JOURNAL OF MATERIALS SCIENCE 8 (1973) 1315-1324

The structure of polyoxymethylene produced by the radiation-induced, solid-state polymerization of trioxane

E. H. ANDREWS, G. E. MARTIN
Department of Materials, Queen Mary College, London

All features of the X-ray diffraction pattern of polyoxymethylene produced by radiation-induced, solid-state polymerization of trioxane have been examined. The heavy radial streaking observed on both our own and on previous workers' patterns has been explained and the hexagonal unit cell dimensions have been calculated.

We have computed sets of parameters for chain configurations which could exist within the accuracy of the measurement, and have shown that each configuration arises as a result of various indexing of the diffraction pattern. In conclusion we argue that such helical structures are better described in terms of their average chain parameters rather than by attempting to define an exact unit cell height or identity period. Finally, we have calculated a set of values for the parameters which exactly describe the polyoxymethylene chain.

1. Introduction

Early work [1-3] on the crystal structure of polyoxymethylene reported a hexagonal unit cell with lattice constants, $a = 4.46$ Å and $c = 17.3$ Å with the space group symmetry of either C_3^2 or C_3^3. Each unit cell was thought to contain one helical molecule with monomer unit (-CH_2-O-).

In 1960 Tadokoro *et al* [1] calculated details of the chain configuration of polyoxymethylene for two contradicting models; one containing nine monomer units in five turns of the helix, proposed by Huggins [2], and an earlier model of nine monomers to four turns due to Sauter [3]. They utilized the method of Cochran, Crick, and Vand [4] to calculate the intensities of diffracted X-rays from a lattice containing helical molecules of the configurations proposed for the two models. On comparing these results with their own X-ray data for polyoxymethylene they found distinct evidence to support the five turns model suggested by Huggins.

Polyoxymethylene obtained from solid-phase polymerization of trioxane, either by radiation-induction or by repeated sublimations, was found [5] to have a fibre pattern suggesting the same nine-five structure. Rotation photographs of this material, however, exhibited many new reflections which could not be indexed on the basis of the structures proposed above which were determined from samples of oriented commercial polymer. These "new" reflections were due to a twin orientation of the hexagonal lattice. The molecules are positioned in the crystal lattice of trioxane such that polymerization may propagate in other fixed directions as well as along the *c*-axis. Carazzolo *et al* [5] showed that the twinned orientation was at an angle of 76° 7′ with the main crystal direction and that it had a three-fold repetition with "twin" crystals growing in the directions of alternative faces of the hexagonal main crystal.

Carazzolo [6] found that his data from X-ray diffraction of oriented and annealed polyoxymethylene were better explained on the basis of a 56.0 Å repeat unit than by the previously established identity distance of 17.3Å. He thus proposed a 29 monomers: 16 turns model for the chain conformation and different assignments for the *l*-indices of the layer lines. The very intense layer line would be indexed $l = 16$ because each helical turn would scatter X-rays in phase. This fixes the assignment of the remaining layer lines in such a way that the first observed layer line has the index $l = 3$. The first and second order lines and many others must be assumed to be missing. However, there are no symmetry operations to account for the absence of so many layer lines, nor could one expect so many absences to occur accidentally as would be required by this model. It is often the case that the accuracy of indexing can be improved by taking sufficiently large, but physically unrealistic identity periods. Although the deficiencies of this model appear to be self evident, several authors [7-11] have subsequently cited 56.0 Å as the currently adopted identity period and 29:16 as the chain configuration.

In view of the widespread adoption of the 56.0 Å repeat unit in preference to the well justified and simpler 17.3 Å unit, we have re-examined all features of the X-ray diffraction patterns obtained from polyoxymethylene produced by solid-state polymerization of trioxane, with the intention of gaining a clearer view of the structure of this material. It will be shown that the apparent conflict may be resolved and the diffraction pattern explained in terms of an average chain configuration of the polymer molecule. We shall show that many chain-models with various identity periods may be derived within the accuracy of the X-ray data and that each of these may be generated as a result of a very small variation in the helical parameters. We have concluded that the polyoxymethylene structure is better described by the average values of the chain parameters rather than by attempting to fit exact repetition periods to the data.

The present work, which forms part of a study of the structure and properties of polyoxymethylene from solid-state polymerization, has also led to the explanation of a striking feature of the X-ray diffraction patterns, namely the strong radial streaks observed to occur on the highest intensity reflections.

2. Experimental procedure

2.1. Specimen preparation

The starting materials, crystals of trioxane, were grown by sublimation in closed and carefully cleaned containers exposed to a temperature gradient over their volume. Hayashi *et al* [12] showed that the presence of small amounts of water could strongly inhibit the post-polymerization of irradiated trioxane hence some phosphorus pentoxide was placed in each vessel to minimize the water content of the material. The needle-shaped crystals of trioxane were sealed in air in glass tubes where they remained until the post-polymerization reaction was completed. The effect of an air atmosphere on the reaction has been studied [13] and shown to increase both the polymerization rate and the ultimate degree of conversion.

The crystals of trioxane were irradiated at room temperature to a dose of 1 Mrad by high energy electrons from a 15 MeV linear accelerator. They were subsequently transferred to a constant temperature bath and held at 55°C for 48 h. We have found that this dose and temperature of post-polymerization maximize the ultimate degree of conversion to polymer. Polymerized specimens were washed in acetone and dried under vacuum for 48 h to remove unreacted monomer. The weight of each specimen was then recorded so that its degree of conversion could be calculated. The average conversion of the batch of specimens prepared for the present study was 78%.

In previous work [1-3, 5, 6] on the X-ray determination of the structure of polyoxymethylene, oriented specimens were produced by drawing and in some cases subsequent annealing of commercial polymer. The degree of alignment achieved by these means was always inferior to that obtained by solid-state polymerization and hence our X-ray diffraction patterns were less arced than those obtained by some previous workers and thus our measurements could be carried out with greater accuracy.

2.2 X-ray diffraction methods

In all cases a copper target tube was used and operated at 40 kV, 16 mA. Transmission diffraction patterns were obtained using a flat plate camera for static measurements and a cylindrical camera (diameter 57.3 mm) for oscillation and rotation patterns. The axis of rotation was the long axis (*c*-molecular axis) of the specimen which coincided with that of the camera.

The same cylindrical camera was in use when the nickel filter used in previous exposures was replaced by a crystal monochromator to obtain both rotation and Weissenberg patterns. The monochromator was a doubly curved crystal of lithium fluoride which was aligned to reflect the copper $K\alpha$ line into the collimator from its (200) planes.

3. Results and discussion

3.1. Initial results

Static fibre patterns obtained on the flat-plate

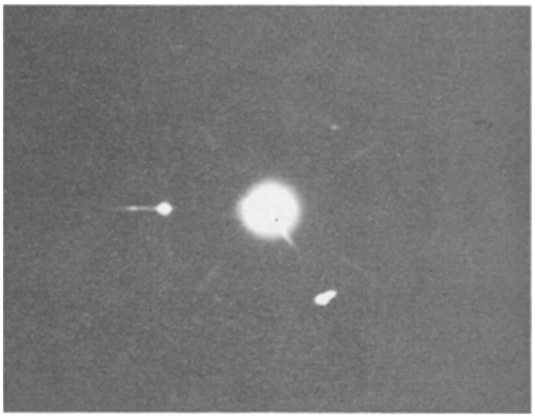

Figure 1 X-ray fibre pattern of polyoxymethylene. Specimen to film distance = 30 mm.

camera exhibited a symmetrical array of sharp spots but with considerable asymmetry in the relative intensities of the reflections (Fig. 1). These photographs revealed little more than that the specimens were all highly oriented and possibly had a single crystal texture.

Oscillation photographs were taken of a single specimen rotated through 20° during each exposure. Each photograph exhibited differing intensities for particular reflections and some had spots not present in the next photograph. This further suggested a single crystal nature for the specimen of polyoxymethylene.

3.2. Rotation patterns

The rotation photographs showed very highly oriented single crystal patterns with no observable "amorphous halo" (Fig. 2). When the photographs were superimposed on a Bernal Chart, many of the spots fell on lines of constant reciprocal lattice co-ordinate ξ, thus having the same *hk* indices, as well as falling on layer lines parallel to the equator of the pattern. Besides these spots there were many others of largely varying intensities which have been attributed to the twin orientations in polyoxymethylene from solid-state polymerized trioxane [5]. Notable features of the pattern are the considerable intensity of the "main crystal" fifth layer-line, the absence of sixth and seventh layers and a strong eighth layer-line. The absence of reflections of the type 00*l* demonstrates the high degree of *c*-axis alignment because the 00*l* reciprocal lattice points lie on the axis of rotation and hence cannot intersect the sphere of reflection.

3.3. Radial streaking

A striking feature of Fig. 2 is the streaking which was observed to radiate from the centre of the pattern and pass through the very strong reflections. Such streaking was present in the X-ray diffraction photographs obtained by some previous workers but was not discussed. This streaking arises from the failure of the nickel

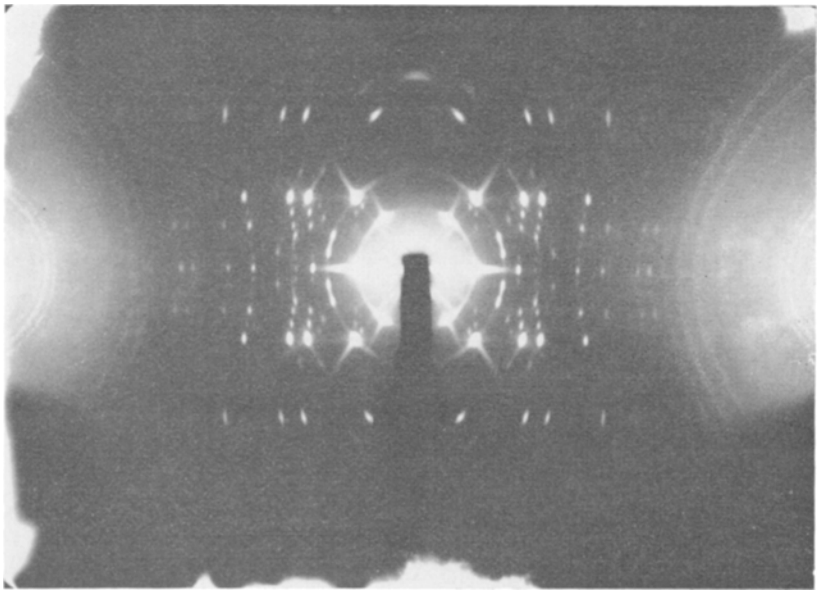

Figure 2 Rotation pattern of polyoxymethylene, nickel filtered copper radiation.

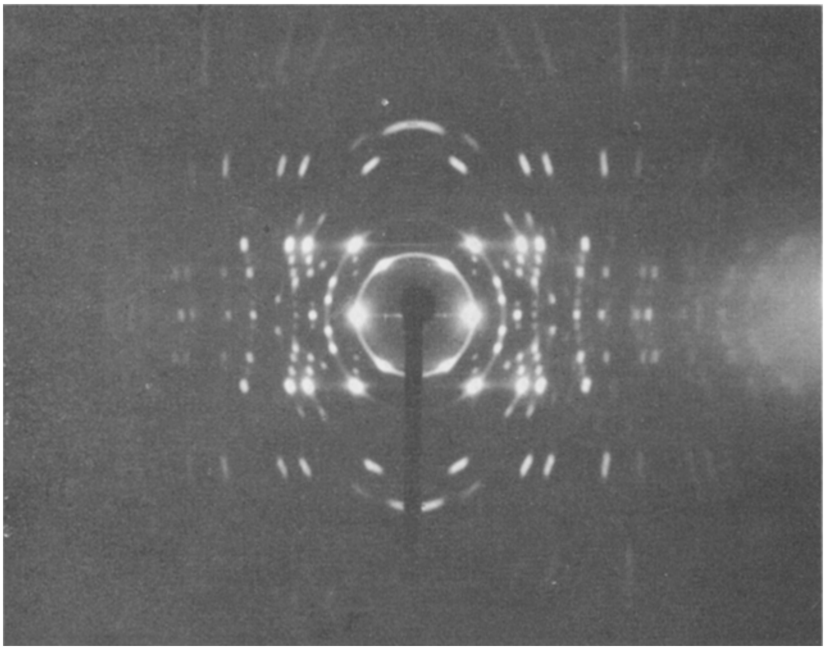

Figure 3 Monochromatic X-ray rotation pattern of polyoxymethylene.

filter to eliminate certain portions of the copper X-ray spectrum, and this was established by using a crystal monochromator instead of a filter. Fig. 3 shows a monochromatic X-ray diffraction photograph of a polyoxymethylene specimen taken under the same conditions as the previous exposure, and the streaks due to incomplete filtering are now completely absent.

The position, intensity and shape of the diffracted spots were not altered when the monochromator was used. However, some new reflections appeared inside the first order ring at positions which were previously obscured by radial streaks. The spots were very weak and at first they appeared to be aligned with a layer line of the second kind, i.e. that they were diffracted from planes with the same *hk* indices. However, a close examination showed that the new reflections occurred as a result of diffraction of X-rays of $\frac{1}{2}$ and $\frac{1}{3}$ the copper $K\alpha$ wavelength originating from the (400) and (600) planes of the monochromating crystal.

3.4. Crystal symmetry and order

To verify the hexagonal symmetry reported for the polyoxymethylene unit cell we used the monochromatic X-rays to obtain a normal beam Weissenberg pattern of the zero layer line. This is shown in Fig. 4 where {100}, {110} and {200} reflections can clearly be seen to have a 60° repetition. The well-defined spots demonstrate the high degree of order in the *ab* plane and their hexagonal repetition taken with the orientation in the *c*-direction all show that polyoxymethylene produced by solid-state polymerization has a single crystal texture. The slight linear spreading observable only in the most intense reflections suggests that there is a small variation in the direction of the crystallographic axes in the plane perpendicular to the rotation axis over the long range of the body of the specimen exposed to X-rays.

4. Interpretation

4.1. Indexing

It is first necessary to index the reflections due to the main crystal so that the lattice parameters can be determined and the crystalline chain configuration defined. To simplify this task we first established which of the reflections were due to the main crystal by taking an X-ray rotation photograph of a polyoxymethylene specimen produced by radiation-induced, solid-state polymerization of tetraoxane $(CH_2O)_4$. The size and spacing of the ring-molecules in the tetraoxane crystal lattice are not as suited to twinning as they are in the trioxane lattice. The resulting diffraction pattern, shown in Fig. 5, was found to

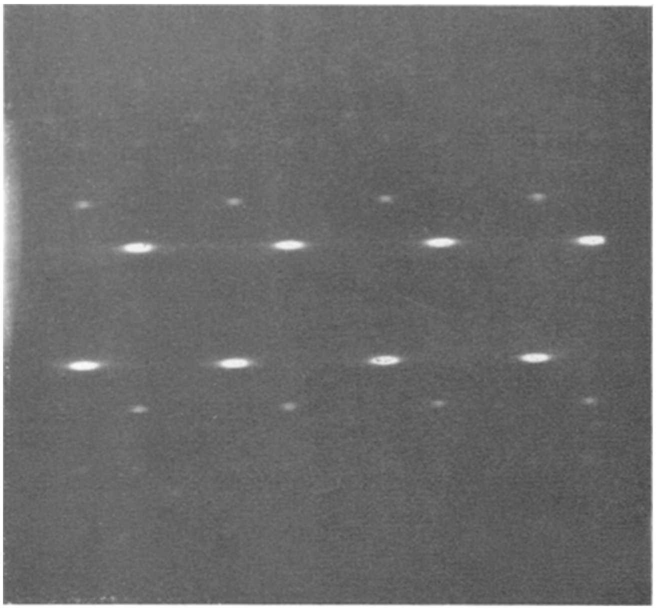

Figure 4 Zero-layer Weissenberg pattern of polyoxymethylene.

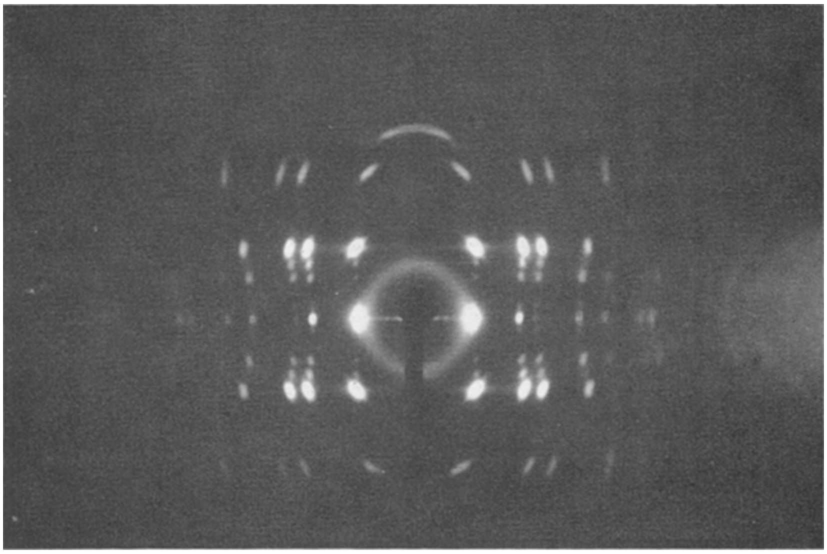

Figure 5 X-ray rotation pattern of polyoxymethylene obtained by solid state polymerization of tetraoxane.

superimpose exactly over a set of the reflections of Fig. 3. These reflections were thus identified as being due to the main crystal. The relative intensities of these particular reflections were also observed to be increased in specimens which were first annealed for 2 h at 168°C. The effect of annealing the specimens was to reduce the quantity of material in the twinned configuration.

The indexing of the main crystal reflections is shown in Table I where the relative intensity of each observed reflection is given under its indices. The reciprocal co-ordinates ζ and ξ are the average values calculated from the positions of the spots on several photographs for five different polyoxymethylene specimens. The intensities are in agreement with those observed

TABLE I Indexing and intensities of main crystal reflections

Layer		hk =	10	11	20	21	30	22	31	40	32	41
line	ζ	ξ =	0.398	0.687	0.794	1.052	1.193	1.378	1.435	1.593	1.736	1.819
0	0		VS	S	W	M	M	M	M	W	W	W
1	0.086		—	W	W	W	—	—	—	—	—	—
2	0.181		—	—	W	W	—	VW	VW	VW	VW	VW
3	0.276		W	M	M	M	W	W	W	VW	VW	VW
4	0.363		W	M	M	W	—	—	—	—	—	—
5	0.441		VS	VS	VS	S	VW	—	—	—	VW	VW
6			—	—	—	—	—	—	—	—	—	—
7			—	—	—	—	—	—	—	—	—	—
8	0.723		S	S	S	M	W	VW	VW	—	—	—
9	0.798		S	VW	—	—	—	—	—	—	—	—
10	0.886		—	W	W	VW	—	—	—	—	—	—

VS = very strong; S = strong; M = medium; W = weak; VW = very weak.

by other workers and with the calculated [5] intensities based on the theoretical structure factors for a helical molecular structure with a repeat unit of five turns containing nine monomeric units.

4.2. Lattice parameters

4.2.1. Unit cell dimension $|\mathbf{a}|$

Using the values of ξ given in Table I and the corresponding indices, h and k, we calculated values for the lattice parameter, $|\mathbf{a}|$ from the expressions:

$$\xi = |\mathbf{a}^*| \sqrt{(h^2 + k^2 + hk)} \quad \text{(hexagonal system)}$$

$$|\mathbf{a}^*| = |\mathbf{b}^*| = \frac{2\lambda}{\sqrt{3}\,|\mathbf{a}|}$$

hence

$$|\mathbf{a}| = |\mathbf{b}| = \frac{2\lambda}{\sqrt{3}\,\xi} \sqrt{(h^2 + k^2 + hk)} \cdot$$

Thus the position of each zero-layer reflection gave a value for $|\mathbf{a}|$. The mean value and standard deviation of these is:

$$|\mathbf{a}| = 4.478 \pm 0.006 \text{ Å}$$

and the corresponding value of $|\mathbf{a}^*|$ is 0.398Å^{-1}.

In Fig. 6 we have constructed a hexagonal reciprocal lattice plane for the equatorial reflections with the lattice-point spacing being the mean value of $|\mathbf{a}^*|$. The figure shows the projections of the average measured values of ξ plotted to the same scale as $|\mathbf{a}^*|$. All of these fall on the appropriate point of the lattice net thus demonstrating the excellent fit between the calculated mean value of $|\mathbf{a}|$ and the measurement of each observable reflection.

4.2.2. Unit cell dimension $|\mathbf{c}|$

There is, as may be expected, very little discrepancy between the measurements of the lattice parameter $|\mathbf{a}|$ made by various workers. However, this is not the case for the unit cell long-dimension $|\mathbf{c}|$ which corresponds to the average repeat distance of the helical molecules. Sauter [3], Huggins [2] and other subsequent workers had found $|\mathbf{c}| = 17.3$ Å whereas more recently, Carazzolo [6] determined $|\mathbf{c}|$ to be 56.0 Å. The structure factors of the configurations corresponding to these repetition periods are almost identical and lead to similar intensities of X-ray reflections provided the layer lines are re-indexed according to a 29:16 helix for the 56.0 Å identity distance.

We measured the separation of all sets of layer lines on several photographs. These were used as data to compute the ζ-co-ordinate of each layer line and the value of $|\mathbf{c}|$ divided by index l from the following expressions which are derived from simple geometry.

$$\zeta = \frac{y_l}{\sqrt{(R^2 + y_l^2)}}$$

$$\frac{|\mathbf{c}|}{l} = \frac{\lambda}{\sin(\tan^{-1} y_l/R)}$$

where y_l is the height of the lth layer line, R is the radius of the camera and λ is the average wavelength for copper $K\alpha$ radiation. A computer programme then generated sets of l-indices for the layer lines and corresponding values of $|\mathbf{c}|$ from the data. The mean values and standard deviations of all measurements yielded the following results as possible values for $|\mathbf{c}|$: (17.3 ± 0.3, 38.1 ± 0.6, 55.7 ± 0.5, 65.9 ± 1.2,

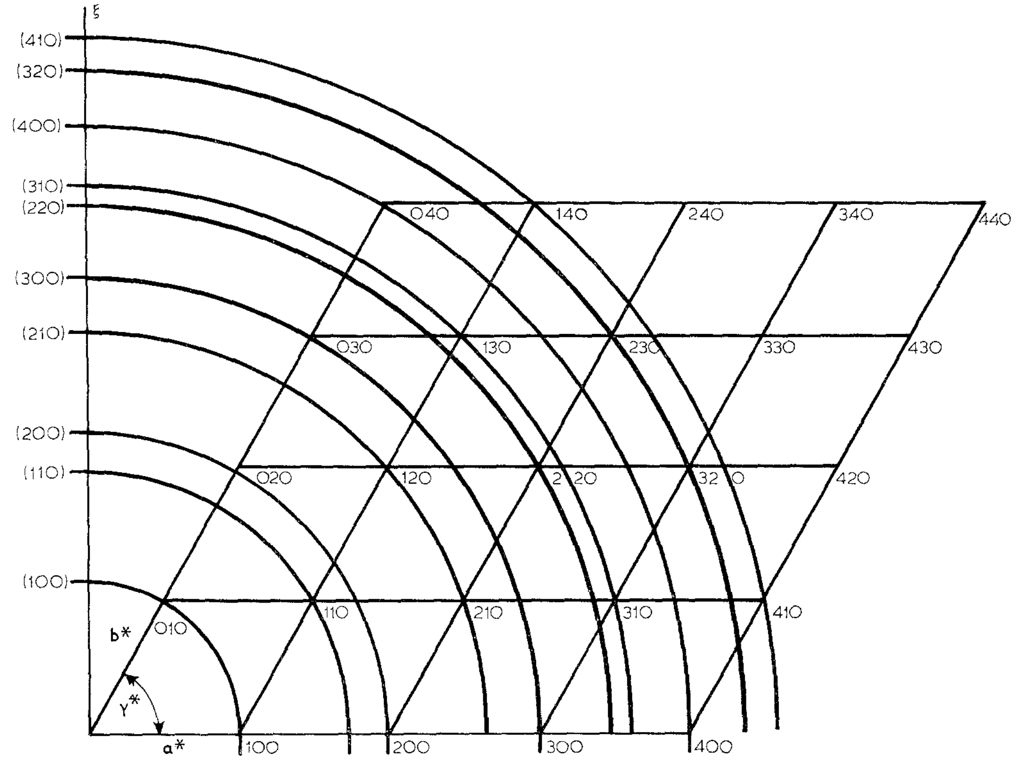

Figure 6 Reciprocal lattice construction for equatorial reflections.

72.8 ± 0.8, 82.9 ± 0.7 and 89.7 ± 1.0) Å. Each of these identity periods would be associated with a chain configuration having a number of helical turns equal to the *l*-index assigned to the very intense layer line, as each turn should scatter X-rays in phase. Dividing the identity periods by the appropriate numbers of turns we found that the translation along the *c*-axis per turn was almost equal for each of the repeat units. In fact the total variation of the translation was between 3.44 and 3.48 Å with a mean of all results of 3.46 Å. That is to say that each of the considerably different identity periods corresponds to an almost infinitesimal variation in the chain configuration.

5. Calculation of the chain-configuration

5.1. General model for a helical molecule

To better understand the structure of polyoxymethylene produced by solid-state polymerization we next calculated the possible parameters for the chain configuration based on the method derived by Eyring [14] and developed for this case by Shimanouchi and Mizushima [15].

In their formalism, the chain configuration is defined in terms of bond lengths, r_{ij}, bond angles, ϕ_{ijk} and internal rotation angle, τ_{jklm}, see Fig. 7a. The latter angle is that between bond *jk* and bond *lm* when viewing along bond *lk*, see Fig. 7b. The helix may be described by the three co-ordinates, ρ_i, θ_{ij} and d_{ij}; the radius of the helix, the rotation angle per bond about the helical axis and the translation along the axis between the ith and *j*th atoms, respectively. Flory and Mark [11] deduced that the C-O-C and O-C-O bond angles of the polyoxymethylene chain should be very nearly equal and approximately tetrahedral. From potential energy considerations, De Santis *et al* [16] have shown that with the assumption of equal bond angles the energetically favoured chain configuration is one with equal internal rotation angles, i.e. $\phi_{\mathrm{coc}} = \phi_{\mathrm{oco}}$ and $\tau_{\mathrm{ococ}} = \tau_{\mathrm{coco}}$, where o and c refer to oxygen and carbon atoms.

To obtain the relationships between r, ϕ, τ and ρ, θ and d, Shimanouchi and Mizushima [15] considered the transformation of co-ordinate systems locating one atom into similar systems locating a neighbouring atom. The variables of one transformation system were r, ϕ

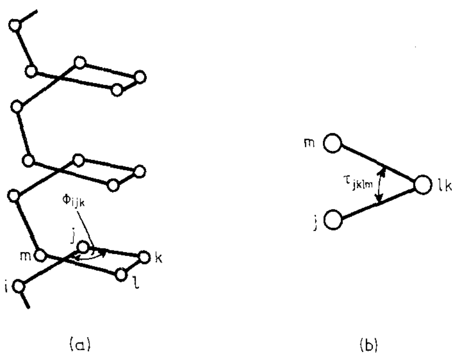

Figure 7 Helical co-ordinates.

and τ and ρ, θ and d were the variables of the other system. Application of Matrix Theory yields the following relationships between the chain parameters:

$$\cos\theta = \tfrac{1}{2}(\cos\tau - \cos\phi\cos\tau - \cos\phi - 1) \tag{1}$$

$$d^2 = \frac{r^2(1-\cos\tau)(1-\cos\phi)}{(3+\cos\phi-\cos\tau+\cos\phi\cos\tau)} \tag{2}$$

$$\rho^2 = \frac{2r^2(1+\cos\phi)}{(3+\cos\phi-\cos\tau+\cos\phi\cos\tau)^2} \tag{3}$$

5.2. Polyoxymethylene chain parameters

In order to apply the equations to the polyoxymethylene chain we need to know a structural factor obtainable from X-ray diffraction data. It can be said on quite general grounds that what is possible to assess with certainty for a helicoidal polymer from X-ray diffraction is the period per monomeric unit and the number of monomers per turn. These are 1.93 ± 0.01Å and 1.81 ± 0.01 respectively for polyoxymethylene. Using the relationships shown above and the data of greatest reliability available to date, i.e bond length, $r = 1.43$ Å [17] which is the length of C-O bonds in ethers and related compounds and the calculated bond angle, $\phi = 110° \, 53'$ [1, 11] and the axial translation between atoms, $d = 0.965$ Å which is half of the period per monomer from X-ray analysis, we have computed the remaining parameters, ρ, τ and θ. Re-arranging Equation 2 we have:

$$\cos\tau = \frac{3d^2 - r^2 + (d^2 + r^2)\cos\phi}{(d^2 - r^2)(1-\cos\phi)}$$

which when evaluated was substituted into Equation 1 to give θ and Equation 3 to yield ρ. The results were;

radius of helix = 0.686 Å
internal rotation angle = 78° 4′
rotation per bond = 100° 28′ .

These, of course, are nominal figures derived by using bond lengths and angles of related compounds. They should be compared with the precise figures derived from the X-ray data below.

5.3. Computation of possible repeat units

Using this nominal data we then wished to generate lengths of chain which would constitute a repeat unit within certain degrees of accuracy. The condition to obtain a repeat, i.e superposition of one atom directly above an atom of the same type in the chain, after n atoms, is satisfied when $n\theta = 2m\pi$; m is an integer and is equal to the number of turns of the helix.

First the models for which $n\theta = 2m\pi \pm 2\%$ were computed. The results are shown in Table II where we also show the percentage difference of the number of monomers per turn from its mean value of 1.81 and the angular deviation from perfect superposition of atoms over the repeat distance as a percentage of the rotation angle per bond. We subsequently computed chain models for which the number of monomers per turn was required to be within 1% of 1.81 but no different models of significance were generated. Models generated within the latter constraints which were also obtained by the first computation were all found to agree with those derived from the X-ray data within the quoted experimental limits. That is the X-ray data would give rise to each identity period in Table II depending on the indexing of the layer-lines and in particular the very intense layer-line which would have the average periodicity of the helix. Although on the basis of the calculated possible chain configuration some models provide better fits than do others, each configuration is indistinguishable from the X-ray data. However, regular repetition blocks with length of 56.0 Å or greater would give rise to a clear maximum in the low-angle X-ray diffraction spectrum but no such maxima are observed [18, 8]. Furthermore, there are no symmetry operations to account for the absence of so many layer lines, nor could one expect so many absences to occur accidentally, as would be required to explain the indexing assigned for any but the shortest, 17.3Å, identity period. It must be remembered that the X-ray diffraction photographs are a result of the

TABLE II

No. of monomer units	No. of turns	Monomers per turn ratio	% difference from mean ratio	% angular deviation	Identity period (Å)
9	5	1.800	0.55	8.30	17.37
16	9	1.788	1.78	25.06	30.88
20	11	1.818	0.45	58.26	38.60
25	14	1.786	1.34	16.76	48.25
29	16	1.812	0.14	66.56	55.97
34	19	1.789	1.13	8.46	65.62
38	21	1.810	0.03	76.86	73.34
41	23	1.783	1.51	41.82	79.13
43	24	1.792	1.01	0.17	82.99
47	26	1.808	0.13	83.15	90.71
52	29	1.793	0.93	8.13	100.36
56	31	1.806	0.20	91.45	108.08
57	32	1.781	1.59	66.89	110.01
59	33	1.788	1.22	25.23	113.87
61	34	1.794	0.88	16.43	117.73
65	36	1.806	0.25	99.75	125.45

average structure of many thousands of chains and that these chains are typically 10^3 monomer units in length. It would be difficult to imagine every helical chain having over its total length the precise configuration to bring about an exact and unambiguous identity period. We propose that the structure of polyoxymethylene must be described by defining the average chain parameters rather than by trying to fit exact repetition periods to data as was attempted in previous studies. From this study it can be said that the average chain configuration is closest to the 9:5 model with an average translation per turn of 3.46 Å, which determines an average identity period of 17.3 Å for that model.

5.4. Average chain parameters

These dimensions fix the remaining parameters of the averaged chain configuration. Substituting from Equation 1 into Equation 2 to solve for $\cos\phi$ we obtain:

$$-(d^2+r^2)\cos^2\phi + [2(d^2-r^2)\cos\theta + (2r^2-1)]\cos\phi + 4d^2 - r^2 + 2(r^2-d^2)\cos\theta = 0\,.$$

This yields a value for ϕ which may be substituted back into Equation 1 to obtain τ and these then give ρ from Equation 3. The resulting parameters for the helical polyoxymethylene molecule are as follows:

Bond length = 1.43 Å
translation per turn = 3.46 Å
bond angle = 106° 53′
internal rotation angle = 73° 42′
rotation per bond = 100° 0′
radius of helix = 0.725 Å.

6. Conclusions

We have found that polyoxymethylene produced by solid-state polymerization is a highly crystalline and well ordered material with hexagonal symmetry. Although there appears to be a small variation in the direction of the crystallographic axes through the body of the specimen and some slight disorder in the *ab* plane we have obtained good single crystal-like diffraction patterns with clearly defined spots. From these photographs we have determined the lattice parameter, $a = 4.478 \pm 0.006$ Å and have found that various identity periods along the molecular axis will fit the X-ray data depending on the indexing of the layer lines. We found that each of the identity periods would occur as a result of very small variations in the chain configuration. However, as the X-rays "see" the average structure of the specimen we argue that such helical structures are better described in terms of their average chain parameters rather than by attempting to define an exact unit cell height or identity period.

Acknowledgements

The authors wish to thank Dr E. Sãndor, Physics Department, Queen Mary College for the use of his X-ray facilities, Dr N. Darlington of the same department for useful discussions and Mr D. White, Physics Department, St Bartholomew's Hospital for his co-operation and assistance in irradiation of samples. The financial support of SRC is also gratefully acknowledged.

References

1. H. TADOKORO, T. YASUMOTO, S. MURAHASHI, and I. NITTA, *J. Polymer Sci.* **44** (1960) 266.
2. M. L. HUGGINS, *J. Chem. Phys.* **13** (1945) 37.
3. E. SAUTER, *Z. Phys. Chem.* **B.18** (1932) 417.
4. W. COCHRAN, F. H. C. CRICK, and V. VAND, *Acta Cryst.* **5** (1952) 581.
5. G. A. CARAZZOLO, S. LEGHISSA, and M. MAMMI, *Die Makromolek Chemie* **60** (1963) 171.
6. G. A. CARAZZOLO, *J. Polymer Sci.* **A1** (1963) 1573.
7. G. ADLER, *ibid* **A1, 4** (1966) 2883.
8. Y. CHATANI, T. UCHIDA, H. TADOKORO, H. HAYASHI, M. NISHII, and S. OKAMURA, *J. Macromol. Sci.* (*Phys.*) **B2** (1968) 567.
9. M. D'ALAGNI, P. DE SANTIS, A. M. LIQUORI, and L. MAZZARELLA, *Nuovo Cimento* **31** (1964) 1368.
10. B. CRIST and A. PETERLIN, *J. Polymer Sci.* **A2, 9** (1971) 557.
11. P. J. FLORY and J. E. MARK, *Makromol. Chem.* **75** (1964) 11.
12. K. HAYASHI H. OCHI, and S. OKAMURA, *J. Polymer Sci.* **A2** (1964) 2929.
13. I. ISHIGAKI, A. ITO, T. IWAI, and K. HAYASHI, *ibid* **A1, 9** (1971) 2511.
14. H. EYRING, *Phys. Rev.* **39** (1932) 746.
15. T. SHIMANOUCHI and S. MIZUSHIMA, *J. Chem. Phys.* **23** (1) (1955) 707.
16. P. DE SANTIS, E. GIGLIO, A. M. LIQUORI, and A. RIPAMONTI, *J. Polymer Sci.* **A1** (1963) 1383.
17. H. J. M. BOWEN and I. E. SUTTON, "Tables of Interatomic Distances and Configurations in Molecules and Ions" (Chem. Soc., London 1958).
18. V. S. RYSKIN and A. I. SLUTSKER, *Polymer Sci., USSR,* **12** (1970) 2068.

Received 8 February and accepted 22 March 1973.