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Local Order in Polymer Glasses and Melts [and Discussion]

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Local order in polymer glasses and melts†

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The molecular organization of polymer melts and glasses remains a challenging area of polymer physics. Recent advances in simulation procedures and quantitative atomistic based X-ray and neutron scattering studies have shown most conclusively that the historical view of some level of local parallelism between chain segments to be ill-founded. There are, however, examples of properties and data which suggest that particular specific local correlations may be a widespread phenomena in disordered polymer systems. We explore how the issues of local order have moved on from a simple consideration of local parallelism of chain segments to a consideration of the relationship between the local chemical order and the molecular arrangements. The possibilities afforded by recent developments in broad Q neutron scattering and where appropriate using selective deuteration coupled with atomistic computer simulations are evaluated.

1. Introduction

Ever since the pioneering proposal of Staudinger that ‘polymers’ were long chain molecules there has been much speculation on the nature of the arrangements of such molecules in the molten and glassy states. The inherent connectivity of chain molecules coupled with the absence of three-dimensional translational order in melts and glasses poses real problems for any structural analysis. Initial concerns centred on the apparent impossibility of packing chain molecules in a dense structure without recourse to structures with high levels of local parallelism between chain segments. This view gained momentum from early diffraction studies (Stewart & Morrow 1927; Warren 1933) and continued to receive support from studies performed in the 1970s (see Mitchell 1989 for references). In fact diffraction studies on polymer melts and glasses before 1978 with the notable exceptions (Charlesby 1953; Voigt-Martin & Mijlhoff 1976), all concluded that some form of local order was required to explain the observed diffraction data. These proposals were made despite the overwhelming evidence for the random coil model proposed by Flory (1949); a concept extended to the solid state through properties such as rubber elasticity. The advent of atomistic modelling procedures for scattering analysis (Lovell *et al.* 1979; Mitchell *et al.* 1982) and off-lattice simulations of dense polymer structures showed that both the features of these early studies were incorrect. Detailed quantitative scattering analysis involving comparison between experimental and calculated scattering functions showed that,

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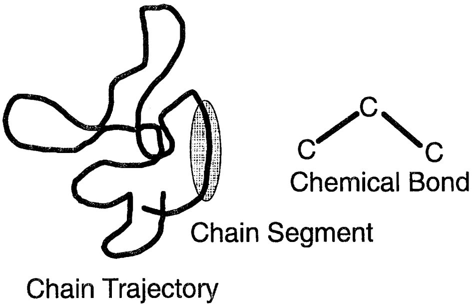

Figure 1. The different length scales relevant to molecular organization of polymer melts and glasses.

for materials such as molten poly(ethylene), any local parallelism between the chain segments must be minimal (Mitchell *et al.* 1982). Moreover the pioneering off-lattice simulations of Ryckaert *et al.* (1978) and Vacatello *et al.* (1980) showed most conclusively that it was possible to achieve structures of the correct density without any requirement for local chain parallelism.

These observations, together with the fact that small-angle neutron scattering studies of deuterium labelled mixtures of molten polymers confirm the essential features of the random coil model (Sadler 1989), give false expectation that all issues with respect to the structure of polymer melts and glasses are settled. Although, we know qualitatively that the configurations of long chain molecules are unperturbed by the requirements of dense packing, this observation provides no information as to the local arrangements of the polymer molecules. It is well established from computer simulations that the introduction of specific strong interactions between chain segments, through for example random copolymerization, still leads to random coil configurations albeit with expanded or restricted dimensions. In other words specific correlations, or local structure, can occur while still providing a random large scale chain configuration. Perhaps the most striking example of this behaviour involves protein molecules.

The recent progress in experimental techniques such as neutron scattering, and in atomistic computer based simulation procedures has resulted in a fresh examination of the local structure of polymer melts and glasses. In this contribution we explore how the issues of local order have moved on from a simple consideration of local parallelism of chain segments to a consideration of the relationship between the local chemical order and the molecular arrangements. Such considerations not only affect our approach to structure in both single and multiple component systems, but also the role of chain interactions in areas such as blends and deformation.

2. Local structure

The chemical connectivity inherent to a long chain molecule results in a number of significant length scales in any consideration of polymer organization.

These are shown schematically in figure 1. We shall be concerned with how the shortest length scale, namely that associated with chemical structure, manifests itself in the local organization of chain segments. Chain segments may be equated with a local persistence of conformation along the chain. The chain trajectory is an assembly of such chain segments. Of course for inhomogeneous materials such as semi-crystalline polymers (Bassett, this volume), liquid crystalline polymers (Windle, this volume) or phase separated blends (Higgins, this volume) there is an additional level of structure associated with the morphology of that inhomogeneity. Here we are concerned with materials which are homogeneous on the large scale as may be deduced from the absence of significant light scattering. The local structure considered here is on a scale of 1–50 Å and hence in terms of scattering on a scale of 0.2–50 Å^{-1}. The latter is often referred to in terms of wide-angle X-ray scattering or broad Q neutron scattering (cf. low Q scattering).

The basic building block for a covalent organic system is the chemical bond. It is the almost universal exhibition of rotation about covalent bonds that gives polymer systems their rich structures. It is usual to consider the possible torsional angles for a particular bond in terms of rotation states (Volkenstein 1963; Birshtein & Pititsyn 1966; Flory 1969) although such an approach need not be restrictive since in principle a large number of states may be considered. Even for systems such as poly(pyrrole), which exhibit just two rotation states, random, albeit planar, chain configurations will result (Mitchell *et al.* 1992).

For relatively simple polymers such as poly(ethylene) or poly(tetrafluoroethylene) the local chain structure or conformation is determined by the populations of the skeletal rotation states. In such cases we can envisage a typical chain segment with a shape anisotropy determined solely by the probabilities of the various rotation states. Various proposals have been made on the critical anisotropy factor which will mark the boundary between an isotropic melt and liquid crystalline order, for example (Bedford *et al.* 1992; Ronca & Ten Bosch 1991).

For chemically more complex polymers, such concepts may not be useful. In the case of poly(styrene) the bulk of the atoms are those associated with the side-groups, and if we extend our consideration to systems such as side-chain liquid crystal polymers, then the side-groups become the dominant feature. In other words for a system with large side-groups or other distinctive structures, it may be the interlocking of those groups to achieve the required density which represents the critical local structure.

In addition to the nature of the chain segment or local conformation we must also consider the interactions between chain segments both in terms of spatial and orientational order. Interchain interactions may arise, in the case of a long chain molecule, between segments belonging to the same chain and to those belonging to different chains as shown in figure 2.

The possibility of local correlation of segmental orientational order has been at the forefront of much structural analysis of polymer melts and glasses. However, we should not neglect the possibility of other particular or specific local interactions which may be much more prevalent than simply parallelism.

3. Evidence for local order

(*a*) *Rubber elasticity*

A most striking result was obtained by Deloche *et al.* (1986) in a study of the development of orientational order with mechanical strain in poly(dimethylsiloxane) based networks using deuterium magnetic resonance spectroscopic techniques. Deloche *et al.* found that similar levels of orientation were found for both deu-

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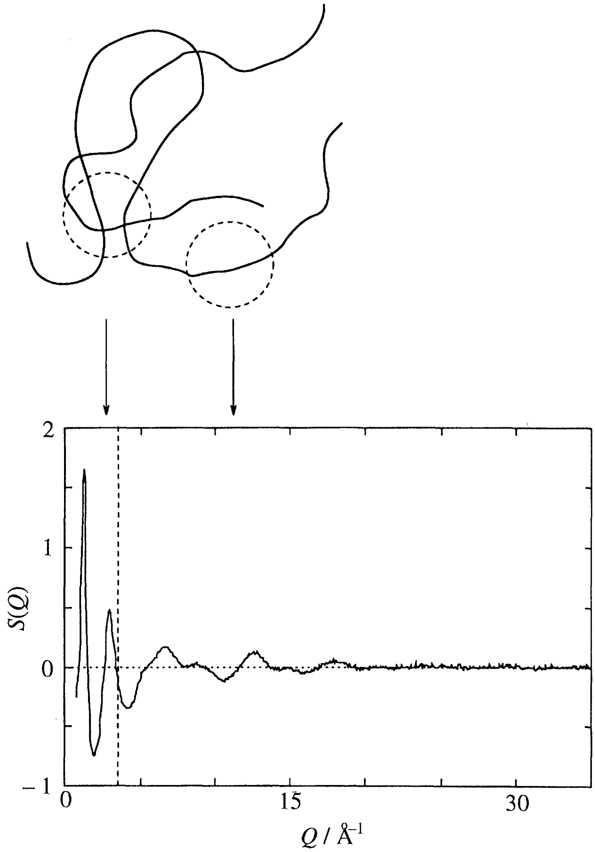

Figure 2. A schematic representation of the concepts of inter- and intrachain structure and their relationship to a broad Q neutron scattering pattern from molten poly(ethylene).

terium labelled chains chemically crossed-linked into the network and for those simply acting as guest molecules. Such a result challenges the notion in the classic approach to rubber elasticity, that all interactions act, in effect, through the movement of junction points. The orientation of the chemically unattached chain can only take place through local segmental interactions. This fascinating work focuses attention on such segmental interactions and therefore onto local order issues.

(*b*) *Miscible blends*

Much of the current work on polymer blends is associated with observations on the phase separation mechanism and little is directed at the more fascinating problem of why some polymer mixtures are miscible. The polystyrene-polyphenylene oxide system shows a negative volume coefficient on mixing (Paul & Newman 1978) and scattering studies have shown that local organization of the miscible blend is different to that displayed by polystyrene or polyphenylene oxide (Mitchell & Windle 1985).

Figure 3 shows the scattering curves for the homopolymers and for a blend of poly(styrene) and poly(phenyleneoxide) (Rosi-Schwartz 1994, unpublished work).

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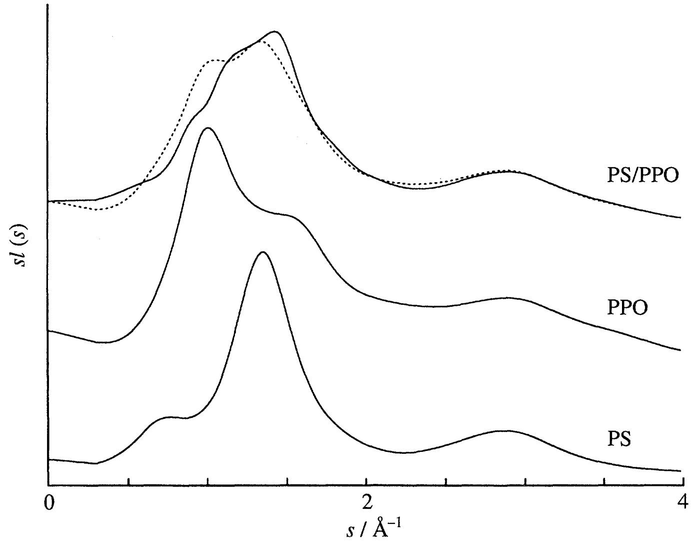

Figure 3. Wide-angle scattering patterns of poly(styrene), poly(dimethylphenyleneoxide) and a 43/67 blend showing the synergistic behaviour of the scattering patterns. The dotted line is obtained by adding the curves for the homopolymers with the appropriate weightings.

The change in structure on blending may be observed by comparing the scattering curve for the blend with that for a 'mixture' obtained by adding the functions for the homopolymers with appropriate weightings. A similar synergism has been observed in the scattering for series of mixtures of styrene and methacrylate formed by copolymerization (Mitchell *et al.* 1990). It is widely accepted that for most blends, strong specific and hence local interactions are required to stabilize miscibility in polymer mixtures. If this is the case then are such specific local structures present in all disordered polymer systems? In other words, we could consider all disordered polymer chains as random copolymers, in which the 'different' units reflect their conformational state and their environment. Such variety in chain segments would result in a considerable variation in the interaction parameter for particular pairs of segments. The structure of random walks in disordered media is topical activity and there may be much to learn from such theoretical studies in which the chemical detail is excluded.

(*c*) *Scattering studies*

Historically much of the evidence for ordered arrangements in polymer melts and glasses has arisen as a result of scattering studies as highlighted in the introduction. It has been shown that in many instances the basis of such conclusions was ill-founded (Lovell *et al.* 1979). However, there are examples of studies of systematic series of polymers which point to the possibilities of local order or special correlations (Miller 1987; Mitchell 1987; Mitchell 1989; Windle 1985), although detailed analysis has not been performed. The particular examples cited involve a series N-alkylmethacrylates (Miller 1987) and a set of polymers containing phenyl rings in their backbones, for example polycarbonate, polyetheretherketone (Mitchell 1989; Windle 1985). The former show a systematic variation in the position of the diffuse maxima in the wide-angle X-ray scattering patterns with increasing length of the alkyl chain length. All the scattering patterns for the phenylene based polymers exhibit a diffuse maxima which was thought to arise from some face-to-face correlations of the aromatic rings.

In X-ray scattering studies of glassy atactic poly(styrene), Mitchell & Windle (1984) proposed that the unusual scattering pattern and its temperature dependence could be explained through a model in which the aromatic rings were segregated on a local scale. Each of these examples highlights the possibilities of some local correlations, each of which is specific to the chemical nature of the particular polymer. Small-angle neutron scattering studies of mixtures containing deuterium labelled chains have shown qualitatively that the trajectories of polymer chains in the melt are not grossly perturbed by the dense packing, for example (Cotton *et al.* 1974; Yoon & Yoon 1976). However, such studies have not been quantitatively pursued and it is unclear what deviations from the random coil model are possible, particularly with regard to local correlations, while retaining good agreement with the neutron scattering data.

4. Scattering approach

The quantitative relationship between the observed scattering, albeit X-ray or neutron based, and the structure is well established. Let us consider the situation in neutron scattering. In the so-called static approximation the measured intensity is proportional to the differential scattering cross section, which in turn can be related to the static structure factor $S(Q)$ characterizing the system. In the simple case of a disordered system composed of N identical nuclei, the differential scattering cross section is given by the following relationship:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = Nb^2 S(Q), \tag{4.1}$$

where b is the scattering amplitude of the identical nuclei and the amplitude of the momentum transfer $\boldsymbol{Q}$ is given by the relationship $Q = 4\pi \sin\theta/\lambda$, 2θ being the scattering angle and λ the incident neutron wavelength. $S(Q)$ is defined as the spatial Fourier transform of the atomic pairwise correlations functions,

$$S(Q) = 1 + \rho_0 \int_0^\infty (g(r) - 1)\mathrm{e}^{\mathrm{i}Qr}\mathrm{d}r, \tag{4.2}$$

where ρ_0 is the average density of the system and $g(r)$ is the pair distribution function, expressing the probability that there exists an atom at a distance r from the origin atom. The radial distribution function and, similarly, $S(Q)$ are split into partial terms for systems containing more than one chemical species.

The structure factor $S(Q)$ is readily determined from the experiment (equation (4.1)), while a model structure factor can be easily derived (equation (4.2)) if the coordinates of the atoms within the model are known. Hence one approach to structural analysis is to devise an algorithm for the generation of atomistic models which are quantitatively evaluated by comparison of their calculated structure factor or radial distribution function with the experimentally derived functions. An alternative approach is to use the scattering data to drive the optimization of the model in a similar manner to that used in energy minimization or Monte Carlo simulations. An example of this approach is described in § 6.

Of course if particular peaks in the experimental real or reciprocal space functions may be identified with features of the structure, it becomes possible to perform direct analysis. However, it is usually only the very local chemical structure which can be deduced in this manner from a consideration of the peaks in the radial distribution function and for a polymer this is usually known in advance. Thus little of the useful intermediate or local structure can be determined directly and hence structural analysis must involve atomistic models.

A great variety of approaches have been used to construct atomistic models. The convenient division in reciprocal space into interchain and intrachain components depicted in figure 2 means that useful analysis may be performed on 'single' chain models as well as dense space filling volumes containing one or more chains.

5. Local chain conformations

We have identified the chain segment as one of the possible building blocks for a polymer melt or glass structure. In this section we consider examples of studies of the local chain structure using broad Q scattering data. The major problem of simulating a polymer chain, thereby describing its conformational correlations, arises because of the internal rotations in molecules. The description is greatly simplified by adopting the rotational isomeric state in which the chain is represented as an equilibrium mixture of the various states, each of which is characterized both by its torsional angle value and by its probability of occurrence. In general these probabilities will be conditional in nature, since the probability for a bond to be in a given isomeric state will depend upon the state associated with the bond's nearest neighbours.

(*a*) *Flexible chains*

The local structure of molten poly(ethylene) has been studied extensively. Successive structural analyses using scattering techniques have confirmed that molten poly(ethylene) consists of highly disordered polymer chains in which the probability of the trans rotation state is 0.50–0.60 (Mitchell *et al.* 1982; Voigt-Martin & Mijlhoff 1976; Narten *et al.* 1992; Misawa *et al.* 1991). Rosi-Schwartz & Mitchell (1994*a*) have developed a quantitative approach to conformational analysis using scattering data. The procedure involves building successive random chains according to particular rules, e.g. bond lengths, valence and torsion angles, rotation states probability matrix. The structure factor $S_{\mathrm{C}}(Q)$ calculated from the model chain is then quantitatively compared to the experimental pattern $S_{\mathrm{E}}(Q)$ via the following χ^2 test:

$$\chi^2 = \frac{1}{n_Q}\sum_{i=1}^{n_Q}(Q_i S_{\mathrm{C}}(Q_i) - Q_i S_{\mathrm{E}}(Q_i))^2, \tag{5.1}$$

where n_Q is the number of Q points in the scattering curve. Obviously this comparison takes place over the portion of scattering pattern containing no appreciable contributions from interchain correlations, namely over Q values higher than *ca.* 2 Å^{-1}. Several models can be built by varying the different parameters defining the simulated chain. The χ^2 corresponding to each generated chain will then measure the accuracy of the model in describing the conformational correlations in the real polymer chain. The most accurate model will simply be the one corresponding to the minimum χ^2 value obtained. This procedure provides twofold information: on the one hand the effect of that particular parameter on the overall structure factor can be studied; on the other hand it is possible to adjust the single chain model of the polymer to 'fit' the experimental results.

By systematically searching throughout the possible parameter space, sets of parameters, which yield the best fit to the data, may be identified. Ward & Mitchell (1994) have applied these techniques to the neutron scattering data obtained for deuterated molten poly(ethylene) over an extensive Q range, namely 0.2–50 Å^{-1}. This analysis confirmed the results of previous scattering studies using X-ray scattering data from a more limited Q range. In essence, in the melt, the chain segments consist of three to four skeletal bonds in the trans conformation which exhibits an equi-axed shape. In that analysis, the concept of rotation states was found to be useful and provided an adequate representation of the conformational properties of the poly(ethylene) chain.

In contrast, earlier X-ray scattering work by Mitchell & Mitchell on molten poly(dimethylsiloxane) showed that for such systems the rotational isomeric state model was inadequate for providing a proper description of the local conformation (Mitchell & Odajima 1984). Through comparison between experimental data and scattering functions calculated from atomistic models, Mitchell *et al.* showed that a chain with largely freely rotating bonds provided the best fit to the data. This contrasts with the conclusions drawn from consideration of properties associated with the large scale configuration of the chains (Flory 1969). This study of poly(dimethylsiloxane) highlights the more exact nature of conformational analysis when considering the local structure. Moreover, it draws attention to the necessity of local distortions in the structure when considering excluded volume effects. The original concern about the problems of dense packing largely arose from the prospect of organizing chains with rotation states distributed in an *a priori* manner. The problem of packing high irregular but rigid objects such as tree branches is well known to all. However, if during growth, such irregular objects are exposed to excluded volume effects then high densities are possible. Such high densities are obtained by the introduction of specific distortions (i.e. bond rotations) into the object. Although such distortions, if independent, will average out over a large distance, locally they remain specific.

(*b*) *Stiff chains*

If polymer chains are sufficiently stiff, i.e. a high persistence of a particular conformation, they may form liquid crystal phases with a high level of orientational order between chain segments. Molten poly(tetrafluoroethylene) is thought to exhibit a chain stiffness at the border of liquid crystal behaviour (Ronca & Yoon 1982). Rosi-Schwartz & Mitchell have used the quantitative approach using broad Q neutron scattering coupled with atomistic modelling, briefly described in the previous section, to provide a concise description of the local conformation of molten poly(tetrafluoroethylene) (Rosi-Schwartz & Mitchell 1994*a*). Model chains were constructed using set bond length, valence and torsion angles, and conditional probability matrix and the calculated structure factor compared with the experimental data through the χ^2 test in equation (5.1). By systematically searching throughout the possible parameter space, sets of parameters, which yield the best fit to the data, may be identified. An example of the procedure used is shown in figure 4 in which the χ^2 is plotted as a function of the trans tor-

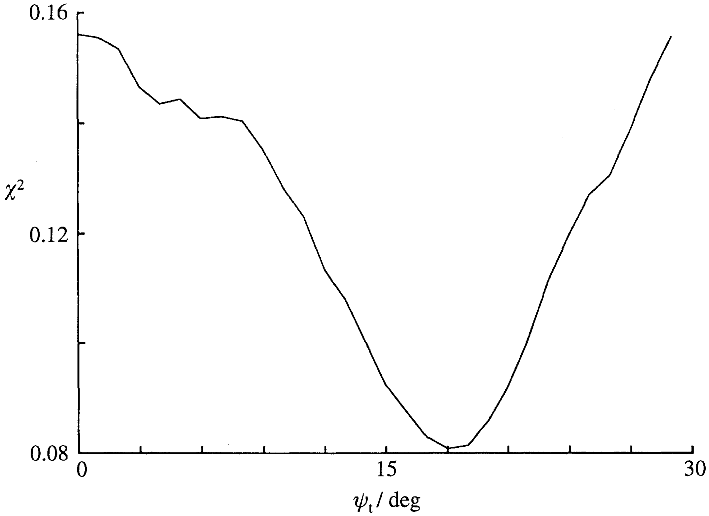

Figure 4. A plot of χ^2 obtained in comparison of the experimental and calculated structure factors for models of poly(tetrafluoroethylene) against the skeletal torsion angle used to generate the model chains.

sion angle. Clearly a minimum value of χ^2 is obtained when the angle is twisted away from the planar zig-zag arrangement.

This analysis showed that the poly(tetrafluoroethylene) chain in the melt could be characterized by four rotation states, in which the probability of a trans conformer was *ca.* 0.86. This gives rise to chain with extended chain segments with an aspect ratio of *ca.* 3.2, which reassuringly, is below the minimum suggested by Bedford *et al.* (1992) for the formation of a liquid crystal phase. A projection of one chain constructed according to these rules is shown in figure 5. It is interesting to note that force fields used in current atomistic modelling severely mis-estimate the conformational characteristics of poly(tetrafluoroethylene), in particular the twisting of the trans conformer away from the planar arrangement, shown clearly by the scattering analysis (figure 4), is not reproduced by such force fields (Rosi-Schwartz & Mitchell 1994*a*). This emphasizes the importance of validation in any significant atomistic simulation.

This study of molten poly(tetrafluoroethylene) highlights the precision possible with the current structural analysis procedures using broad Q neutron scattering data coupled with appropriate quantitative atomistic modelling procedures especially for systems with a highly persistent conformation.

The X-ray scattering study of Lovell *et al.* on glassy poly(methylmethacrylate) showed a similar persistence of chain conformation, consisting of largely all-trans conformation extending over some 20 Å (Lovell & Windle 1981). However, in this case the steric crowding arising from the multiple substitution in the backbone leads to an increase in the valence angle about one of the skeletal carbon atoms in the repeat and hence a curved chain segment. Such an analysis has been confirmed by recent broad Q neutron scattering by Ward & Mitchell (unpublished work, 1994). The nature of the curved chain segment for poly(methylmethacrylate) not only raises intriguing questions of how such curved chain segments pack in a dense glass, but also draws attention to the specific nature of local structure. Clearly

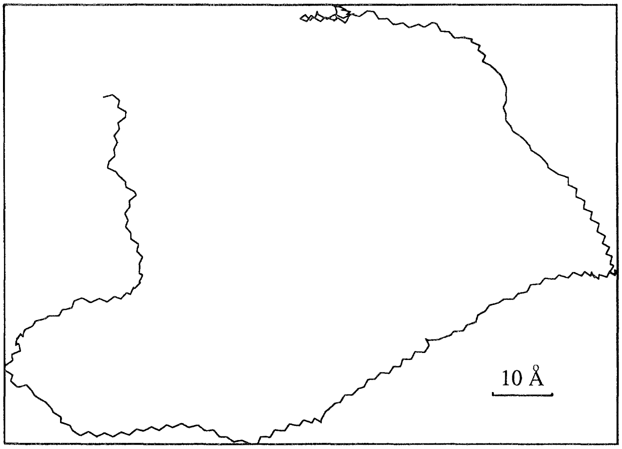

Figure 5. Typical chain trajectory for molten polytetrafluoroethylene generated using the geometrical information and the conditional probability matrix obtained from the scattering analysis described in the text.

the possibility of parallelism is almost irrelevant for poly(methylmethacrylate), but this does not exclude the possibility of other local correlations specific to poly(methylmethacrylate).

(*c*) *Chains with bulky side-groups*

Scattering studies of polymers with bulky sidegroups have largely been unsuccessful. The dominating influence of the side-groups on the scattering pattern results in little sensitivity of the calculated scattering functions to variations in the backbone conformation. A wide-angle X-ray scattering study of poly(styrene) was unable to identify any particular local conformations although highly regular sequences could be ruled out (Mitchell & Windle 1984). Rosi-Schwartz *et al.* have developed a novel approach to this problem using the particular advantages of selective deuteration to yield specific partial correlation functions which may be more sensitive to the backbone conformation, since the contributions from the side-groups have been removed using the complete set of experimental data (Rosi-Schwartz & Mitchell 1994*c*; del Val *et al.* 1992). This approach is discussed in more detail in § 6.

6. Interchain correlations

The breadth of the diffuse interchain peaks in scattering patterns from polymer melts and glasses (for example figure 2), typically $\Delta Q \approx 0.3$–0.5 Å^{-1}, indicates particularly limited spatial correlations between chain segments. For most materials such limited spatial correlations extend over three to four chain segments. Early diffraction studies of interchain correlations had to rely on subjective formulas or in the case of quantitative models, approximations were used to yield the interchain scattering. The rapidly developing field has provided more satisfactory procedures through either complete atomistic models, for example (Clarke & Brown 1994), or through analytical solutions to the classic approach used in simple fluids via the Percus–Yevick formulation (Hansen & 1986). In the following sections the success of these approaches is considered and the possibilities for more complex systems examined.

(*a*) *Flexible chains*

Previous X-ray diffraction experiments on molten poly(ethylene) (Mitchell *et al.* 1982) used an approximation for the interchain correlations based on the random packing of spheres. Such analysis indicated that any orientational order must be minimal. This type of approach has been considered in a more formal manner for molten poly(ethylene) in terms of the recently developed polymer reference interaction site model (Schweizer & Curro 1987; Curro & 1987). This allows a calculation of complete scattering or correlation functions using an analytical form for the interchain correlations. Indeed such an approach allows a separation of the interchain contribution to be made (Narten *et al.* 1992; Honnell *et al.* 1991).

The methods for generating bulk atomistic models, albeit for a cube with length 20–30 Å, are now widely established for example (Roe 1991). In such models a low energy atomistic model is obtained using Monte Carlo or molecular dynamics procedures (Clarke & Brown 1994). Although in principle any starting configuration could be used a number of studies have used the so-called amorphous growth procedure which is now available through commercially available software packages (e.g. QUANTA from Molecular Simulations, Burlington, U.S.A.). In a recent study, Rosi-Schwartz & Mitchell (1994*b*) created bulk polyethylene specimens by placing a PE chain in a unit cell and by representing other chains as images in the same cell through the use of periodic boundary conditions. A 700 CH_2 monomer chain was grown in an amorphous structure in a cubic box, whose dimensions were determined by the required bulk density, which gave a cell dimension of *ca.* 28 Å. The amorphous growth algorithm used generates the polymer by placing one repeat unit, or residue, at a time, till the complete chain is packed in the cell. Torsion angles are assigned values by random sampling, according to a RIS model, representing the equilibrium conformational states of the polymer. The energy added through the placement of each residue is then computed. If the new conformation is of lower energy, then it is selected; if it is of higher energy, it is accepted with probability equal to the Boltzmann factor $\exp(-\Delta E/k_BT)$, where T is the temperature of the system, k_B is the Boltzmann constant and ΔE is the energy difference between current and previous conformations. If the conformation is rejected, the random placing process continues until a new conformation is accepted or a specified maximum number of trials is reached. In this last case, the previous residue is erased and randomly placed again, according to a procedure called ‘backtracking’. The structure generated by such procedures are in a high energy state, and therefore unrealistic, mainly due to the steric interactions related to non-bonded Van der Waals forces. Minimization and molecular dynamic procedures were used to drive the model towards equilibrium.

The structure factors calculated for models prepared in that manner were in good agreement with the observed structure factor for molten poly(ethylene). A potential hazard with these amorphous growth procedures arises from the fact that the local conformation is modified by the excluded volume interactions. It is therefore quite likely that the conformation of the chain at the start of growth will be different to that at the end of the growth cycle. A second restriction of such simulations is that they depend critically on the force fields used in the calculations of the energy as each residue is added and in the force calculations during the subsequent molecular dynamics. Essentially, the force fields represent small scale structure rules, from which the larger dense polymer structure is constructed. The comparison between the calculated scattering and the experimental data serve to validate the model if good agreement is reached and hence validate the force fields chosen. It is a weakness in many such simulations in the literature that quantitative comparisons of the calculated structure factor with experiment are not made.

We have adopted a second approach in which we use the scattering data to drive the model (Rosi-Schwartz & Mitchell 1994*b*). This is a reverse Monte Carlo type procedure in which random moves applied to individual atoms in the starting structure are accepted or rejected on the basis of whether such a move increases the match between observed and experimental data, in other words whether χ^2 in equation (5.1) is reduced. In a conventional Monte Carlo type simulation such moves are accepted or rejected on the basis of the calculated energy. The reverse Monte Carlo type of approach has been successfully exploited in the field of simple fluids and amorphous metals (McGreevy 1993). We have used as a starting point models built using the amorphous growth procedures described above, but without any minimization or molecular dynamics cycles. The initial fit is very poor, but after some 10^7 moves the χ^2 reaches a plateau value. Of course it is expected that an excellent fit is obtained and indeed this is the case. To produce this model we have simply defined the coordination numbers for each atom, the final model is based entirely on the scattering data with no input based on force fields. Evaluation of the model in terms of bond lengths, bond angles and torsion angles yields the expected results (Rosi-Schwartz & Mitchell 1994*b*) and these are the same as observed in models in which the optimization has been driven in terms of energy calculated from specific force fields. The fact that both approaches, based on quite different criteria yield equivalent models suggests that we should have strong confidence in the results.

From such an atomistic model we can calculate parameters which can not be directly obtained from the experimental observation. A key parameter is the local orientational order calculated as sketched in figure 6.

Chain segments (i and j in figure 6) are identified by three backbone atoms. 'Directors' are then associated to each segment and the distance r_{ij} between each pair of chain segments is calculated. The orientational order parameter $f(r)$, averaged over all chain segments, is finally evaluated:

$$f(r) = \langle \tfrac{1}{2}(3\cos^2 \alpha_{ij}^r - 1)\rangle_{ij}.$$

Figure 6 shows a plot of $f(r)$ as a function of r. The most prominent features of this curve, i.e. the first three narrow peaks, merely represent intrachain correlations arising from regularities within the chain. The interchain orientational correlations are represented by the broad peak centred on a distance scale of about 4 Å. It is significant that a peak corresponding to second nearest neighbours is not observed. The low value of 0.1 is in agreement with earlier X-ray investigations (Mitchell *et al.* 1982; Mitchell et al 1980). This level of orientational order may be thought as arising from an excluded volume effect around the near neighbour chain segments. In other words, as anticipated there are no substantial local orientational correlations in molten poly(ethylene)

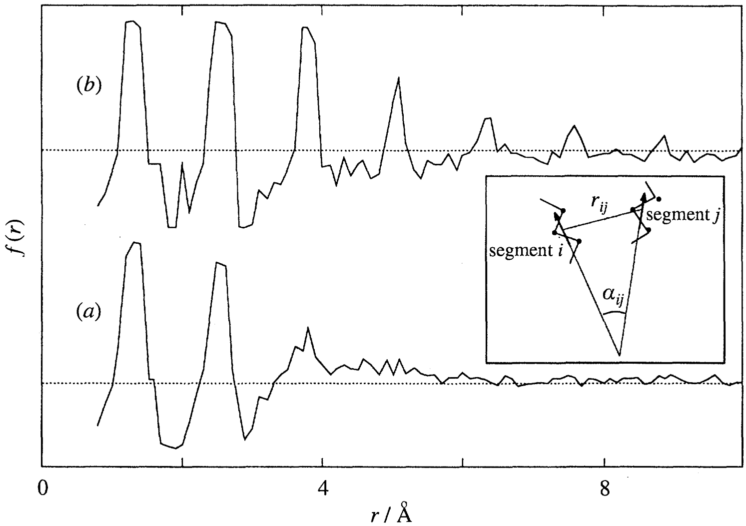

Figure 6. Orientational correlation function $f(r)$ plotted as a function of distance r for the model structures described in the text for (a) molten poly(ethylene) and (b) poly(tetrafluoroethylene).

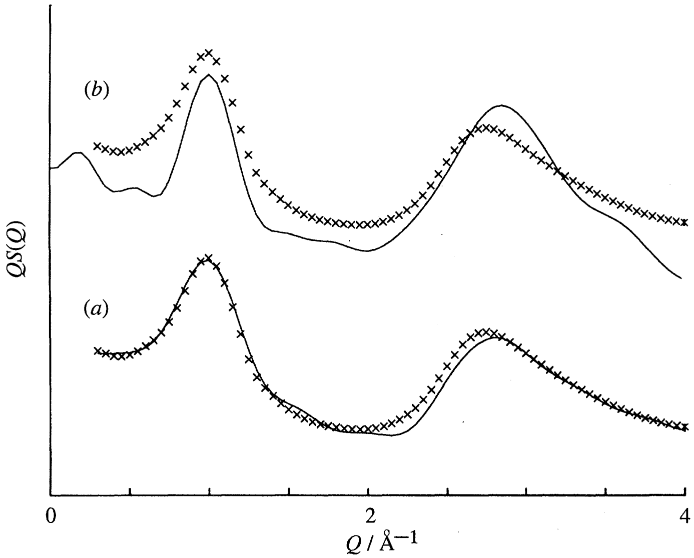

Figure 7. A comparison of the experimental structure factor for molten poly(tetrafluoroethylene) with those calculated from models (a) a model generated using the reverse Monte Carlo procedure described in the text with minimal orientational correlations (b) a model with a high level of orientational order.

(b) *Stiff chains*

We have applied a similar procedure to that described in the preceeding section to the structural analysis of molten poly(tetrafluoroethylene) (Rosi-Schwartz & Mitchell 1994a). Models built using the amorphous growth procedure provide structure factors which are in poor agreement with the observed data. However, models produced as a result of the reverse Monte Carlo showed excellent fit between the observed and calculated structure factors as shown in figure 7

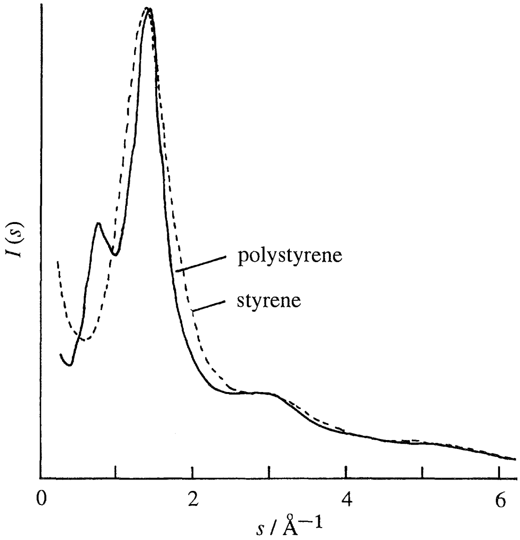

Figure 8. A comparison of the wide-angle X-ray scattering curves for styrene and glassy atactic poly(styrene).

Evaluation of the model in terms of bond angles and lengths together with torsion angles yielded values similar to those obtained in the single chain analysis described in § 5. Figure 6 shows a plot of the orientational correlation function $f(r)$ defined as for the poly(ethylene) study. It is clear that the level of orientational order observed for molten poly(tetrafluoroethylene) is very similar to that found for molten poly(ethylene), that is minimal. This lack of orientational order is perhaps surprising given the anisotropic chain segments. However, inspection of a model shows that for relatively stiff segments, in a non-ordered model, segmental orientational order will inevitably be lower than that for systems with highly flexible chains. This is, in part, the origin of an interesting correlation shown, for a series of chemically different polymers, between the extent of spatial correlations in a polymer melt and the glass transition temperature in which the 'order' drops as the glass transition of the polymer rises (Mitchell 1987).

To reinforce the excellent fit shown in figure 7*a*, a comparison is shown in figure 7*b* between experimental data and structure factors derived from models built with a high level of segmental orientation. It is clear that such models do not provide a particularly satisfactory fit (Rosi-Schwartz & Mitchell 1992).

(*c*) *Chains with bulky side-groups*

We have set out to develop procedures based on the amorphous growth approach for the construction of atomistic models of glassy atactic polystyrene. Although models produced in this way provide structure factors which qualitatively match the observed functions, such structure factors do not exhibit the distinctive peak in the scattering pattern for polystyrene at $Q \approx 0.7$ Å^{-1}. In fact this peak is one of the few differences between the scattering pattern observed for the monomer styrene and the resultant polymer as shown in figure 8.

It essential therefore that any realistic polymeric model of glassy poly(styrene) reproduces this feature. The fact that it corresponds to a length scale of 8–12 Å

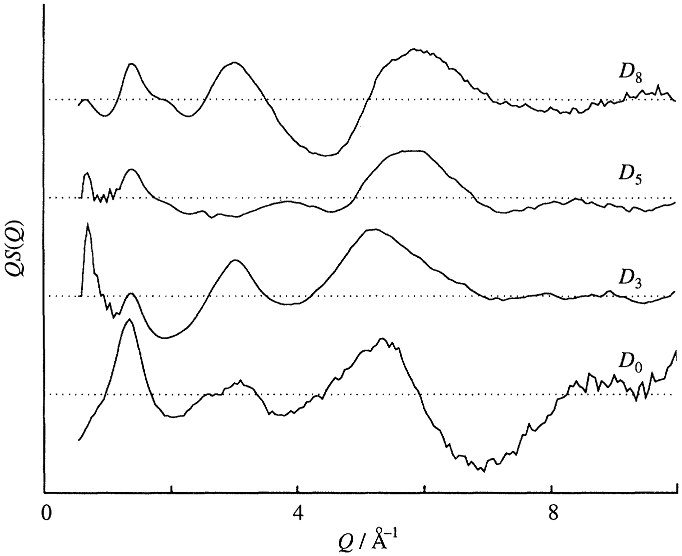

Figure 9. The structure factors for selectively deuterated glassy atactic poly(styrene) obtained by using neutron scattering procedures.

means that any model will need to be sufficiently large to satisfactorily reproduce this type of correlation. As a consequence we have adopted a new experimental approach which attempts to differentiate between the various structural correlations present in glassy polystyrene (del Val *et al.* 1992; Rosi-Schwartz & Mitchell 1994*c*). In a polymer such as poly(styrene) we can partition the structure into the polymer backbone and the side group. As a consequence the structural correlations may be represented by several partial correlation functions each related to interactions between the specific sites, i.e. $g_{\rm bb}(r)$, $g_{\rm bs}(r)$, $g_{\rm ss}(r)$ where b denotes the backbone site and s is the side-group site. We may access these partial correlations in the same manner as atomic partial correlation functions are obtained from the scattering from polyatomic fluids, namely through isotopic substitution or by anomalous scattering.

The latter is not really possible for hydrocarbon systems and so we have adopted selective deuteration as the way forward. Accordingly broad Q neutron scattering data was obtained for four glassy polystyrene samples with differing levels of deuteration labelled as D0, D3, D5 and D8 in which the number denotes the level of deuteration in terms of a monomer unit. The resultant structure factors are shown in figure 9. Such quantitative measurements over a broad Q range of polymers with a significant hydrogen content and hence a large incoherent background, are only possible with recent advances in neutron instrumentation, in this case at ISIS, Rutherford Laboratory, U.K. (Rosi *et al.* 1992). The changing levels of deuteration clearly result in substantial changes to the structure factor, although X-ray scattering measurements revealed that each sample exhibited an equivalent structure. Manipulation of these functions yields a partial correlation function in which only the correlations involving atoms in the backbone unit are included; we have labelled this $S_{\rm bb}(Q)$ and the corresponding real space function as $g_{\rm bb}(r)$. Figure 10*a* shows the radial distribution function obtained by Fourier transformation of the structure factor for D8; this includes all correlations. Figure

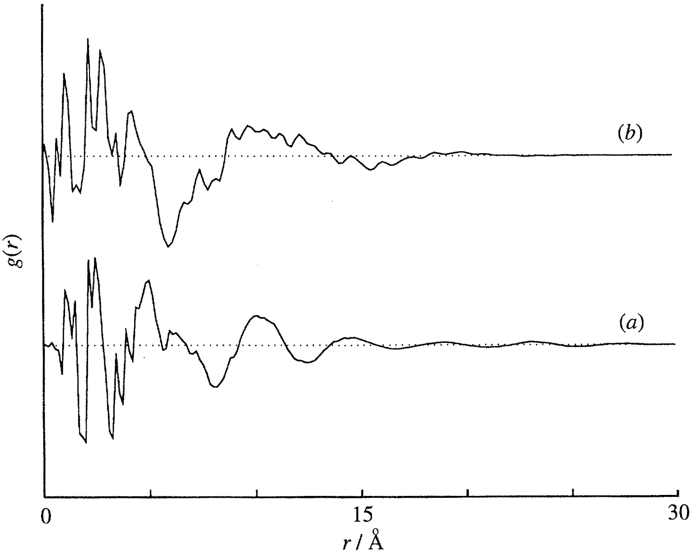

Figure 10. Real space correlations functions for glassy PS (*a*) total correlation function for D8, (*b*) partial correlation function g_{bb} describing the correlations involving the backbone atoms only.

10*b* shows the corresponding pair correlation $g_{\mathrm{bb}}(r)$ for the backbone sites. Comparison with model functions (Rosi-Schwartz & Mitchell 1994*c*) confirms that the short range peaks in $g_{\mathrm{bb}}(r)$ correspond to the intrachain correlation involving just the backbone atoms. Using such an approach, a detailed conformational analysis will be possible and this work is in progress. The partial correlation function shows a broad feature at $r \approx 10$–12 Å, which is clearly not discernible in the total correlation function and illustrates the particular power of the new approach to structural studies. This corresponds to the correlations between the polymer backbones.

It is noticeable that it is a broad and weak peak indicating very limited backbone correlations. This feature is much weaker than the corresponding features in simple polymers such as molten poly(ethylene) or poly(tetrafluoroethylene). We may conclude that no substantial chain segment correlations are present in glassy polystyrene. Moreover, it suggests that the correlations between the side-groups are the overiding features as proposed previously (Mitchell & Windle 1984) and thus the polymer chains are forced into highly disordered conformations with limited spatial correlations. This type of neutron scattering has powerful advantages when unravelling the complex structural correlations present in polymeric materials with both backbone and side-group units. Coupled with atomistic modelling procedures it provides a positive way forward.

7. Résumé

We have shown that there is still much to be discovered about the local arrangements of polymer melts and glasses. Current computer simulations provide the prospect of yielding useful atomistic models, but it is essential that such models are validated through quantitative comparison with experimental data for which broad Q X-ray and neutron scattering are most useful. The detailed studies on molten poly(ethylene) and poly(tetrafluoroethylene) show that such scattering data may be exploited to drive the optimization of the model thus avoiding the dependence on particular force fields. Such studies show that for simple polymer melts the level of local orientational ordering in minimal. However, it is clear that our attention is being drawn to more complex local interactions which arise from the specific chemistry of the polymer units. These correlations may have an important role in the stabilization of miscible mixtures and other properties such as deformation. Despite the challenges posed by structural studies of disordered polymers, the use of selective site-based deuteration coupled with atomistic modelling procedures, provide a positive approach which may unravel many of the mysteries of polymer melts and glasses.

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Discussion

M. Warner (Cavendish Laboratory, U.K.). Depolarized light scattering measurements on fluids of anisotropic molecules can reveal angular correlations induced by packing. Your illustration of the packing of the benzene rings in molten polystyrene is reminiscent of problems investigated by light scattering in the 1960s by Botherell. The intrinsic depolarization per molecule is measured in dilute solution. The depolarized light scattering per molecule in the melt is then enhanced or suppressed with respect to this value according to the correlations between the depolarising species. Such scattering would be a direct test of the packing model you and Windle propose.