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A new approach to neutron scattering for non-crystalline hydrogenous polymers

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We report a wide angle neutron scattering experiment on atactic polystyrene, recently performed on the novel small angle neutron diffractometer for amorphous and liquid samples (SANDALS) commissioned at the pulsed neutron facility ISIS (UK). The use of SANDALS allows for the first time true quantitative neutron scattering data to be obtained over a large scattering vector range for hydrogenous polymers. Results for samples of both totally deuterated and totally protonated polystyrene are presented and compared with predictions from statistical models for the chain configuration. The possibility offered by SANDALS of investigating the local structure of hydrogenous polymers offers exciting prospects, particularly in the study of polymers of technological or commercial importance.

(Keywords: neutron scattering; polystyrene; hydrogenous polymers)

Introduction

The study of short range order (in the range 1–100 Å) in disordered polymers is particularly challenging due both to the structural complexity of these materials and to the absence of a periodic lattice. The complexities of the structural organization arise from the variety of intrachain structures possible in addition to the interchain correlations. To some extent the problem may be eased by considering the polymer molecule to be made up of a series of representative chain segments. Wide angle diffraction techniques have been used to obtain quantitative information on the nature of the chain segments, in terms of local chain conformation and chemical configuration, and on the spatial and orientational correlations of segments[1,2].

In this context neutrons are a particularly interesting probe. Neutron diffraction has proved to be a very successful structural technique for the study of many types of materials. Neutrons are very penetrating, and they are scattered with comparable intensity by both light and heavy elements. This is an important feature when the materials of interest are organic compounds, such as polymers. Furthermore, the neutron diffractometers currently available allow the structural features to be explored over a very large region in reciprocal space ($Q_{\max} \sim 100\,\text{Å}^{-1}$), and therefore with a high spatial resolution, certainly higher than that obtained by the more traditional X-ray based approach.

A particular drawback of neutron diffraction is the presence of inelasticity effects, whereby energy is exchanged between the neutron and the nucleus, and a variable portion of the observed scattering is not truly elastic[3,4]. This inelastic scattering provides no useful information on the static structures of the materials, although of course there is in principle much information to be gained concerning the dynamics of the system. A correction procedure may be used to eliminate the inelastic contributions, however it is not completely satisfactory when the inelasticity effects are severe, i.e. for low mass atoms and for high scattering angles. In such cases, particularly at large scattering vector (Q) values this effect can predominate to the point of preventing the extraction of any useful information from the experimental data.

In a hydrogenous material, the problem can be at least reduced by substituting the hydrogen atoms with heavier deuterium ones. This approach depends of course on the fact that this substitution has no effect on the static structural arrangements. Besides being very expensive, in some polymeric systems deuteration is very difficult to achieve, if not impossible. Even where deuteration is possible through, for example, polymerization of deuterated monomers, it may be difficult to reproduce the conditions and characteristics of the hydrogenous polymer, especially with polymers of technological or commercial importance. This creates a great obstacle to the utilization of the otherwise powerful technique on many polymeric materials.

A few reports of neutron diffraction experiments performed on hydrogenated polymers can be found in the literature, but in all of the reported data the inelastic term turns out not to be particularly crucial, either because the investigated sample is a crystalline material[5], and the intensity of the Bragg peaks of interest outweighs any other contribution, or because, although the polymer under study is amorphous, the very limited Q range of interest (typically 0–5 Å^{-1}) is certainly not dominated by inelasticity effects[6–8].

In this paper we show the possibility of performing useful neutron diffraction experiments on hydrogenated amorphous polymers over an extremely wide Q range, by exploiting the particular features of the new small

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angle neutron diffractometer for amorphous and liquid samples (SANDALS) installed at the pulsed neutron facility ISIS (Rutherford Appleton Laboratory, UK).

The aim of this work is not a presentation of a detailed study of the local chain organization in polystyrene. What we intend to establish here is the viability of neutron diffraction in heavily hydrogenated materials, thanks to new experimental facilities that are only now available to the community.

Neutron diffraction theory

Thermal neutrons can exchange both energy and momentum with the system in study, due to their wavelength and energy characteristics. However, if the incoming neutron energy is large compared to the typical values of energy exchange with the system, the collision can be considered elastic, and hence $|\vec{k}_f| = |\vec{k}_i|$, where $\vec{k}_f$ and $\vec{k}_i$ are the wave vectors characterizing the scattered and incident neutron, respectively. This is the so-called 'Static Approximation'.

The amplitude of the momentum transfer $\vec{Q} = \vec{k}_f - \vec{k}_i$ is then given by the relationship $Q = 4\pi \sin\theta/\lambda$, with 2θ being the scattering angle and λ the incident neutron wavelength. The measured intensity is proportional to the differential scattering cross-section, which is in turn related to the spatial Fourier transform of the atomic pairwise correlation functions. In the simple case of a system composed of N identical nuclei, the differential scattering cross-section is given by the following relationship:

$$\frac{d\sigma}{d\Omega} = \left\langle \sum_{i,j} b_i b_j \, e^{i\vec{Q}\cdot(\vec{r}_i - \vec{r}_j)} \right\rangle \qquad (1)$$

where b_i and b_j are the scattering amplitudes of the nuclei in positions $\vec{r}_i$ and $\vec{r}_j$, respectively, and the angular brackets indicate an ensemble average.

The double sum in equation (1) may be separated into two parts, which give rise to a self term ($i = j$) and a distinct one ($i \neq j$):

$$\frac{d\sigma}{d\Omega} = \left(\frac{d\sigma}{d\Omega}\right)^{\text{self}} + \left(\frac{d\sigma}{d\Omega}\right)^{\text{distinct}}$$

$$= N\langle b^2 \rangle + \sum_{i \neq j} \langle b_i \rangle \langle b_j \rangle \langle e^{i\vec{Q}\cdot(\vec{r}_i - \vec{r}_j)} \rangle \qquad (2)$$

The self term contributes therefore an incoherent background containing no structural information, whose intensity depends on the chemical nature of the polymer under study, and which needs to be removed from the experimental data in order to obtain the quantity of interest, the pairwise term (generalization to the case of a polyatomic system is straightforward, and the above considerations remain valid).

As already mentioned, one of the most difficult problems in the determination of the coherent scattering cross-section from experimental data is the fact that the Static Approximation, assumed so far, is rarely satisfied in neutron measurements, especially when the system under investigation is composed of low mass nuclei.

The reason for this is the fact that real neutron diffractometers for amorphous materials are far from ideal, in that they do not measure diffraction as total scattering along a path of constant Q, but rather along a path of constant time-of-flight. This Q variation brings into the experimentally measured structure factor a spurious Q-dependent inelastic contribution that needs to be evaluated and removed.

A method to correct for these inelasticity effects was originally proposed by Placzek[9] and further developed by others[10–13]. The correction procedure is approximate, and to first order it can be shown to affect only the self term in equation (2)[14].

The most important point is that this correction increases with decreasing nuclear mass of the scattering entity and with increasing scattering angle.

For hydrogen-rich materials, the effect can be rather extreme, and the resulting experimental data can therefore be quite meaningless. This is especially true on reactor diffractometers, where a high Q range can only be achieved by performing the measurements at large scattering angles.

The main purpose of the substitution of hydrogen with deuterium is that, besides producing an overall reduction in the incoherent 'background' level, due to the great difference in the incoherent scattering cross-sections of the two isotopes ($\sigma^{\mathrm{H}}_{\mathrm{incoh}} = 79.7 \times 10^{-24}$ cm^2, $\sigma^{\mathrm{D}}_{\mathrm{incoh}} = 2.0 \times 10^{-24}$ cm^2), the increase in nuclear mass reduces somewhat the inelasticity problem.

One approach to the problem is the attempt to eliminate the incoherent component experimentally, through polarization analysis. At present, the available spectrometers are limited in Q range and offer rather poor signal-to-noise data[15].

At a pulsed neutron source, a relatively high flux of short wavelength epithermal neutrons (which are not present in neutron beams derived from a reactor) is available. The short wavelength neutrons enable a wide range of Q values to be explored at small scattering angles. This provides a method for estimating the inelasticity correction. The new spectrometer SANDALS is designed specifically for this purpose.

Using SANDALS

Contrary to a conventional diffractometer, in which a monochromatic incident neutron beam is employed and Q is scanned by varying the scattering angle 2θ, on a pulsed source this is achieved by employing a broad range of incident neutron wavelengths and using the time-of-flight technique.

The essence of time-of-flight diffraction is therefore the possibility of obtaining a full scattering pattern over a wide Q range at a fixed scattering angle 2θ. As a consequence, a number of detectors placed around the sample will record a complete scattering function. The potential of the time-of-flight method in the study of oriented polymers has been described elsewhere[16].

SANDALS exploits the epithermal flux from ISIS: the usage of neutrons of energies up to 10 eV allows a broad and continuous momentum transfer range ($Q \sim 0.2$–50 Å^{-1}) to be explored at low scattering angles (between 3° and 41° at the time of the experiment). This geometry minimizes the inelastic scattering effect, which can be corrected in a relatively straightforward way even for light atoms[17,18].

Figure 1 shows a schematic diagram of the instrument. It consists of a large vacuum tank. Its shape is designed to scan all scattering angles with continuous angular coverage. The detector banks are approximately on the surface of a cylinder of radius 0.8 m, to minimize the variation of resolution with scattering angle.

The disadvantage of using a small angle geometry is

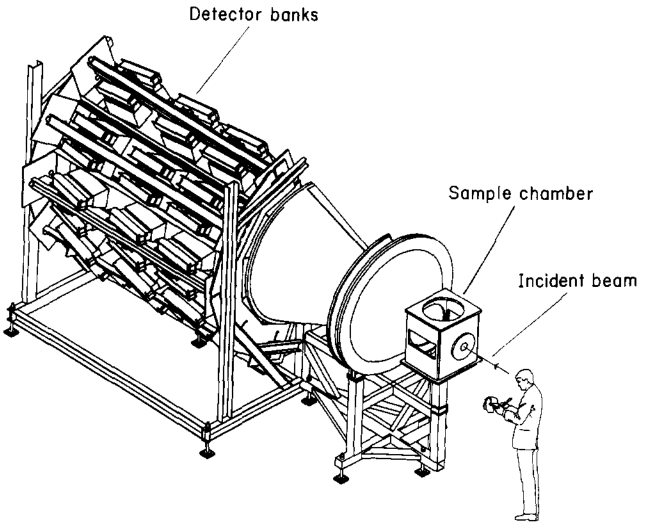

Figure 1 Schematic three-dimensional view of SANDALS

the loss in resolution, due to the fact that the resolution $\Delta Q/Q$ is dominated by the value of $\Delta\theta \cot\theta$, which becomes large at small angles, where $2\Delta\theta$ is the angular range probed by the detector. Therefore high resolution can only be achieved by using small detectors and long flight paths, with a resulting loss in the count rate. Hence an appropriate compromise has to be achieved between count rate and resolution. On SANDALS it is $\Delta Q/Q \sim 2.5\%$, which is adequate for most investigations of disordered materials.

The potential of this spectrometer is evident: the possibility of studying amorphous polymers of scientific and technological importance in their natural composition offers exciting prospects for both structure and structure–property relationship studies.

Experimental

The measurements reported here were made on two samples of undeformed polystyrene, one totally deuterated (d-PS) and one totally hydrogenated (h-PS), in the form of flat sheets ~0.7 mm thick. The polymers were obtained by free radical polymerization at 55°C, using AIBN as initiator. These conditions produce atactic configurations.

The choice of the system was dictated by the fact that this polymer has already been the subject of many investigations and X-ray studies[19], which have shown that this polymer exhibits unusual local structural arrangements.

At the time of the experiment, only one of the four detector banks was installed, with an angle coverage between 11° and 21°. For this reason, in order to obtain a good signal-to-noise ratio, the measurements were rather long (~24 h). Each measurement was performed in 2 h runs, which were afterwards compared with each other, in order to check the time reproducibility of the results. Since then a larger number of detectors has been installed and measurements now take ~8 h.

Results and discussion

The experimental data were reduced using standard procedures: after normalization for the incident beam flux, the data were converted to an absolute scale by means of a standard vanadium sample and corrected for absorption and multiple scattering using standard routines[20]. The inelasticity effects were dealt with in a similar way to that used in a previous experiment on liquid hydrogen sulphide[21].

The features in the $QS(Q)$ curve for $Q < 3$ Å^{-1} can be related to spatial correlations between segments of different polymer molecules (interchain correlations), whereas the scattering at higher Q arises from intrachain correlations, i.e. correlations within the chain segments. In fact, the first two peaks are due to group phenyl interactions and phenyl–phenyl interactions, respectively (interchain), while the peaks at 3 and 6 Å^{-1} arise from correlations corresponding to C–C and C–H bonds (intrachain)[19].

Figures 2 and *3* clearly show the uniqueness of neutrons as a structural probe. Chain correlations are explored up to very high Q values, compared with the maximum of 12 Å^{-1} which has been reached in the best X-ray diffraction experiments on polystyrene. In principle, the new additional information enables very short range correlations to be investigated and structural parameters of the chain to be accurately determined. Furthermore, any analysis in real space profits from the very high spatial resolution achieved by Fourier-transforming the high Q curves in *Figures 2* and *3*. It is also to be noted

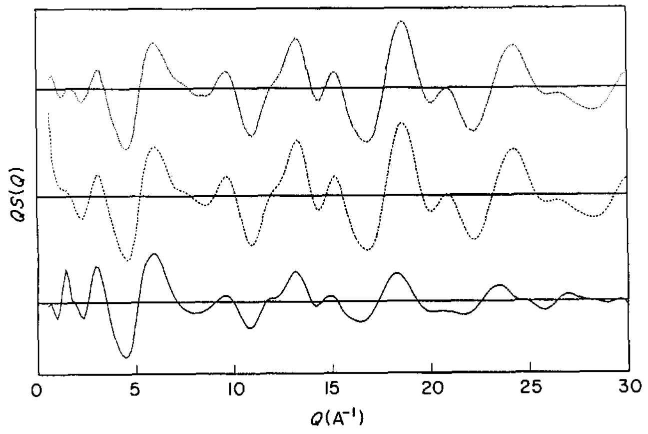

Figure 2 Plots of the experimental and calculated Q-weighted scattering frunction $QS(Q)$ for d-PS: (——) experimental data; (– – –) simulated polymer as a single chain; (· · ·) simulated polymer in the box

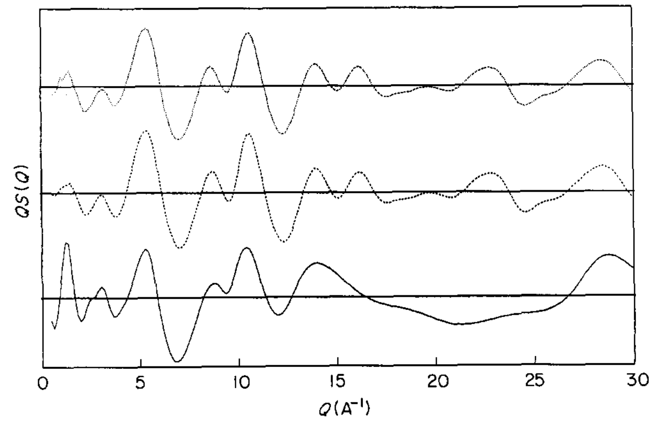

Figure 3 Same as *Figure 2* but for h-PS

that, due to the direct character of the neutron–nucleus interaction, the experimental data are not convoluted with coupling functions (such as the electron cloud distribution in the case of X-ray diffraction), thereby providing very straightforward information. Finally, *Figures 2* and *3* clearly show a remarkable variation of the features in the diffraction pattern with deuteration. This indicates the great advantage offered by the availability of selective deuteration, that is the possibility to obtain multiple independent data sets for a given material, once again increasing the amount of information available. All of this provides a very stringent test on any possible model of the polymer, which must match simultaneously all this new wealth of information, if it is to realistically represent the detailed structure of the chain.

Scattering data interpretation for amorphous polymers is a complicated task. We have found that the most productive route is to compare the experimental data with scattering patterns calculated from computer generated models of the polystyrene chain. *Figures 2* and *3* show the model which seems at present to best represent the experimental results. It was obtained from a simulation of the polymer chain through growth of the amorphous material in a cubic box, subject to periodic boundary conditions and to statistical constraints on the allowed values for the bond torsional angles[22]. The growth was carried on to the proper bulk density, i.e. $1050\,\mathrm{kg\,m^{-3}}$. The chain was constituted of 200 C_8H_8 units.

Figures 2 and *3* show the comparison between the experimental Q-weighted structure factors and the model calculation for both d-PS (*Figure 2*) and h-PS (*Figure 3*). The model prediction is presented both for the calculated single chain and for the 'unwrapped' polymer in the box.

As can be seen, the correspondence between experimental data and model prediction is not yet quantitatively correct, due to inaccuracies still present in the model. Nevertheless, the main features in the experimental diffraction patterns are qualitatively reproduced by the model calculation up to $\sim 20\,\mathrm{Å}^{-1}$. In particular, the model in the box seems to account better for the scattering observed at very low Q values, as could be expected, due to the bigger contribution in this case by the interchain correlations.

What is most important is the fact that the calculated structure factor changes in accordance with the experimental observation when all the hydrogen atoms are substituted with deuterium in the simulated chain. This represents a further confirmation of the validity of the experimental method in the determination of the structure of hydrogenous materials.

Conclusions

In our study we have shown, we believe for the first time, that an extensive and complete structural investigation of hydrogenous amorphous materials through neutron scattering is indeed feasible with the availability of the new spectrometer SANDALS.

The potential of this instrument in the field of polymer science is evident: the possibility of studying materials in their natural composition represents a major step forward, especially for new polymers of technological or commercial importance.

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