

The structure of amorphous polystyrene by X-ray scattering and simple conformational analysis

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The X-ray diffraction patterns of amorphous (glassy) polystyrene are interpreted by means of intensity functions calculated from model structures of isotactic polystyrene, incorporating only intra-chain interactions. The range of chain conformations or possible complexions is explained by means of the agreement between theoretical and experimental functions and in relation to published data for the conformational energy of polystyrene in solution. The calculations indicate that in the glassy state, isotactic chains adopt conformations characterized by a large phenyl group separation and a degree of rotational disorder defined about skeletal bonds.

1. Introduction

The structural investigation of amorphous polymer assemblies of biological and synthetic origin and of known chemical structure concerns the quantitative description of the degree of disorder. Disordered systems may be defined within a spectrum of structures from the paracrystalline to the amorphous† and it is necessary to study the factors responsible for variations in structural regularity. At the atomic level of structure these factors may be identified with constraints imposed by covalent bonding characteristics. Discussion of a higher level of structural complexity requires a description of the influence of hydrogen bonding and coulomb and Van der Waals forces. By considering the effect of these constraints on the energy available for chain distortion it is possible to investigate the relationships between short-range order and parameters descriptive of overall chain conformation.

The X-ray scattering method has been used with some success for the study of both ordered [1] and disordered polymer systems [2-6], the analyses leading to discussion of the extent of

short-range order, and the influence of intra- and inter-chain scattering interactions. The two principal methods of interpretation [2] involve either Fourier transformation of intensity data or the calculation of theoretical intensity functions based on model structures. Differences [2] between experimental reduced intensity functions and those calculated from models arise from the exclusion of regions of rigid structure beyond the limits of the model. The effects of flexibility along a disordered chain were emphasised by Bjornhaug *et al.* [6], who, in their selection of suitable forms of polymer for study, chose those which had the greatest degree of chain flexibility. This had the consequence that intra-monomer scattering contributions were enhanced at the expense of inter-monomer and inter-chain effects. An important result of the work of Arndt and Riley [1] is that for a range of protein structures with α , β and other conformations, the effects of inter-chain interactions on the intensities of amorphous X-ray scattering were found to be significant only at small scattering angles ($s = 4\pi/\lambda \sin \theta < 1 \text{ \AA}^{-1}$, see later).

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†The term amorphous is used to describe those structures which give a continuum of X-ray scattering rather than a series of discrete X-ray reflections, interpreting 'discrete' in a general way to include all stereoregular possibilities of repeating unit cells subjected to distortion, disorientation or strain.

In the present work, calculations of theoretical intensity functions which include the effects of chain disorder, have been used for the structural study of amorphous (glassy) polystyrene as a preliminary to further work [7] on bacterial cell wall structure by the X-ray scattering method. This polymer system was considered to be particularly appropriate for investigation, owing to the absence of branching, the inclusion of bulky side-groups and the possibility of both atactic and isotactic forms. The philosophy is that a disordered chain conformation may be regarded as derived by processes of distortion from a notional regularly repeating chain conformation which may be identified. In reverse, the problem appears as a search for a stereochemically acceptable initial regular structure which may be distorted within an ensemble of individually acceptable structures, all different, but each generically related to the original regular structure. Generalization of this concept leads to the consideration of a number of regular structures, each forming a starting point for the process of distortion, but with some fundamental relationship between them – such as is involved in the complexion of structures with large phenyl group separation.

High quality scattering data obtained for both isotactic and atactic amorphous polystyrene were available [3]. In earlier work [6, 8] on non-crystalline polystyrene, radial distribution function methods were adopted. Emphasis has been laid [8] on the structural importance of side-group interactions in determining polystyrene configurations and it has been suggested that intra-chain contributions dominate the total scattering. Finally [3], calculations of theoretical radial distribution functions have been carried out for models based on limited regions of crystalline isotactic polystyrene.

Recently the conformational energies of meso and racemic dyads of polystyrene have been calculated [9] in terms of skeletal bond rotations using the Lennard–Jones 6–12 potential for non-bonded atom pairs. This analysis has allowed likely conformations for polystyrene chains in solution to be deduced in relation to the separation of nearest neighbour phenyl groups and the possible effect of solvent molecules.

2. Theory and computational details

Theoretical reduced intensity functions $si(s)$ were calculated according to the Debye equation applied

to an atomic model:

$$i(s) = \sum_{p=1}^N \sum_{q=1}^N f_p(s) f_q(s) \frac{\sin sr_{pq}}{sr_{pq}}, \quad (1)$$

where $f_p(s)$ is the atomic scattering factor for an atom p , r_{pq} is the separation of atoms p and q . $s = 4\pi\sin\theta/\lambda$ where λ is the X-ray wavelength and 2θ the scattering angle. The summations in Equation 1 extend over all atom pairs in the model and the effect of atomic thermal vibration is introduced by an experimental temperature factor [10] of the form $\exp(-b_{ij}s^2)$ where $b_{ij} = \frac{1}{2}(\bar{u}_i^2 + \bar{u}_j^2) = \frac{1}{2}\bar{u}_{ij}^2$ describes the variance of the separations of atoms i and j . Test calculations showed that a reasonable value for \bar{u}_{ij} was 0.05 Å.

Comparison of a theoretical reduced function, $si(s)$, may be made with an equivalent experimental function calculated from the measured intensity data, $I_m(s)$, according to the equation;

$$si(s) = s \{ \alpha I_m(s) - I_{\text{ind}}(s) - I_{\text{inc}}(s) \} \quad (2)$$

where α is a scaling factor, $I_{\text{ind}}(s)$ represents the independent atomic scattering component and $I_{\text{inc}}(s)$ represents the incoherent scattering. The use of Equation 2 in this form assumes that $I_m(s)$ is corrected for specimen absorption and background scattering (see [3]).

A difficulty of the model approach is the finite model size and the exclusion of scattering effects associated with interatomic distances greater than the model dimensions. The effect of finite model size obscures the features of the “small s ” region owing to the presence of a large intensity maximum. Although correction functions have been developed [11], the most effective means of reducing this effect is to increase the model dimensions, resulting in a compression of the spurious maximum towards the origin.

In the present analysis of a disordered polymer system, the effects of differences in chain regularity from chain to chain were approximated by using the equation, referred to $s \gg 1 \text{ \AA}^{-1}$;

$$si(s) = \langle si_I(s) \rangle, \quad (3)$$

where $i_I(s)$ is the intensity associated with a single model chain with a disordered configuration defined in terms of a range of single bond rotations applied between monomer units. The extent of such disorder may be varied between limits to structural complexions set by considering the Van der Waals repulsions between adjacent monomer

units. The average in Equation 3 was calculated over several different configurations, the number being limited by the availability of computer time. Thus the calculation of theoretical intensity functions includes contributions arising from inter-monomer scattering interactions in single chains, and extends beyond first nearest neighbour effects, but bearing earlier work in mind (especially [1]), excludes inter-chain interactions.

The analysis was divided into three stages. The first involved the calculation of sterically allowed angular ranges for single bond rotations between monomer units ($\text{CH}_2 \cdot \text{CH} \cdot \text{C}_6\text{H}_5$). Using the absolute minimum Van der Waals non-bonded atomic separations, and adopting a method similar to that used to study conformations of polysaccharides [12] and proteins [13], a map of sterically acceptable angular positions was constructed in terms of dihedral angles ϕ and ψ . These describe the mutual orientation of adjacent monomer units in relation to two linkage, single covalent bonds. Thus, regions of (ϕ, ψ) plot which define sterically unacceptable conformations may be eliminated from the calculations.

The second stage involved the calculation of theoretical intensity functions for single regular chains within the domain of sterically acceptable conformations; this allowed, in principle, the identification of possible underlying structural complexions which might provide a basis for disordered chains. Conformations containing severe steric restrictions associated with non-adjacent monomer units were eliminated from computer generated model polymer chains at this stage by inspection.

The final stage involved the generation of disordered configurations varying the dihedral angles within assigned ranges using a random number generator. The ranges were based on the previously calculated sterically allowed regions and an initially regular chain configuration was assumed. Clearly, the application of fixed rotations ϕ_i and ψ_i to each pair of linkage bonds in a polymer system will lead to a well defined regular configuration.

If the rotations are not fixed and vary randomly within angular intervals $\Delta\phi$ and $\Delta\psi$ for each successive linkage, then the resultant configuration

will be irregular in form. Suitable ranges of the angular variations are considered later.

A series of computer routines was then used for the location of any further sources of steric hindrance which might arise from second and third nearest neighbour monomer interactions, any clashes being relieved by sidegroup manipulation. A logical tree representation, similar to that used by Hermans and Ferro [14] for protein molecules, allowed efficient storage of chain configurations. The details of computation and the application to different polymer types are described elsewhere [15]. Theoretical intensity functions were calculated from disordered chain coordinates using Equation 1.

Atomic coordinates have been published by Natta and Corradini [16] for crystalline isotactic polystyrene. Their results were based on a two dimensional projection of electron density and indicated the presence of a hexagonal unit cell, with space group $R3c$ or $R\bar{3}c$ and lattice parameters, $a = b = 21.9 \text{ \AA}$ and $c = 6.65 \text{ \AA}$. This analysis suggested that the polymer carbon backbone assumes a *tg* configuration in the form of a three-fold helix* parallel to the z axis. The longest model chain used in the present work for calculation using Equation 3 consisted of 24 monomer units extending in the crystalline form over an axial distance of 53.2 \AA . The resolution of the electron density map of Natta and Corradini did not enable the locations of chain or phenyl group hydrogen atoms to be determined. Therefore, the position of each hydrogen atom was calculated assuming standard bond lengths and ideal tetrahedral coordination for hydrogen atoms attached to the backbone. The positions of phenyl ring atoms defined in a three dimensional cartesian co-ordinate system were determined by considering the magnitude of inter-atomic distances projected on the $X-Y$ plane.

3. Experimental data

Experimental data collected from a quenched sample of atactic glassy polystyrene were kindly supplied by Drs Wecker, Davidson and Cohen. These authors [3] demonstrate (their Fig. 4) virtually identical X-ray scattering from different specimens of atactic polystyrene with different

* In the following the term "helix" does not necessarily carry the connotation of an *extended* series of monomers on a cylindrical surface. A distorted helical structure expresses the fact that irregular distortions are applied in modelling to an initially regular structure.

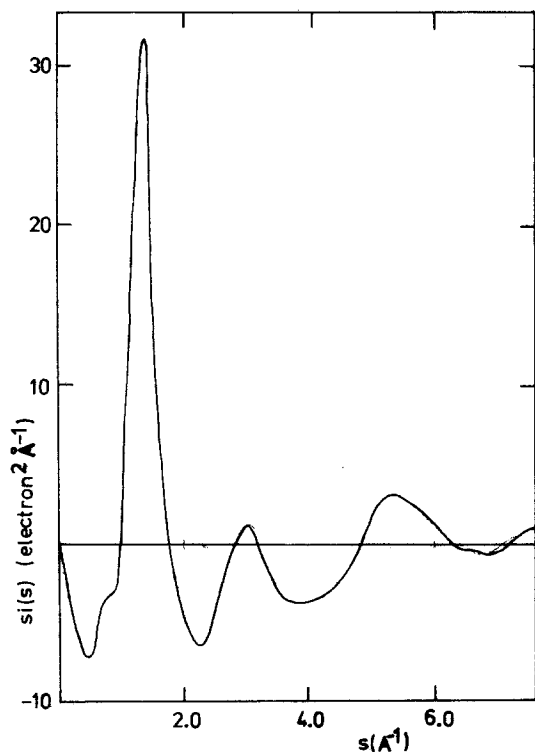


Figure 1 Reduced intensity function for glassy atactic polystyrene (calculated from results supplied by Wecker *et al.*).

thermal histories. Fig. 1 shows an unsharpened reduced intensity function calculated from their data. This function was obtained by subtracting contributions due to independent scattering using the sum of fitted atomic scattering factors [17] weighted by the molar fractions for the material; corrections for absorption, polarization, incoherent scattering and multiple scattering had been applied by Wecker *et al.* The corrected curve was refined following a procedure similar to that reported by Kaplow *et al.* [18] and using the published material density of 1.048 g cm^{-3} .

The reduced intensity function is of a slowly varying form, extending from $s=0.0$ to $s=7.6 \text{ \AA}^{-1}$ with broad peaks situated in the region of 1.4 , 3.0 and 5.4 \AA^{-1} . There is also an indication of a "shoulder" to the first peak at approximately $s=0.7 \text{ \AA}^{-1}$.

In view of the very small differences observed by Wecker *et al.* between experimental scattering data for atactic and quenched isotactic samples, the intensity function shown in Fig. 1 was considered suitable for the structural analysis of quenched isotactic polystyrene; regularity in side-group substitution found in the isotactic form was

considered more suitable for computer modelling. Thus, in the calculation of theoretical functions no attempt was made to investigate quantitatively the structural consequences of differing tacticities.

4. Results and calculations

4.1. (ϕ, ψ) plots for isotactic polystyrene

Fig. 2 shows (ϕ, ψ) plots for two monomer units of isotactic polystyrene calculated on a simple Van der Waals contact basis and at angular intervals of 10° in both ϕ and ψ . The origin of the plot coincides with the main chain backbone in a staggered *tt* configuration. The *tg* configuration found in crystalline isotactic polystyrene corresponds to the position, $\phi = 0^\circ$, $\psi = 120^\circ$.

Regions I and II (Fig. 2) describe ranges of single bond rotations which, for a fixed side-group orientation, allow conformations free from all steric restrictions; these are defined by Van der Waals minimum separations [19] and involve only those inter-atomic interactions associated with adjacent monomer units (R_i and R_{i+1} in Fig. 4a). Phenyl side-groups assume fixed orientations defined in accordance with the data of Natta and Corradini [16]; this removes the element of symmetry about the line $\phi = \psi$ which would be expected for regions I and II if the side-groups were oriented perpendicular to the plane of the carbon backbone.

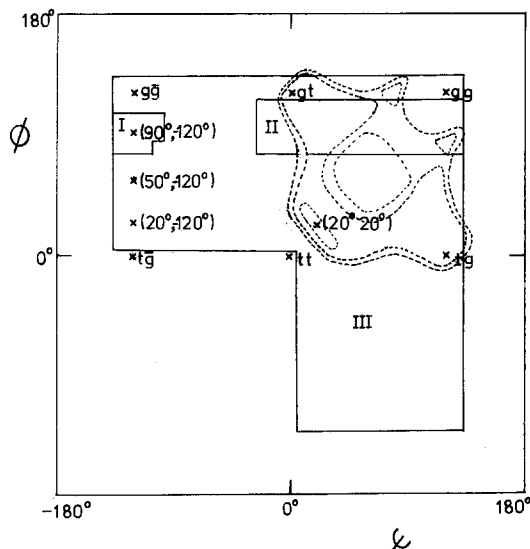


Figure 2 Calculated (ϕ, ψ) conformational plot for isotactic polystyrene. Regions I, II and III were assessed using minimum hard sphere Van der Waals contact distances [19]. Energy contours for the *g* domain are those published by Yoon *et al* [9] for a meso dyad of isotactic polystyrene.

Area III describes configurations which do not initially satisfy the Van der Waals criteria but may do so after adjustments to the orientation of phenyl side-groups. Such adjustments may be made by a rotation about the linkage covalent bond between a phenyl ring and the carbon backbone (χ_i in Fig. 4a). The allowed regions were calculated by considering the magnitudes of interatomic distances while excluding those whose position in space is dependent upon χ_i . In contrast to regions I and II, this results in an element of symmetry about the line $\phi = \psi$. Thus it was possible to define an absolute maximum domain (region III) which includes the possibility of flexibility in side group orientation. Within this

region are situated regions I and II which may be identified with a particular fixed side-group orientation.

The large allowed regions and the associated large degrees of rotational flexibility originate in part from the exclusion of interactions between non-adjacent phenyl groups. These effects are particularly important in polystyrene owing to the presence of bulky side-groups and their short separation along the backbone of 2.5 Å.

Inspection of (ϕ, ψ) plots show that tt and $t\bar{g}$ conformations lie just outside region III; however, the position of the three fold helix found in crystalline isotactic polystyrene (tg) falls within the maximum allowed region. The difference in status assigned on this basis to the tg and $t\bar{g}$ conformations may reflect the uncertainty in the analysis particularly in relation to the orientation of the phenyl side groups or relate to differences in energy attributed to g and \bar{g} domains by Flory and co-workers [9] for the meso dyad. An energy contour map for the g domain calculated by these workers using the Lennard-Jones potential function is also shown in Fig. 2. A potential minimum at $\phi = \psi = 20^\circ$ is apparent, together with subsidiary minima associated with tg , gt , and gg conformations.

On the basis of (ϕ, ψ) plots and the conclusions of Yoon *et al.* [9] it was decided to investigate initially the forms of the intensity functions for polystyrene chains in regular tg , $t\bar{g}$ configurations, together with regular conformations based upon the potential minimum at $\phi = \psi = 20^\circ$. The function for distorted chains in areas I and II in Fig. 2 are considered later.

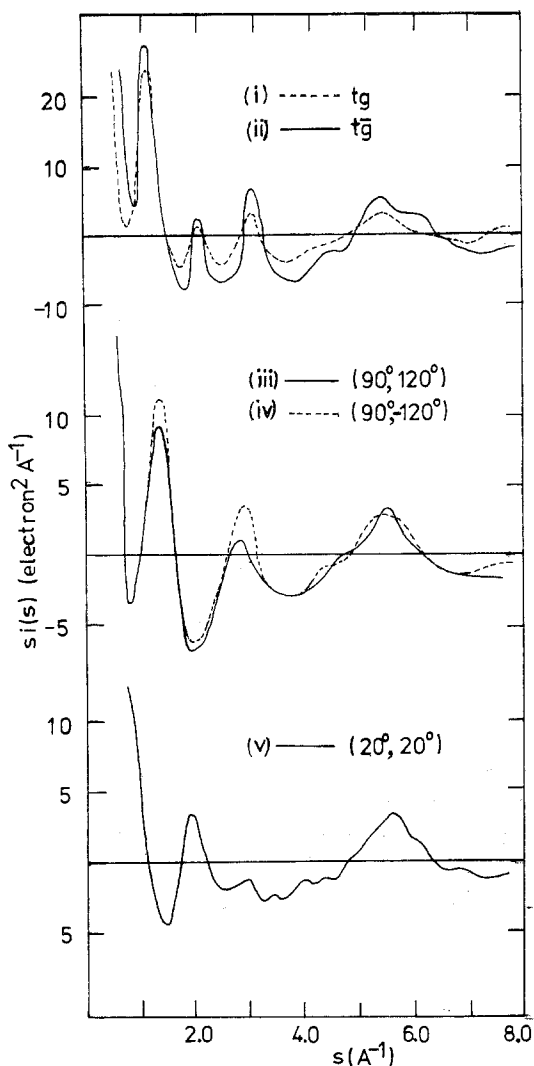


Figure 3 Theoretical reduced intensity functions calculated for isotactic polystyrene chains (12 phenyl groups) adopting, (i) tg , (ii) $t\bar{g}$, (iii) $(90^\circ, 120^\circ)$, (iv) $(90^\circ, -120^\circ)$, and (v) $(20^\circ, 20^\circ)$ conformations

4.2. Theoretical intensity functions: regular chains

4.2.1. Changes in chain conformation

Fig. 3 shows theoretical intensities calculated for a range of single isotactic chains (12 phenyl groups per chain), defined as follows: (a) $(0^\circ, +120^\circ)$, tg conformation (cf. Yoon *et al.* [9]); (b) $(0^\circ, -120^\circ)$, $t\bar{g}$ conformation; (c) $(90^\circ, +120^\circ)$, $\sim gg$ conformation; (d) $(90^\circ, -120^\circ)$, $\sim g\bar{g}$ conformation; (e) $(20^\circ, 20^\circ)$ conformation based upon the principal energy minimum for a meso dyad [9].

Similarities between functions describing left and right handed helices (tg and $t\bar{g}$ conformations) are not unexpected from considerations of symmetry; the relative orientation of adjacent phenyl groups will be similar although the structural

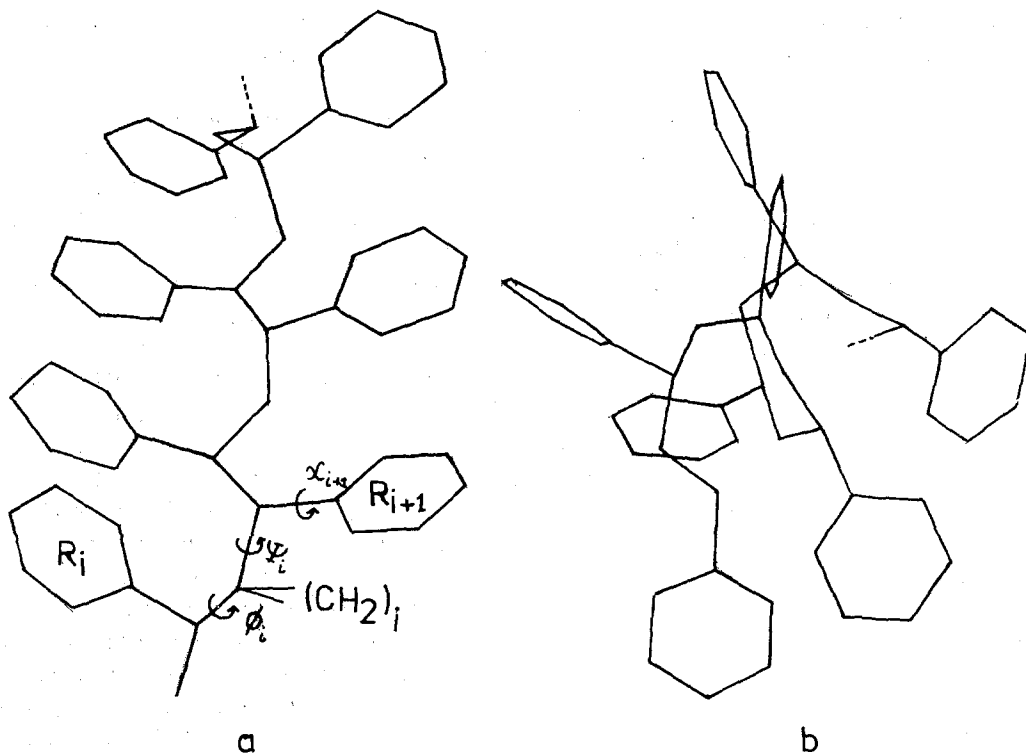


Figure 4 Molecular diagram showing isotactic chains adopting (a) $(90^\circ, -120^\circ)$ and (b) $(90^\circ, +120^\circ)$ conformations. Also shown in (a) are the three principal angles of rotation which allow the unique description of conformational changes.

relationship between R_{i+1} and $(CH_2)_i$ groups will be different (see Fig. 4a). The principal features within the theoretical functions (intensity peaks positioned at 1.1 , 2.0 and 3.0 \AA^{-1}) are not in agreement with those obtained experimentally (Fig. 1); this suggests that a notional regular structure in the form of a three-fold helix is unsuitable as a basis for the application of axial disorder in relation to the glassy state. It should be stressed that a statement of this kind rests upon the assumption that chain disorder in amorphous polystyrene does not completely obscure intensity features characteristic of the underlying regular conformation (see below).

In order to compare the experimental X-ray scattering from glassy polystyrene with the preferred structure from conformational energy analysis [9], a theoretical intensity function was calculated for an isotactic chain based upon the principal energy minimum observed by Yoon *et al.* ($20^\circ, 20^\circ$ in Fig. 2). This conformation, which allows sufficient separation of adjacent phenyl groups to relieve severe steric repulsions, is characterized by a broad maximum at $s = 1.9 \text{ \AA}^{-1}$ and

less well defined features in the range $s = 3.0$ to 5.0 \AA^{-1} . The principal features of the calculated curve are inconsistent with the form of the experimental function.

Theoretical intensity functions corresponding to chain conformations defined by positions $(90^\circ, 120^\circ)$ and $(90^\circ, -120^\circ)$ are also shown in Fig. 3; the former conformation is in the proximity of the *gg* minimum discussed by Yoon *et al.* There is a clear measure of agreement between these functions and the experimental data (calculated peaks positioned at $s = 1.6, 3.0$, and 5.5 \AA^{-1}) suggesting that disordered chain conformations based on these positions may provide an adequate structural description of amorphous polystyrene.

Drawings of atomic models of computer generated isotactic chains adopting $(90^\circ, 120^\circ)$ and $(90^\circ, -120^\circ)$ conformations are shown in Fig. 4, there being considerable differences in tertiary structure. The $(90^\circ, 120^\circ)$ conformation is characterized by a convoluted chain resulting in a tightly compacted structure. Alternatively, the $(90^\circ, -120^\circ)$ conformations results in a linear chain with approximately opposing adjacent phenyl groups.

4.2.2. Sensitivity of intensities to chain length

The influence of chain length was assessed by calculating intensity functions as examples, for single isotactic chains consisting of 1, 2, 4 and 8 crystallographic repeats ($t\bar{g}$ conformation); each repeat has three phenyl units. The analysis allows in principle an estimation of the longest region of rigid structure consistent with the experimental intensities; this is equivalent to the identification of a persistence length [20] with magnitude dependent upon the degree of axial disorder between successive monomer units.

The addition of regularly repeating units to a regular chain results in a progressive increase in detail in the intensity function, particularly in relation to the appearance and sharpening of peaks centred at $s = 1.1, 2.0$ and 3.0 \AA^{-1} (Fig. 5). For the longer chains, intensity modulations are also apparent in the region of $s = 4.0$ to 7.0 \AA^{-1} . The increased detail shown in the intensity functions for 4 and 8 repeat units (as compared with the results for smaller numbers) is inconsistent with the slowly varying profile of the experimental function calculated from the data of Wecker *et al.*;

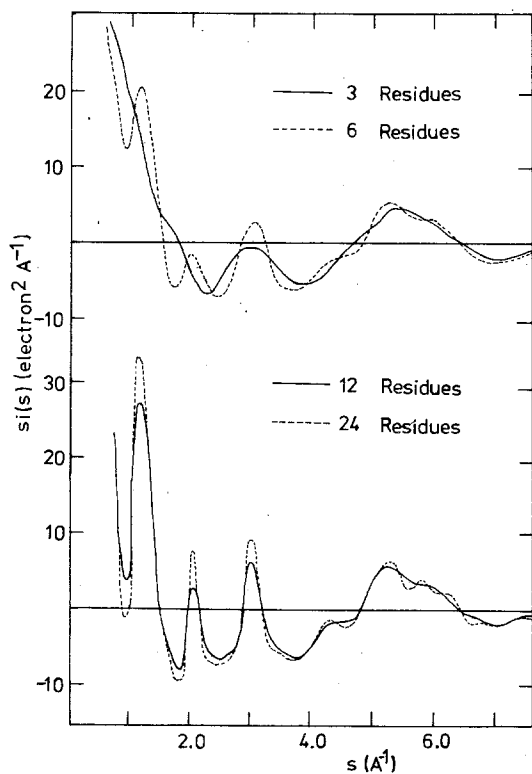


Figure 5 Theoretical reduced intensity functions for different lengths of extended isotactic chains ($t\bar{g}$ conformation).

such a comparison relies upon changes in the form of intensity features (height, sharpness etc.) rather than upon their position. On this basis, and without limitation to a particular model conformation, it appears that in the experimental sample any rigid structural order must be confined to regions of chain containing not more than 6 phenyl groups. Alternatively, the fine intensity features might be effectively 'smoothed out' by the application of a degree of axial disorder to a longer chain by means of distortions taking the form of single bond rotations. Further, it is significant that the onset of peaks characteristic of a three fold helix occurs for chains with 3 and more phenyl groups. For a string of 6 phenyl groups the peaks at $1.1, 2.0$ and 3.0 \AA^{-1} are very well defined. These observations have a central importance in the present study as they suggest that very long chains containing a relatively high degree of disorder (consistent with a short persistence length) will retain an X-ray scattering profile characteristic of the underlying regular structure.

4.3. Theoretical intensity functions: disordered chains

On the basis of the above results, as an example, disordered conformations (24 phenyl groups) described by the allowed region centred at $(90^\circ, -120^\circ)$ were investigated. Ranges of bond rotations $\Delta\phi, \Delta\psi$ about the $(90^\circ, -120^\circ)$ position were selected such that the sharp intensity features characteristic of X-ray scattering from long (or longer) chains were smoothed out. The ranges are not critical, and after some trials were restricted to the ranges $\phi = 75^\circ$ to 105° and $\psi = -100^\circ$ to -140° and values were selected within the ranges using a random number generator. Relatively few conformation rejections occurred (less than 20%), steric clashes being removed by sidegroup adjustment. Steric clashes, which in some cases resulted in conformation rejections, originated from the simplification involved in the enclosure of irregularly shaped allowed regions by rectangles (Fig. 2) involving the possibility of introducing unacceptable configurations. When considering the effect of non-adjacent phenyl groups on the (ϕ, ψ) plots the particular rotations ϕ_i and ψ_i under investigation were also applied to the next pair of linkage bonds in the chain. The consequence of avoiding a complete investigation incorporating four interdependent variables was therefore to introduce the possibility of steric clashes between second nearest

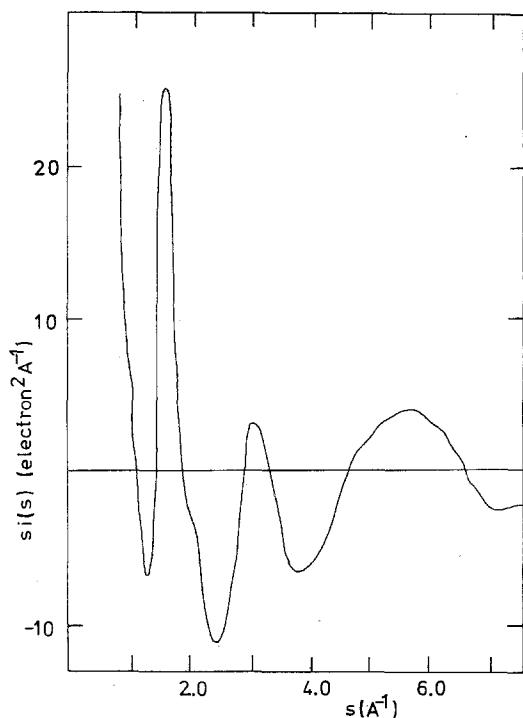


Figure 6 Averaged theoretical reduced intensity function for disordered isotactic polystyrene (24 phenyl groups).

neighbour phenyl groups when applying random rotations to any four successive bonds.

Fig. 6 shows a theoretical reduced intensity function averaged over five independent configurations of chains each containing 24 phenyl groups with bond angles defined within the above angular ranges. The overall form of this function and the experimental function are similar, there being three broad peaks occupying the regions of $s = 1.6$, 3.0 and 5.5 \AA^{-1} of the calculated function. The 3.0 and 5.5 \AA^{-1} peaks are at almost identical positions, there being a deviation of $s = 0.2 \text{ \AA}^{-1}$ between peaks in the 1.6 \AA^{-1} region. However, differences in peak shape are apparent as might be expected for a model system with a single starting configuration and with, necessarily, a small number of chains. In the theoretical function, as compared with the experimental function, the 5.5 \AA^{-1} peak is broader while the width of the 1.6 \AA^{-1} peak is relatively reduced. The heights of peaks at 3.0 and 5.5 \AA^{-1} within the theoretical function are greater, involving differences of 47% and 70% respectively and the heights of the 1.6 \AA^{-1} peak reduced as compared with the experimental result by approximately 25%. Similarly, minima at $s = 2.4$ and 4.0 \AA^{-1} show small differences. The averaged function which includes the effects of disorder

relative to a regular, $(90^\circ, -120^\circ)$ configuration, is therefore in much closer agreement with the experimental data than corresponding results calculated on distortion of, for example, a three fold helix. This suggests a more open structure for glassy isotactic polystyrene than earlier proposals [3], with a larger separation between phenyl groups.

4.4. Theoretical intensity functions: systematic changes in chain configuration

Having achieved a measure of agreement between the experimental and theoretical intensity functions, it was considered appropriate to investigate the X-ray scattering from various regular structures each representing a particular departure from a given initial regular structure. The starting configuration was chosen at the centre of the angular ranges within which disorder was constrained (Fig. 2). Functions were calculated for single isotactic polystyrene chains assuming configurations defined on the (ϕ, ψ) plot by a line joining the positions $(0^\circ, -120^\circ)$ and $(90^\circ, -120^\circ)$. Each chain consisted of 24 phenyl groups with a structurally regular configuration.

Fig. 7 shows intensity functions calculated for regular conformations defined at positions $(20^\circ, -120^\circ)$ and $(50^\circ, -120^\circ)$. Also shown is a theoretical function defined by the position $(90^\circ, -120^\circ)$ (the centre of region I). This describes sterically sound conformations for a single polystyrene chain assuming fixed side group orientation. The final intensity function in the series $(0^\circ, -120^\circ)$ is shown in Fig. 5 (8 crystallographic repeats) and corresponds to the three-fold helical conformation found in crystalline polystyrene. The changes in detail of the reduced intensity functions reflect the sensitivity of intensity features to conformational changes. These changes are manifested as the occurrence or removal of fine features within the intensity function together with changes in shape and the displacement of existing peaks. Further, by considering the variations of features apparent in intensity functions calculated for the $(0^\circ, -120^\circ)$, $(20^\circ, -120^\circ)$ and $(50^\circ, -120^\circ)$ configurations it is possible to deduce the origin of broader peaks observed for the $(90^\circ, -120^\circ)$ configuration.

In particular, the broad peak centred at $s = 1.6 \text{ \AA}^{-1}$ appears to be the result of the merging of peaks observed at $s = 1.25$ and 1.7 \AA^{-1} ob-

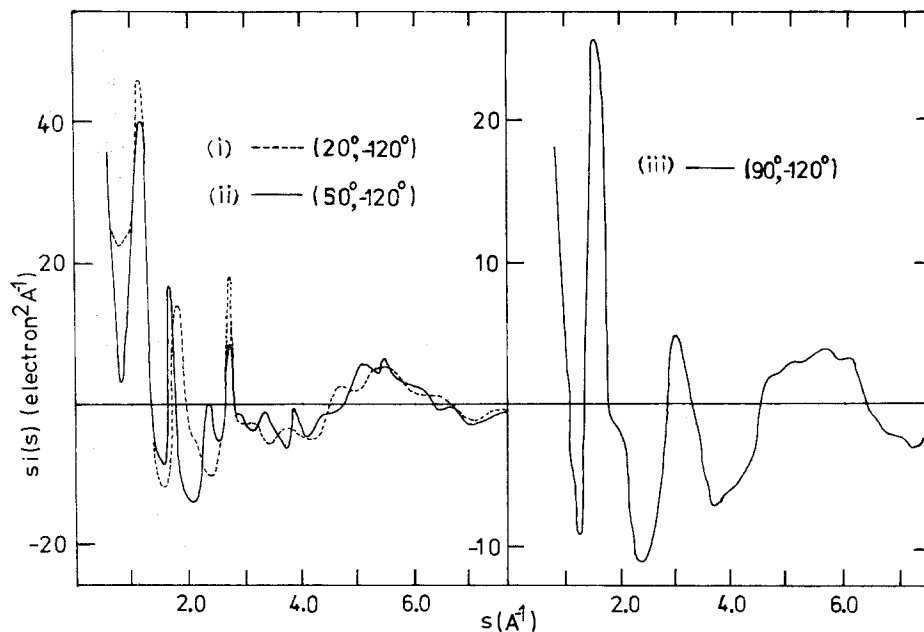


Figure 7 Theoretical reduced intensity functions for single isotactic chain formations (24 phenyl groups) defined by (i) $(20^\circ, -120^\circ)$, (ii) $(50^\circ, -120^\circ)$ and (iii) $(90^\circ, -120^\circ)$.

served for $(50^\circ, -120^\circ)$ configuration. These peaks have positions, $s = 1.1$ and 2.0 \AA^{-1} within the $(t\bar{g})$ intensity function, their separation progressively decreasing as ϕ increases.

However, as is apparent in Figs. 3 and 7, a systematic assessment of changes within the intensity functions with differing ϕ and ψ is not possible. Although the chain configuration in this series of calculations is altered in a regular manner the changes reflected in the intensity function are in general complex. However, the averaged intensity function calculated for disordered configurations defined within the region I of the (ϕ, ψ) plot appears to have a form associated uniquely with those positions defined within the \bar{g} region. This lends support to conclusions concerning likely isotactic polystyrene conformations, drawn from the measure of agreement between theoretical and experimental functions.

5. Conclusions

Wecker *et al.* [3] suggested that atactic and isotactic polystyrene adopt significantly different structural forms. They pointed out that atactic polystyrene may contain regions of syndiotactic linkage which make possible planar, staggered chain configurations involving maximum side-group separation. The small differences observed between radial distribution functions obtained for atactic

and isotactic polystyrene were attributed by Wecker *et al.* to the masking effect of a large number of similar interatomic distances. These were thought to originate from intra-phenyl group and phenyl group/main chain interactions which are independent of the tacticity of the polymer. Such a masking effect is difficult to reconcile with the sensitivity to conformation found in the present work using an intensity space approach.

A possible description of glassy polystyrene might be made in terms of a wide range of unrelated conformations without a predominant underlying defined structure. Such a possibility is not supported by the calculated intensity functions which represent essentially the structural relationships between adjacent phenyl groups. The addition of intensity curves arising from more than a limited range of fairly closely defined (Section 4.4) structural complexions would not produce a resultant curve with the sharp intensity peaks of the experimental distribution. On the other hand, it is unrealistic to expect that a model representing a range of distortions from a *single* regular starting point will provide a complete explanation for a complicated structure like glassy polystyrene. Nor is it realistic to assume that there are no other conformations within the stereochemically allowed regions (Fig. 2) besides those somewhat adventitiously identified here as giving reasonable,

rather than total, agreement with the experimental results.

If isotactic polystyrene, however, does assume predominantly the form of a disordered helix characterized by either or both the positions ($90^\circ \pm 120^\circ$) on the (ϕ, ψ) space, then only small differences between RDFs for the isotactic and atactic forms would be expected in agreement with experimental results. These small differences may be viewed in relation to phenyl group separations in atactic and isotactic polystyrene. Within the postulated planar regions of atactic polystyrene [3] the separation of phenyl groups associated with adjacent linkages takes a maximum value, successive groups being situated on opposite sides of the main backbone chain. The ($90^\circ \pm 120^\circ$) structures which provide a suitable basis for the application of disorder within the isotactic chain as indicated by the measure of agreement between calculated and experimental X-ray intensities, involve phenyl group separations which have magnitudes only slightly less than those of the atactic form. This suggests a distinct similarity between the two forms of disordered polystyrene and a common factor within a range of structural complexions.

Obviously any discussion of suitable conformations for glassy polystyrene must relate to determinations of conformational energy. Yoon *et al.* have suggested that conformations in solution within the \bar{g} domain are sterically unfavourable owing to repulsions between the phenyl ring and the backbone CH_2 group; energies throughout the \bar{g} domain were calculated to be at least 5kcal mol^{-1} greater than the principal *tt* minimum. On the basis of these calculations for a meso dyad, a two state rotational scheme ($\phi_t = 10^\circ, \psi_g = 110^\circ$) was considered appropriate for a structural description of polystyrene; by introducing the effect of solvent molecules preference was shifted away from the ($20^\circ, 20^\circ$) conformation.

The results of the present work for the solid state disagree with the predictions of Yoon *et al.* in the following respects:

(1) X-ray intensities calculated for the *tg* conformation (equivalent to the two state rotational system of Yoon *et al.*) are inconsistent with experimental data. The retention of intensity features characteristic of the *tg* conformation in calculations for short chains suggests that even in the case of a high degree of axial disorder the experimental function would provide evidence for the systematic

presence, as distinct from the occasional occurrence, of conformations derived from *tg* is present.

(2) The ($90^\circ, \pm 120^\circ$) conformations lead to reasonable agreement with experimental intensities but are inconsistent with the energy analysis of Yoon *et al.* In particular, the ($90^\circ, -120^\circ$) conformation lies within the \bar{g} domain. The ($90^\circ, +120^\circ$) conformation, relevant for the short chain lengths, cannot be discounted, however, especially in view of the lower value of conformational energy.

In summary, the results of this analysis suggest that the three-fold helix, although present in the crystalline phase, is an unsuitable description of short range structure in amorphous polystyrene. Further, model calculations based on a range of structural complexions, defined within the proximity of either *gg* or $\bar{g}\bar{g}$ conformations, and characterized by a large phenyl group separation, show reasonable agreement with experimental data. Such a view reconciles difficulties in a comparative interpretation of radial distribution functions for glassy atactic and isotactic polystyrene.

Other evidence concerning the overall chain conformation of glassy polystyrene includes the results of low angle neutron diffraction experiments [21] which suggest a radius of gyration of approximately 90 \AA for atactic polystyrene chains. It was also shown [22] that the radius of gyration determined for the bulk polymer is very similar to values published for dispersions of polystyrene in a solvent. Furthermore, the requirement for short chain lengths defined relative to an underlying regular conformation is consistent with an experimentally determined persistence length of 10 \AA which Wignall *et al.* [21] suggest eliminates the meander model of Pechold [23]. A consequence of this complementary work [21, 22] is the suggestion that inter-chain interactions do not contribute significantly to the total coherent scattering from polystyrene in the amorphous forms. This supports the earlier conclusions of Kilian and Bourke [8].

Lovell and Windle [24] have obtained "fibre type" X-ray diffraction patterns for aligned samples of atactic and quenched isotactic polystyrene. Their analysis which involved a numerical desmearing technique suggest that in atactic polystyrene, *tttt* and $(\text{ttgg})_2$ conformations occur in approximately equal proportions; for a syndiotactic linkage this will lead to a wide sidegroup separation. In contrast, diffraction data obtained from quenched isotactic polystyrene were consistent

with the occurrence of $(tg)_3$ conformations and possibly a small proportion of the isotactic equivalent of the $(ttgg)_2$ conformation found in the atactic case. On the basis of our investigations using an intensity space representation for the $(tg)_3$ conformation, we suggest that the alignment process is responsible for the introduction of chain conformations similar to those found in the crystalline case [16]. It is perhaps not unreasonable that the presence of syndiotactic linkages in atactic polystyrene should restrict any equivalent transition to 3/1 helices during alignment.

In conclusion, polystyrene appears to be a particularly good example of a structural class of polymers suitable for investigation using the intensity function method and the observed sensitivity to conformational change results from the presence of large sidegroups. Such side-groups produce a higher concentration of interatomic vectors over a given chain length, changes in their mutual orientation resulting in an effective redistribution of intensity allowing discrimination between different backbone conformations. The general applicability of the method applied to different polymer systems probably relates to the presence of structural groups of this type or any other structure within the backbone chain which allows an effective concentration of interatomic vectors.

Acknowledgements

We are grateful to Professor C. B. Cohen for the experimental scattering data for atactic polystyrene and for helpful suggestions, and to the Medical Research Council for a research studentship for R. A. and support for the general programme of work on bacterial cell wall structure. We would also like to thank Professor P. J. Flory for useful comments and Dr D. Armytage for much valuable discussion.

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Received 29 April and accepted 8 July 1977.