from isotactic to syndiotactic and the pattern from the atactic material which contains 80% racemic dyads[16,17] is indistinguishable from that of the syndiotactic glass[13].

Figure 2 shows the coefficients of different orders of the spherical harmonics $\langle P_{2n}(\cos\alpha)\rangle_{Iu}$ plotted as a function of the scattering vector s. The zero order curve is the scattering function which would correspond to an assembly of unoriented and uncorrelated units. In fact the conformational model used was principally selected by comparing such a function with experimentally determined scattering functions for unoriented samples.

The second curve for $n=1$, that is $\langle P_2(\cos\alpha)\rangle_{Iu}$ is positive for values of s where the intensity is concentrated on the meridian. The fact that it is mainly positive even in the region of the interchain peak in the experimental scattering results from the ommission of interchain correlations in the scattering calculations. Such correlations lead to equatorial scattering and hence negative values for $\langle P_2(\cos\alpha)\rangle$ in the lower s range. The peaks at $s=2.1$ Å^{-1} and 3 Å^{-1} confirm the meridional character of both these maxima which is echoed by the higher harmonics.

Spherical harmonics of experimental scattering function

The experimental two-dimensional scattering pattern from a-PMMA extruded at 100°C to a draw ratio of 3:1 is shown in *Figure 3*. It is expressed as a reduced intensity function $si(s,\alpha)$. The data were collected using a symmetrical transmission diffractometer equipped with an Eulerian cradle[15] to rotate the specimen in its own plane. Application of equation (3) to the intensity function in *Figure 3* generated the coefficients of the experimental spherical harmonics, $\langle P_{2n}(\cos\alpha)\rangle_I$, which are drawn as a function of s in *Figure 4*. These curves can be compared with those from the model in *Figure 2*. The experimental data contains, not surprisingly, interchain as well as intrachain information and there is thus a substantial peak at $s=1.1$ Å^{-1} which corresponds to a negative maximum in $P_2(\cos\alpha)$ as befits its equatorial character. However this equatorial peak represents the upper s limit of the equatorial information[18] and so comparisons between model and experimental harmonic coefficients appear valid for values of s greater than about $s=1.5$ Å^{-1}.

Equation (5) indicates that the ratio of the model and experimental coefficients should be constant for a particular harmonic or n value, this ratio being the corresponding coefficient of the derived distribution

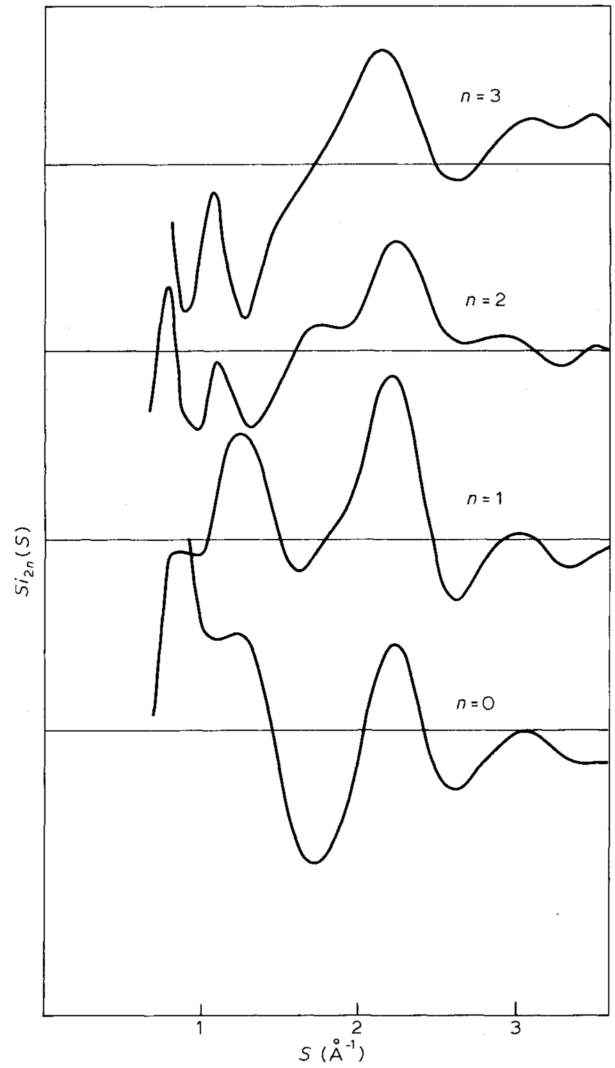

Figure 2 Plots of the amplitudes of spherical harmonics of the calculated intensity function (*Figure 1*)

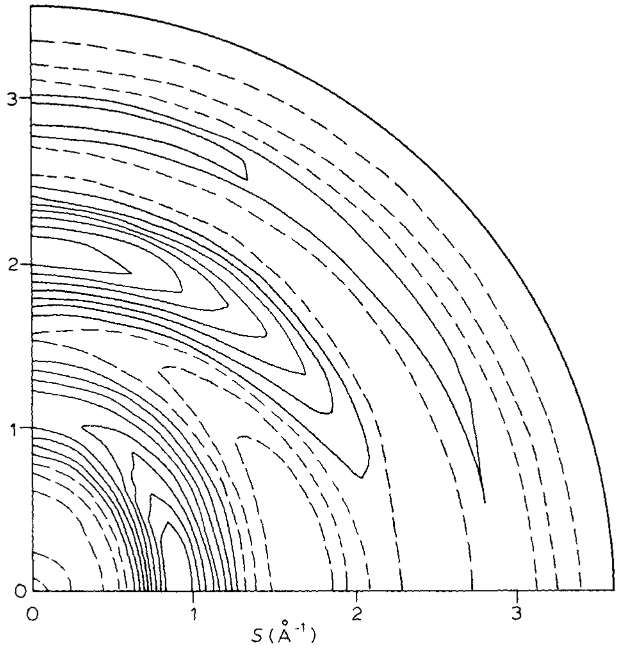

Figure 3 s weighted reduced intensity function $si(s, \alpha)$ for a-PMMA extruded at 100°C to a draw ratio of 3 : 1. The extrusion axis is vertical

function. It thus implies that, for example, the $n=1$ curves of *Figures 2* and *4* should have identical forms, at least above $s=1.5$ Å^{-1}. Comparison shows a clear similarity in shape, but the actual value of the ratio is obviously not independent of s. The scatter of the ratio will be particularly severe where both curves cross the zero axis, so although averaging routines could no doubt be applied which take into account data over a wide range of s, we have chosen to calculate the ratio at the most intense meridional maximum that at $s=2.1$ Å^{-1}. The greatest disparity between the calculated and experimental curve is for $s \sim 1.5$ Å^{-1}. In this region there is some interchain contribution to the scattering and so this conflict should not be taken as evidence against the preferred conformation.

Probably the most difficult step in the analysis of the oriented data is the scaling and reduction of the original intensity plot to give the reduced intensity function $i(s,\alpha)$:

$$i(s,\alpha)=kI(s,\alpha)-\sum_i f_i^2(s)-I\mathrm{comp}(s) \qquad (6)$$

where I is the corrected experimental intensity, k the scaling factor, $\sum_i f_i^2(s)$ the independent scattering from one unit of composition and $I\mathrm{comp}(s)$ the incoherent Compton scattering. The latter component can either be removed experimentally[19] or by scaling with $\sum_i f_i^2(s)$. For the determination of local conformation by comparison of the experimental scattering and that calculated for models for both aligned and unoriented samples, such scaling and reduction is necessary and must be carried through with considerable care. However equation (6) is based on the reasonable assumption that both $f(s)$ and $I\mathrm{comp}(s)$ are isotropic. Hence they have no influence on $\langle P_2(\cos\alpha)\rangle^I$ and higher orders of the spherical harmonics of the scattering, these values of course having been appropriately normalized at all values of s, equation (3). Thus it is possible to determine the harmonics of the orientation function directly from the ratio between the $\langle P_{2n}(\cos\alpha)\rangle$ values from the as-recorded unreduced intensity and the corresponding values from the model scattering. The factors calculated for the scattering vector of 2.1 Å^{-1} used in this work are $\langle P_2 \cos\alpha\rangle_{Iu}=0.2$ and $\langle P_4 \cos\alpha\rangle_{Iu}=0.07$.

These simplified procedures have been adopted in the calculation of the orientation components recorded in the next section.

Strain induced orientation of PMMA molecules

Figure 5 shows the values of the coefficient of the spherical harmonics $\langle P_{2n}(\cos\alpha)\rangle$ and $\langle P_4(\cos\alpha)\rangle$ of the orientation function measured from PMMA specimens deformed in uniaxial compression to different strains at 20°C. Higher harmonics were calculated, but they were of very low magnitude and the precision of the data was not sufficient to ensure their reliability.

The choice of a uniaxial geometry was influenced by the readiness with which the results could be compared with the prediction of theories, while compression was preferable to tension in that relatively high uniform plastic strains could be readily achieved without the complications of plastic instability. The consequence of increasing compressive strain was to render $\langle P_2(\cos\alpha)\rangle$ increasingly negative, and $\langle P_4(\cos\alpha)\rangle$ to a lesser extent

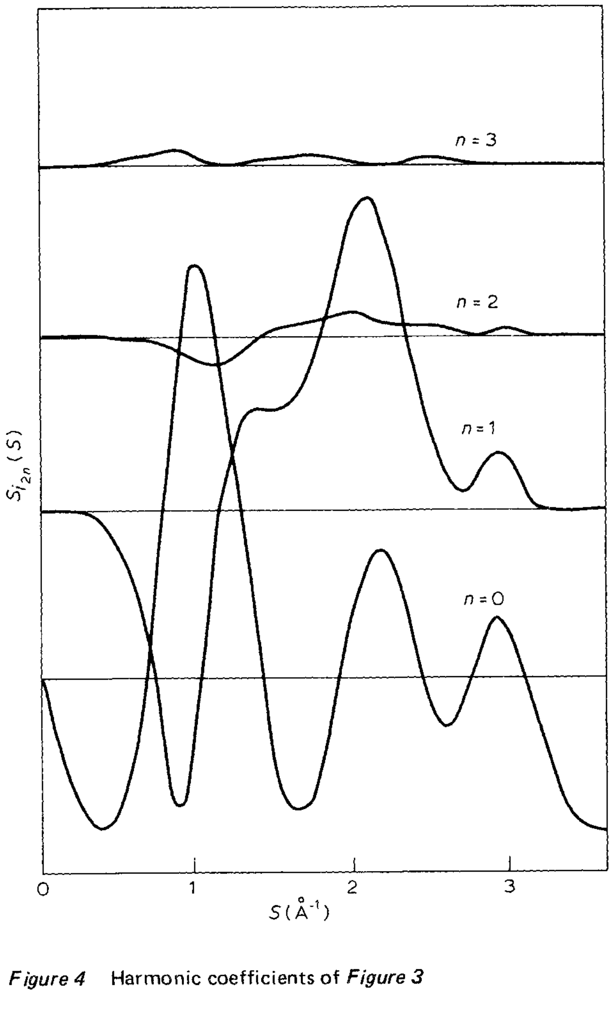

Figure 4 Harmonic coefficients of *Figure 3*

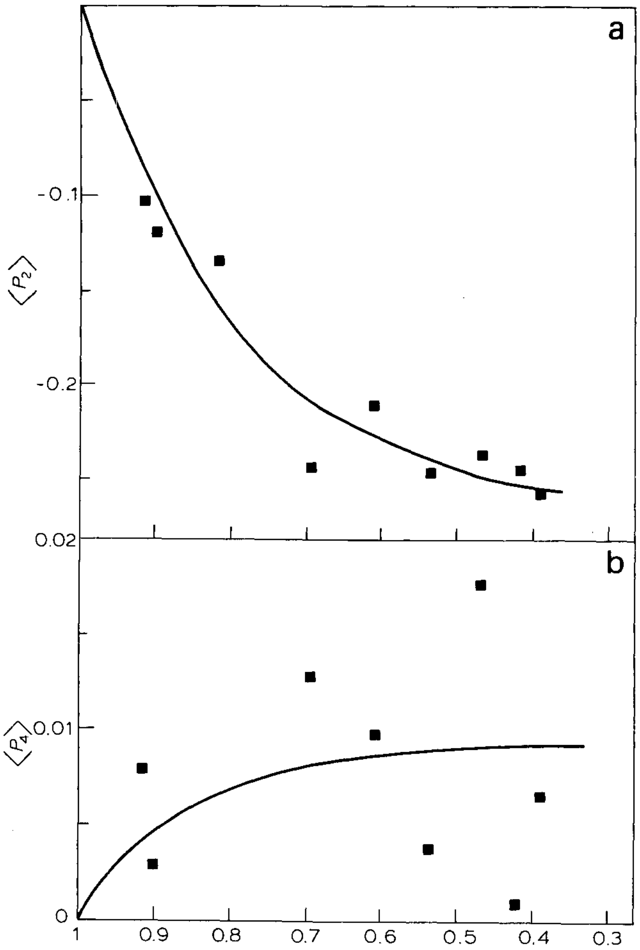

Figure 5 Plots of the coefficients (a) $\langle P_2 \rangle$ and (b) $\langle P_4 \rangle$ of the orientation function, of PMMA against the strain ratio. The specimens were uniaxially compressed at 20°C. The line represents a reasonable fit to the data points

increasingly positive. The maximum recorded values for the harmonic components of the orientation function were -0.25 and around $+0.015$ for $\langle P_2(\cos\alpha) \rangle$ and $\langle P_4(\cos\alpha) \rangle$ respectively. For perfect planar orientation where all the molecules are assumed to be normal to the compression axis, the limiting values of P_2 and P_4 are -0.500 and $+0.375$. It is therefore apparent that even for compression ratios of 0.385 the highest strain obtained at room temperatures, the state of perfect planar orientation is not even approached and judging by the flattening of both $\langle P_2(\cos\alpha) \rangle$ and $\langle P_4(\cos\alpha) \rangle$ curves with strain is unlikely to be obtained.

PREDICTED ORIENTATION/STRAIN BEHAVIOUR

The next step is to compare the development of orientation on deformation with possible molecular models. It is generally recognized that there are two limiting models in the field. The pseudo-affine model, due originally to Kratky[20], is based on an assemblage of orienting units which rotate towards the extension axis in the same manner as lines joining points marked on the bulk material but without the units increasing their length. The model has no adjustable parameters. At the other extreme we have chosen to compare the data with the orientaton predictions of the random chain model, calculated using Treloar's expansion of the inverse Langevin function[21,22]. The model used is affine and can be considered as representing the convolution of the pseudo-affine orientation function, with the orientation distribution of chain units about the chain end to end vector. The random chain function also depends on the number of orienting units in the segments between crosslinks, n, and calculations are made for different values of this parameter.

Figures 6a and *6b* show the comparison for $\langle P_2(\cos\alpha) \rangle$ and $\langle P_4(\cos\alpha) \rangle$ respectively. At low strain ratios that is, $\lambda = 1.0$ to 0.9, the pseudo-affine model appears to predict the development of orientation fairly successfully in terms of $\langle P_2 \rangle$. At larger strain ratios (0.9 to 0.4) the pseudo-affine model gives orientation functions much higher than those observed. The random chain model generates, for what might be taken as a reasonable value of n between 10 and 100, values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ which are too small even at high strains. In fact only the curves for $n < 10$ may be usefully plotted on the same scale as the experimental data (*Figure 6a*, *6b*) and additionally these curves are of totally different shape from that observed. By setting the value of n unrealistically low (the model is only truly valid for large n, i.e. > 10), the $\langle P_{2n} \rangle$ model curve will cross the

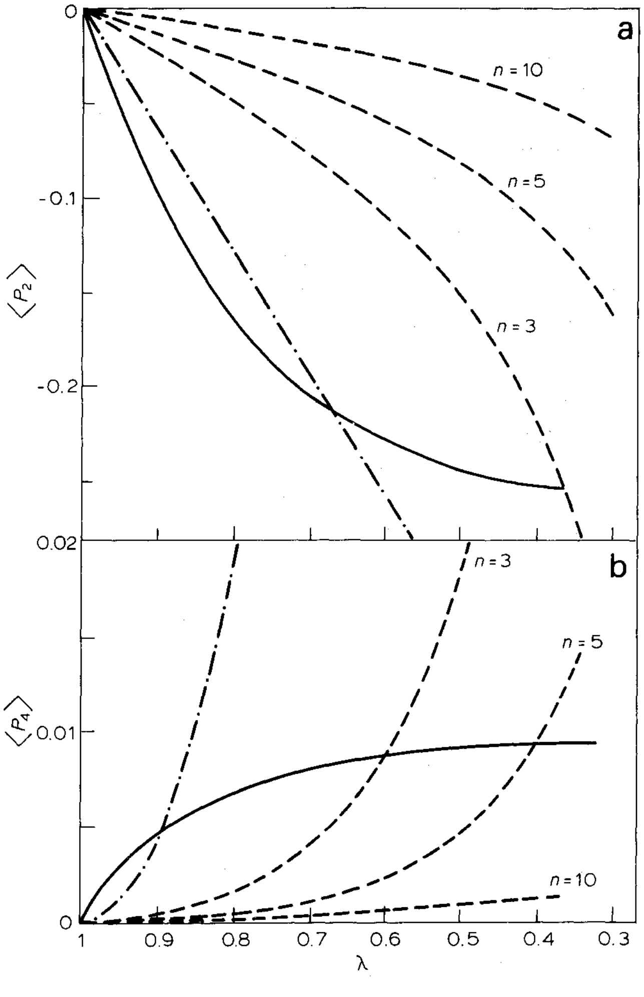

Figure 6 Experimental plots of (a) $\langle P_2 \rangle$ and (b) $\langle P_4 \rangle$ (solid line) against that of *Figure 5* compared with the prediction of the pseudo affine model (—·—·—) and the random chain model (— — — —) for different values of n, the number of chain links per segment

experimental curves at medium to high strains. In essence the random chain model is equivalent in mechanism (but not mathematically) to the pseudo-affine case when $n=1$, which for lower strains is apparent for the increasing similarity of the model curves in *Figure 6* with decreasing n. It is possible[23] to modify the random chain model by calculating values of n which would provide a fit to the $\langle P_2 \rangle$ observed for each particular strain. It is evident from *Figure 6a* that such n values would be extremely low and it is not profitable to proceed further with this model.

It is not our intention to discuss the implications of different models in any further detail at this juncture. However, it appears clear that for the deformation of PMMA glass the pseudo-affine model is reasonably successful at low strains (below 10 to 20% nominal) but at higher strains and particularly for the $\langle P_4 \rangle$ component, it predicts orientation components which are far too large. However, the affine model could only be made to fit the data by choosing a value of n which not only is unrealistically small, but also varies drastically as a function of strain.

CONCLUSIONS

(1) A readily applicable procedure has been introduced which considerably simplifies the extraction of orientation information from X-ray scattering patterns from deformed samples of PMMA.

(2) In principle the procedure enables all components of the orientation function to be derived, although for non-crystalline polymers the limited degree of overall alignment which can be introduced may only permit $\langle P_2 \rangle$ and $\langle P_4 \rangle$ to be obtained reliably in practice.

(3) The approach introduced for PMMA may be applied to any polymer system.

(4) For uniaxially compressed samples of PMMA the results obtained using the new procedures are in poor agreement with both the pseudo affine and affine deformation schemes, although the pseudo affine predicts the initial development of orientation with strain more successfully.

ACKNOWLEDGEMENTS

We thank Mr D. J. Brown for preparing the samples, Professor R. W. K. Honeycombe FRS for provision of facilities and the Science and Engineering Research Council for funding (GRB 28088).

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