On the assessment of incoherent neutron scattering intensities from polymer systems

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The problem of assessing incoherent scattering intensities from polymer systems is outlined. The incoherent cross-sections of some hydrogenous polymers have been measured. The measurements show that the incoherent scattering is anisotropic and the cross-section is temperature- and wavelength-dependent. The change in cross-section is due to changes in the mobility of the polymers which affects the inelastic contribution to the scattering. Without an accurate knowledge of the polymer cross-sections as a function of temperature and wavelength, it is impossible to calculate the incoherent scattering.

INTRODUCTION

Recently the analysis of small-angle neutron scattering (SANS) data from polymers has been considerably refined so that it is now possible to obtain single chain information from polymer mixtures containing high concentrations of deuterated polymers[1-3]. The theoretical treatments described by Akcasu *et al.*[1] and Warner *et al.*[2] rely on the fact that the incoherent contribution to the scattering has been subtracted before the coherent scattering is analysed. The coherent scattering can then be interpreted in terms of single chain structure factors and concentration fluctuations from which the interaction parameter between the components can be obtained. Gawrisch *et al.*[3] have devised a method for single component systems, where there are no concentration fluctuations, from which the single chain term plus the density fluctuations can be obtained without first subtracting the incoherent scattering. However, this method requires measurements to be made on a number of different concentrations of deuterated chains which greatly increases the cost of the experiments. When applied to a two component system, such as a polymer blend, it is not possible to separate the single chain term and the interaction term because of the complex nature of the coefficients which occur. It is therefore essential to be able to subtract the incoherent scattering from these systems before analysing the coherent scattering.

For a dilute mixture of a deuterated polymer in a hydrogenous 'solvent' (where the 'solvent' could be another polymer or a low molecular weight solvent) this is normally achieved by subtracting the scattering from the 'solvent' alone since the small amount of incoherent scattering from the deuterium will be negligible. For the case where there is a high concentration of deuterated polymer the incoherent scattering from the deuterium is no longer negligible and the amount of incoherent scattering from the hydrogenous polymer can no longer be subtracted in this simple way.

A number of methods have been used to obtain the correct level of incoherent scattering. The scattering from a random copolymer of the deuterated and hydrogenous monomers containing the correct ratio of hydrogen to deuterium should have the same amount of incoherent scattering without the coherent signal[2]. Difficulties associated with this method are encountered in the very precise chemistry which has to be performed in order to prepare the appropriate copolymer. A second method of estimating the level of incoherent scattering is that of measuring the scattering from the sample at high scattering angles where the coherent scattering is negligible. This method relies on the assumption that the incoherent scattering is isotropic and therefore results at high q can be applied to the low q range. Since these measurements have usually to be performed on two different instruments to cover a wide enough angular range there can be difficulties in normalizing the data from one instrument to the other. A third method which can be used is polarization analysis.

Use of polarized neutrons to distinguish between coherent and incoherent scattering processes has been employed for a few specialized measurements on one instrument[4]. An increased use of this technique together with extensions to cover the wavelength range used in conventional SANS experiments offers an interesting way to approach the problem of incoherent background scattering. Finally, it should be possible to calculate the level of incoherent scattering from a knowledge of the appropriate cross-sections. In principle, this latter method should be the easiest way of estimating the level of incoherent scattering; however, only the bound atom cross-sections are known for polymers.

To the author's knowledge, no systematic measurements have been made of the polymer total cross-sections as a function of temperature and wavelength. As a first step in this process, an attempt has been made to calculate the scattering from hydrogenous polymers where the

dominant scattering process is incoherent. This paper presents calculated values of this scattering which are compared with measured values.

THEORY

The scattered intensity from any substance comprises two components—coherent and incoherent scattering—so that provided no absorption takes place,

$$I(\theta) = I^{coh}(\theta) + I^{inc}(\theta) \tag{1}$$

Here we are considering only small-angle elastic scattering.

For the case where incoherent scattering predominates and the only multiple scattering is incoherent multiple scattering, then all neutrons which are not transmitted are scattered over 4π steradiens and the scattered intensity can be written as

$$I(\theta) = \phi_0 \Omega_0 T S^{coh}(\theta) + \phi_0 \Omega_0 A \frac{(1-T)}{4\pi} \tag{2}$$

where ϕ_0 is the incident neutron flux, Ω_0 is the solid angle subtended by the detector, A is the area of the sample in the beam, T is the transmission of the sample and $S^{coh}(\theta)$ is its coherent differential cross-section.

If, as in the case of water or a hydrogeneous polymer, the coherent scattering is negligible equation (2) becomes

$$I(\theta) = \phi_0 \Omega_0 A \frac{(1-T)}{4\pi} \tag{3}$$

where the transmission $T = \exp(-n\sigma_e d)$, n is the number density of scatters in the sample which have an effective total scattering cross-section σ_e and d is the thickness of the sample. For incoherent scatterers $\sigma_e = \sigma_{e,inc}$, the effective incoherent scattering cross-section.

Equation (3) assumes that the scattering is totally elastic but, in practice, there is an inelastic contribution to the scattering which is not isotropic. In order to account for the scattering a factor $f(\sigma, \lambda)$ is introduced[5] so that

$$I(\theta) = \phi_0 \Omega_0 A \frac{(1-T)}{4\pi} f(\sigma, \lambda) \tag{4}$$

$f(\sigma, \lambda)$ is a function of the cross-section of the sample and the wavelength of the incident neutrons.

Consider the scattering from two incoherent scatterers under identical experimental conditions, thus

$$I_1(\theta) = \phi_0 \Omega_0 A \frac{(1-T_1)}{4\pi} f_1(\sigma_1, \lambda) \tag{5}$$

and

$$I_2(\theta) = \phi_0 \Omega_0 A \frac{(1-T_2)}{4\pi} f_2(\sigma_2, \lambda) \tag{6}$$

dividing equation (5) by equation (6) gives

$$I_1 = I_2 \frac{(1-T_1)}{(1-T_2)} \frac{f_1(\sigma_1, \lambda)}{f_2(\sigma_2, \lambda)} \tag{7}$$

Therefore, it should be possible to determine I_1 given all the other factors in equation (7). Normally for polymers $f(\sigma, \lambda)$ has been taken to be unity. Current measurements involving detailed comparisons of polymers over wide temperature ranges require careful measurement of this factor to obtain correct results. *Ab initio* calculation of $f(\sigma, \lambda)$ involves many complex terms simply to derive a value for an isotropic diffuse background intensity.

EXPERIMENTAL

Small-angle neutron scattering (SANS) experiments have been carried out on a number of polymers during the past few years. The details of the various instruments used together with a list of polymers investigated are listed in *Table 1*. A description of the basic SANS measurement has been given elsewhere[6].

The transmission of the polymers were calculated from measurements of the transmitted and incident beam. The intensity was measured close to the beam centre to avoid any scattered radiation. Measurements were made with

Table 1 List of samples and experimental conditions

| Polymer	Instrument	Sample to detector distance (m)	Wavelength (A)	Temperature (°C)	Sample thickness (cm)
Polystyrene	ILL, Grenoble	5.66	10	104	0.2
Polystyrene	ILL, Grenoble	5.66	10	128	0.2
Polystyrene	ILL, Grenoble	5.66	10	152	0.2
Polystyrene	ILL, Grenoble	5.66	10	173	0.2
Polystryene	ILL, Grenoble	5.66	10	203	0.2
Polystyrene	ILL, Grenoble	5.66	10	225	0.2
Polystyrene	ILL, Grenoble	5.66	10	247	0.2
Polystyrene	ILL, Grenoble	5.66	10	273	0.2
Polybutadiene	ILL, Grenoble	1.43	12	17	0.2
Polybutadiene	ILL, Grenoble	1.43	12	45	0.2
Polybutadiene	ILL, Grenoble	1.43	12	73	0.2
Polybutadiene	ILL, Grenoble	1.43	12	110	0.2
Polybutadiene	ILL, Grenoble	1.43	12	140	0.2
Poly(methyl methacrylate)	SAS	2.1	10	Room temperature	0.11
Poly(methyl methacrylate)	Harwell	2.1	6	Room temperature	0.11
Poly(methyl methacrylate)	Harwell	2.1	5	Room temperature	0.11
Poly(methyl methacrylate)	Oakridge	14.7	4.75	Room temperature	0.11
Poly(butylacrylate)	SAS Harwell	2.1	10	Room temperature	0.1
Poly(butylacrylate)	SAS Harwell	2.1	5	Room temperature	0.1
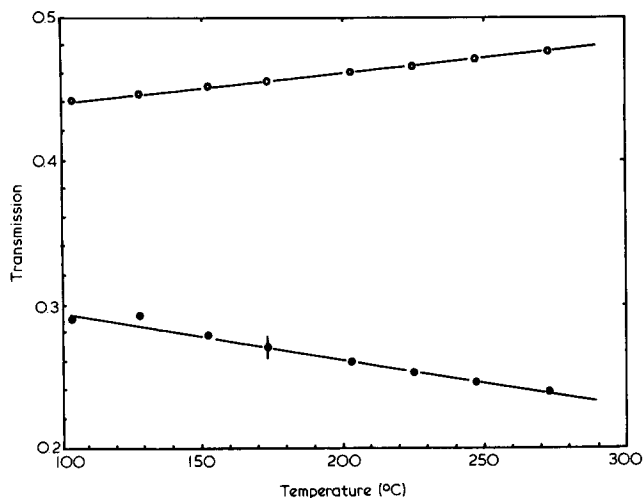
Figure 1 Transmission of 0.2 cm of polystyrene as a function of temperature. (●), T_{meas} (measured transmission) and (○), T_{calc} transmission calculated from bound atom cross-sections

and without the sample in the beam to give I and I_0 respectively. Then

$$T = \frac{I}{I_0} = \exp(-n\sigma_e d)$$

Calculated values of T, T_{calc} were obtained by using bound atom cross-sections thus

$$\sigma_e^{calc} = \sum_i \sigma_{T,i}$$

and

$$n = \frac{\rho N_A}{m}$$

where $\sigma_{T,i}$ is the total bound atom cross-section of atom i in the scattering unit, ρ is its density and m is its molecular weight. For polymers the scattering unit was taken to be a monomer and the density used was that of the polymer.

The values of the scattered intensity used in the calculations of $f(\sigma, \lambda)$ were obtained by taking the average level of intensity across the detector. Over the small angular range covered in the experiment, the intensity appears to be isotropic. The calculations were also carried out using the total scattered intensity and a value of the intensity towards the edge of the detector. All three methods gave the same results within experimental error.

RESULTS AND DISCUSSION

In *Figure 1* the results are shown of transmission measurements carried out on polystyrene as a function of temperature. The calculated values of the transmissions, assuming a constant bound atom cross-section and that only the density changes with temperature, are also plotted on the same Figure. The calculated values of T are greater than the measured values and have the inverse temperature dependence, T_{calc} increases with increasing temperature whereas T_{meas} decreases.

In *Figure 2* the effective cross-section, σ_e, calculated

from the measured transmissions is plotted as a function of temperature. The cross-section increases with the increasing temperature and is always greater than the bound atom cross-section which, for polystyrene, is 696.08 barns. All these measurements were carried out at temperatures above the glass transition temperature of polystyrene so that side-group motion and diffusion will be occurring and both these types of motion will increase with temperature. It should therefore be expected that the measured cross-section is greater than the bound atom cross-section since the scatterers are no longer rigid. The variation of the total cross-section with temperature is well known for small molecules and a number of theoretical treatments have been used to try and calculate the measured cross-sections[7]. The change in cross-section is essentially due to a change in the inelastic scattering contribution. It is also known that the inelastic incoherent scattering from polymers depends on temperature[8] thus changing the total cross-section. The coherent cross-section of most hydrogeneous polymers accounts for only about 10% of the bound atom cross-section, therefore any increase in the cross-section will be dominated by the inelastic incoherent contribution.

Since the scattering from hydrogeneous polystyrene is dominated by the incoherent scattering then it is possible to apply equations (4) and (7). Component 1 is polystyrene and component 2 is water. The scattering from water has already been shown to be anisotropic due to inelastic effects and $f(\sigma, \lambda)$ has been measured[5]. Equation (7) becomes

$$f_{PS}(\sigma_{PS}, \lambda) = \frac{I_{PS}(1 - T_{H_2O})}{I_{H_2O}(1 - T_{PS})} f_{H_2O}(\sigma_{H_2O}, \lambda) \qquad (8)$$

$f_{PS}(\sigma_{PS}, 10 \text{ Å})$ has been calculated for polystyrene and is plotted as a function of temperature in *Figure 3*. $f_{PS}(\sigma_{PS}, 10 \text{ Å})$ is close to unity at the lowest temperature but decreases as the temperature increases. Therefore in order to calculate the incoherent scattering from polystyrene it is necessary to know both the transmission and $f(\sigma, \lambda)$ at the temperature of the measurements for the particular
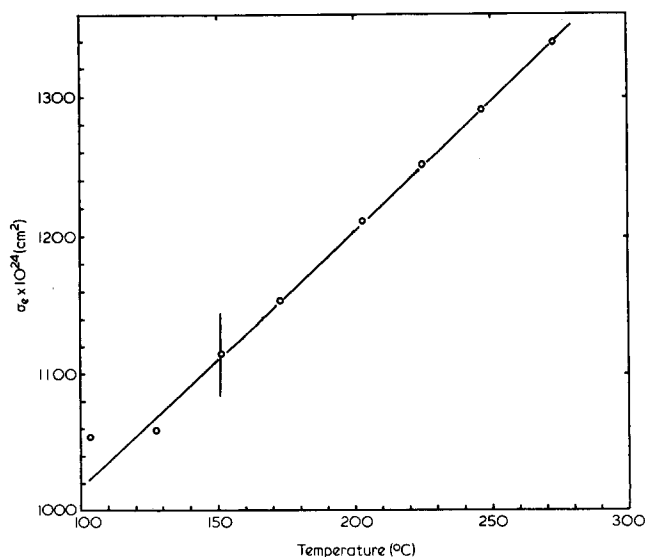

Figure 2 Effective cross-sections, σ_e, of polystyrene as a function of temperature. Bound atom cross-section for polystyrene is 696.08 barns
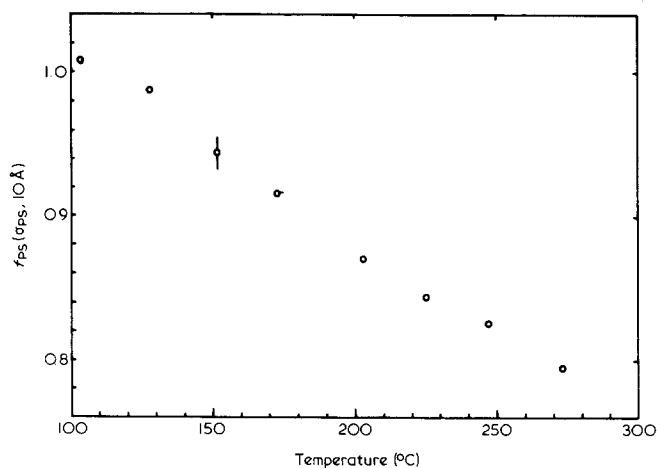
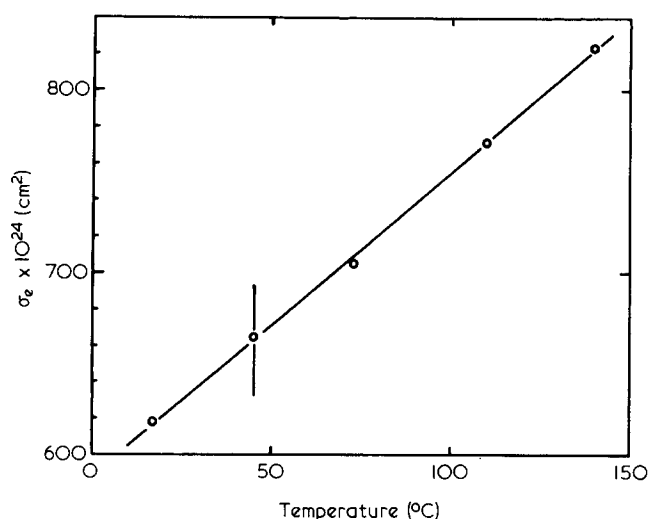**Figure 3** $f_{PS}(\sigma_{PS}, 10\,\text{Å})$ values for 0.2 cm of polystyrene as a function of temperature

neutron wavelength. Data for two polymers, poly(methyl methacrylate) and poly(butylacrylate), are listed in *Table 2*. As the neutron wavelength increases so does the effective cross-section, thus reducing the transmission. One would therefore expect that the cross-section for polybutadiene at 10 Å would be smaller and therefore the shift between σ_H for polystyrene and polybutadiene at the same wavelength to be even greater. Since the increase in σ_e is most probably due to inelastic scattering, the relative values of σ_H may well be indicative of the type of motions involved. Polystyrene has a large side-group whereas polybutadiene has none. It would be interesting to extend these measurements to other polymers to see if there is any systematic trend associated with the type of side-groups involved.
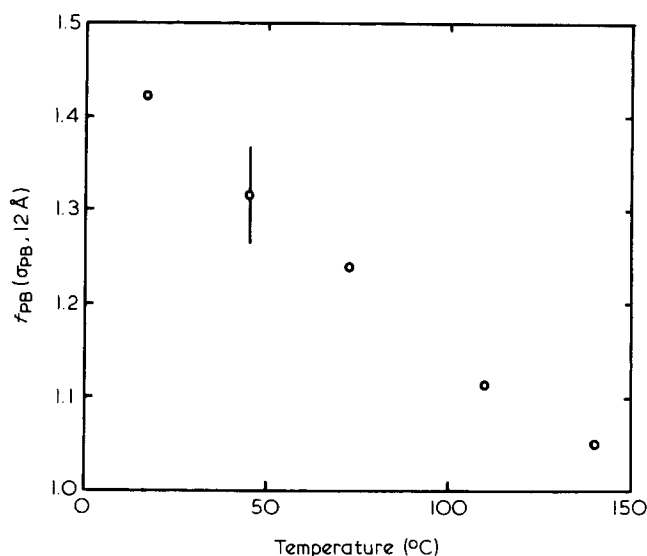

Figure 5 $f_{PB}(\sigma_{PB}, 12\,\text{Å})$ values for 0.2 cm of polybutadiene as a function of temperature
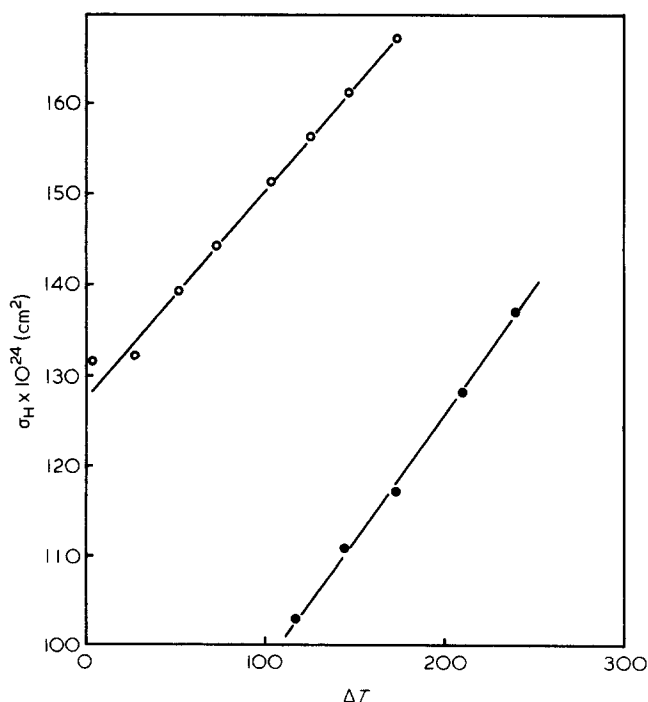

Figure 4 Effective cross-section σ_e, of polybutadiene as a function of temperature. Bound atom cross-section for polybutadiene is 511.05 barns

wavelength being used. It is also worth noting the $f(\sigma, \lambda)$ for water changes with sample thickness and therefore there will be a similar dependence in the case of polymer systems too.

Measurements of σ_e and $f(\sigma, \lambda)$ have also been made for polybutadiene as a function of temperature and these results are plotted in *Figures 4* and *5*. The results exhibit a similar dependence on temperature to the data for polystyrene. In order to compare the results for these two quite different polymers an effective hydrogen cross-section σ_H has been calculated which is the effective cross-section divided by the number of hydrogens in the monomer. In *Figure 6* σ_H is plotted against ΔT, the difference between the measurement temperature and the glass transition temperature of the polymer; thus the results are compared at the same temperature relative to their glass transition temperatures. The slopes of the two lines are essentially the same but the polystyrene values are shifted to higher values of σ_H at the same value of ΔT. These measurements were made at two different wavelengths (10 Å for polystyrene and 12 Å for polybutadiene) so that they are not directly comparable, since it has been found that, as is the case for water[5] and other molecules[7], the cross-sections measured for polymers change with

Figure 6 Effective hydrogen cross-section, σ_H, for polystyrene and polybutadiene as a function of ΔT

Table 2 Transmissions as a function of λ for poly(methyl methacrylate) and poly(butylacrylate)

Polymer	λ (Å)	Transmission
Poly(methyl methacrylate)	10	0.493
Poly(methyl methacrylate)	6	0.520
Poly(methyl methacrylate)	5	0.565
Poly(methyl methacrylate)	4.75	0.577
Poly(butylacrylate)	10	0.473
Poly(butylacrylate)	5	0.564

CONCLUSIONS

Information derived from the coherent scattering component depends on an accurate assessment of background and incoherent scattering. The measurements described in this paper show the importance of inelastic scattering and its effect on the cross-sections of polymers and the measured incoherent scattering. In order to calculate the incoherent scattering from a particular polymer, it is necessary to know not only the transmission, but also $f(\sigma, \lambda)$. Since the effective cross-section depends on details of the motion of the main chain and side-groups, it is logical to expect that the incoherent scattering from a polymer blend or solution, in which the chain mobility can be altered by its surroundings, is not the same as the sum of the incoherent scattering from the individual components.

There clearly remains scope for systematic experiments since calculation of the incoherent scattering is fraught with problems. Out of the four methods initially described in the Introduction, two may be considered as possible standard ways of estimating incoherent levels of scattering: (1) measurement of the scattering at high q and (2) polarizing analysis. Though not a routine technique at present, since it is not available on any small-angle scattering instrument, polarization analysis should be the most accurate technique to quantify the incoherent scattering. Once the incoherent scattering contribution is understood as a function of group motion, temperature and wavelength, it would greatly facilitate coherent scattering analysis from polymer systems.

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