A model for structural inhomogeneities in hexagonal polyoxymethylene (POM)

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Recently samples of POM have been prepared which have the X-ray powder diffraction pattern of the hexagonal form, but have a distinctly different i.r. spectrum. These observations are interpreted here as being due to a difference in the packing of the helical molecules, rather than to the presence of significantly non-standard conformations which is the usual interpretation.

Keywords Hexagonal polyoxymethylene; crystal packing; inhomogeneities; chain conformation; X-ray powder diffraction pattern; infra-red spectra

Polyoxymethylene is perhaps the simplest polymer to have a methylene group alternating with a hetero atom along the backbone. If the bonds were to adopt *trans* conformations then adjacent dipoles would be parallel. It is in part, presumably, to avoid such an unfavourable electrostatic situation that the C–O bonds have the *gauche* conformation predominantly in solution[1] and that *gauche* conformations occur exclusively in the crystals whose structures have been reported[2–4]. The existence of the two well-known solid state forms, the hexagonal or trigonal and the orthorhombic, whose helical pitches are 9/5 and 2/1 respectively, indicate that there is a fine balance between intramolecular energies and chain packing energies. Depending upon which conditions prevail at the nucleation stage of crystallization (which may also coincide with the polymerization itself) one may obtain the stable hexagonal form with one molecule per unit cell, or the metastable orthorhombic form with two molecules per unit cell. A modification of the hexagonal form has recently been found: it can be prepared by the acid-catalysed polymerization of trioxane in nitrobenzene provided that the monomer concentration is above a certain value[5–7], and is recognized by the presence in the i.r. spectrum of a number of bands which are not seen in the spectrum of normal hexagonal POM. These bands have been taken to indicate the presence of unusual conformations, with bond rotation angles other than the conventional 78° 13′, in line with an earlier study of the vibrational spectrum of oligomeric molecules[8]. In this communication we suggest an alternative structure for the modified hexagonal POM which may equally well account for the experimental observations. The extra bands in the i.r. spectrum are attributed to the influence of interchain packing effects such as might arise when one chain in a predominantly hexagonal lattice is advanced in the direction of the chain contour by half a repeat unit (or for the one chain the –O– and the –CH_2– units are interchanged).

Figure 1 is a section cut through a number of POM chains grouped in a hexagonal pattern and lying in the plane perpendicular to the axes of their helices. Above the line C the predominant structure corresponds to the usual hexagonal crystalline form. The chains near A and B are out of register with their neighbours in simple illustration of the proposal. It is consistent with the statement[5] that 'the basic conformation of the chain must be very similar in the two types', that is the normal and modified hexagonal forms. There are three pieces of experimental evidence which are relevant and which are now discussed.

Firstly the modified hexagonal form is characterized by i.r. bands at (*inter alia*) about 1138 cm^{-1} and 988 cm^{-1} which are often as prominent as other bands (for example at 1092 cm^{-1} and at 896 cm^{-1}) which are found in the spectrum of the normal hexagonal form[5–7]. Whatever the nature of the inhomogeneity in the modified form, its extent may be quite large. However, the X-ray powder diffraction pattern of such a sample displays three prominent peaks and has been shown to be almost identical to that of an authentic hexagonal sample[6]. The modified form was highly crystalline: the inhomogeneity in its structure was not associated with a significant fraction of amorphous phase according to this X-ray evidence. Elsewhere it has been stated that the X-ray pattern of a sample rich in inhomogeneities showed it to be 96 to 98% crystalline[5]. As the X-ray diffracting power of an atom is to a first approximation proportional to the

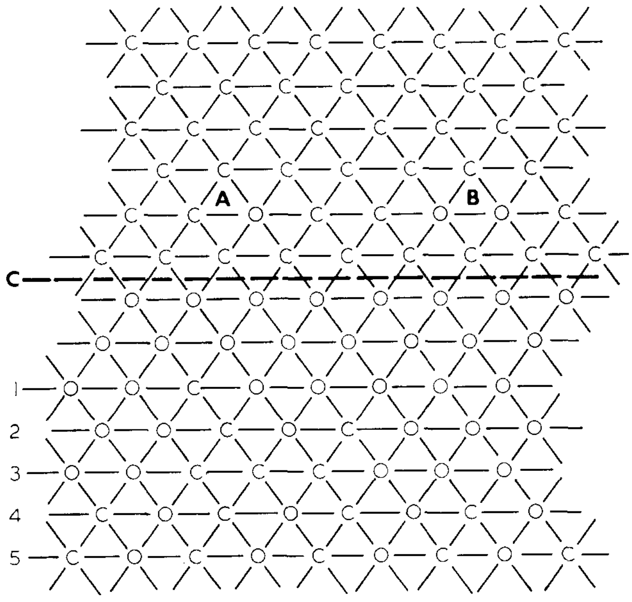

Figure 1 Section cut at right angles to the cylindrical axis of a number of polyoxymethylene chains arranged in a hexagonal pattern O and C indicate the –O– atoms and –CH_2– groups which lie in that plane in the different molecules. **A, B** and **C** indicate where different packing forces arise because adjacent chains are out of register in various ways. On lines 1, 2, 3, 4, 5 there are that number of chains misregistered with an O chain matrix

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number of electrons in the atom[9], and as the –O– and –CH_2– units of POM are isoelectronic, the modification to hexagonal POM caused by exchanging the location of the two units in a substantial fraction of the chains would not be readily detected by the simple X-ray experiment, so long as the basic hexagonal structure had not been disrupted[10]. The vibrational spectrum, however, might well be sensitive to these changes, as the following considerations will show. The simple condition of one molecule per unit cell would lapse, indeed the concept of the unit cell no longer applies. Despite the difference in bond angle between the hexagonal and orthorhombic structures, group vibrations have similar frequencies in the two structures, but in the latter certain i.r. vibrations occur as doublets because of intermolecular interactions in the unit cell containing two polymer chains[3].

A second piece of evidence was provided in this Journal recently when it was shown[7], in agreement with earlier indications[5], that the features in the i.r. spectrum, which characterize the structural irregularity, develop progressively from one sample to another. The absorbances at 1095 cm^{-1}, 1000 cm^{-1} and 900 cm^{-1} correlate roughly with each other over a wide range of samples prepared by different means and obtained from different sources. In terms of the proposed model, normal hexagonal POM corresponds to the top four lines of the figure, while the modified form may contain a variable proportion of such irregularities as are associated with A and B in *Figure 1*. It has been observed that the broadness and shape of each peak varied between samples[7]. The type of inhomogeneity suggested here could produce such an effect. Near A all the contacts between the irregular 'O' chain and the surrounding 'C' chains are identical and would make a single and characteristic contribution to the vibrational spectrum. The modes of vibration of at least 7 chains would be altered by the presence of a single misregistered chain. Near B, where the contacts between the chains are of a different nature, for two irregular 'O' chains are present, the interchain forces will be different and so a different modification of the vibrational spectrum might result. Besides the quasi slip plain imperfection indicated by C in *Figure 1*, other types of imperfection might be imagined, each of which would make a characteristic contribution to the vibration spectrum. Changes in band shape thus indicate different proportions of these irregular structures.

A final piece of evidence for the present proposal is that the crystalline POM obtained from a feed containing 1,3,5-trioxan together with 5% dioxolan with the aid of an acid catalyst has the structural inhomogeneities, whereas in the absence of the dioxolan the normal hexagonal form would be obtained[11]. If two adjacent POM chains were in register for part of their lengths, the incorporation into one of them of a dioxolane unit would introduce one C–C sequence and cause the compositions of the chains to be out of register from then onwards provided that in the solid the chain with the C–C bond maintained approximately the usual pitch of the helix structure. Even a very small proportion of dioxolane would cause up to half of the pairs of chain contacts to be of a modified form.

It is interesting to consider the relationship between hexagonal POM, the out-of-register hexagonal POM and orthorhombic POM. In the lower half of the figure the lines labelled 1 to 5 show an increasing proportion of out-of-register 'C' chains in an 'O' chain matrix. If the proportion of out-of-register chains is about 50% and if they are arranged alternatively, as on line 5, rather than in blocks as on line 3, then the system would leave the hexagonal lattice and adopt the orthorhombic form.

A careful X-ray study of a sample of the modified hexagonal POM might find further experimental support for the model proposed here. Extra meridional reflections have been found in X-ray diffraction photographs of drawn POM[12]. Some were attributed to small distortions in the ideal structure of the 9/5 helix produced by packing effects, but others were associated with metastable regions of unknown structure and organization, and may be compatible with the present model. A neutron scattering study would not be subject to the ambiguities to which the X-ray method is subject because of the isoelectronic character of –O– and –CH_2–. A proof of the present model would be the observation that the irregularities in the i.r. spectrum of a sample of POM containing a proportion of dioxolane units could not be removed by the application of pressure[8,10] or by cold working[8], procedures which have been shown to remove the inhomogeneities from the i.r. spectrum of hexagonal POM. By providing an alternative interpretation of already published work this article may encourage such experimental studies.

References

1 Mark, J. E. *Acc. Chem. Res.* 1979, **12**, 49
2 Huggins, M. L. *J. Chem. Phys.* 1945, **13**, 37
3 Carazzolo, G. and Mammi, M. *J. Polym. Sci. A* 1963, **1**, 965
4 Tadokoro, H. 'Structure of Crystalline Polymers', J. Wiley and Son, New York, 1979
5 Terlemezyan, L., Mihailov, M., Schmidt, P. and Schneider, B. *Makromol. Chem.* 1978, **1979**, 807
6 Terlemezyan, L. and Mihailov, M. *Eur. Polym. J.* 1981, **17**, 1115
7 Shimomura, M. and Iguchi, M. *Polymer* 1982, **23**, 509
8 Oleinik, E. F. and Enikolopyan, N. S. *J. Polym. Sci. C* 1968, **16**, 3677
9 Bunn, C. W. 'Chemical Crystallography', O.U.P., 2nd Edn., 1961
10 The isoelectronic character of KCl gives rise to a similar ambiguity. Brock, C. P. and Lingafelter, E. C. *J. Chem. Edn.*, 1980, **57**, 552
11 Terlemezyan, L., Mihailov, M., Schmidt, P. and Schneider, B. *Makromol. Chem.* 1978, **1979**, 2315
12 Saruyama, Y., Miyaji, H. and Asai, K. *J. Polym. Sci. Polym. Phys. Edn.* 1979, **17**, 1163