

# Measurements of single chain form factors by small-angle neutron scattering from polystyrene blends containing high concentrations of labelled molecules<sup>†</sup>

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A series of small angle neutron scattering measurements on blends of normal polystyrene (PSH) and labelled (deuterated) polystyrene (PSD) have been made with concentrations of PSD from 5 to 50 mol %. It is shown that the single chain form factor of the polymer in bulk can be obtained from a single concentration measurement for any concentration of labelled molecules, providing the molecular weights of the parent and labelled molecules are the same and the molecular weight distributions are narrow.

## INTRODUCTION

Small-angle neutron scattering (SANS) measurements on samples made up of a host polymer matrix in which a proportion of isotopically labelled molecules are dispersed have been used in a wide variety of studies of amorphous<sup>1-4</sup> and crystalline<sup>5-8</sup> polymers. These measurements have conventionally been performed with small relative concentrations of labelled molecules and have involved an extrapolation to zero concentration in order to eliminate interchain interference effects. The intensity of the scattering signal is limited by the small number of labelled chains, and this has restricted the SANS measurements to strongly scattering systems in order to achieve a reasonable signal-to-noise ratio.

Recent developments in scattering theory have indicated that it is possible to extract both the single-chain and interchain (interference) functions by performing measurements at high relative concentrations of labelled polymer, and Williams *et al.*<sup>9</sup> first reported SANS experiments on concentrated solutions of polyelectrolytes. They obtained the single chain form factor by extrapolation of the scattered intensity per labelled monomer to zero content of labelled chains at constant total solution concentration, and the interchain factor from the slope of the extrapolation line. Akcasu *et al.*<sup>10</sup> generalized the technique of Williams *et al.*<sup>9</sup> noting that a concentration

extrapolation procedure was not necessary, and measured the radius of gyration of polyisoprene in the bulk by extracting the intrachain signal using scattering data from two different concentrations (6.9 and 14.5 wt %) of labelled molecules. In this paper we show, with well-defined polystyrenes, that the single chain form factor of the polymer in bulk may be obtained from a single concentration measurement for any concentration of labelled molecules, provided the molecular weights of the parent and labelled molecules are the same and the molecular weight distributions are narrow.

## THEORY

The intensity  $I(K)$  of coherent elastic neutron scattering from a pure unlabelled system consisting of one component (type 1) can be written as

$$I(K) = Na_1^2 P_1(K) + N^2 a_1^2 Q_{11}(K) \quad (1)$$

where  $K = 4\pi/\lambda \sin\theta$  is the neutron scattering vector,  $\lambda$  is the wavelength of the neutron,  $2\theta$  is the angle of scatter,  $a_1$  is the scattering length of a monomer of component 1,  $N$  is the number of molecules per unit volume,  $P_1(K)$  is the intrachain signal which originates from the scattering of the monomer pairs belonging to the same polymer chain and  $Q_{11}(K)$  is the interchain signal which originates from the scattering by intermolecular monomer pairs. For a pure single component which contains no residual voids or heterogeneities (catalyst residues, impurities, stabilizers, etc.), the scattering is due simply to density fluctuations. For amorphous polymers the density fluctuation scattering is small<sup>11,12</sup> and, neglecting this component, we may write, following Benoit<sup>13</sup>:

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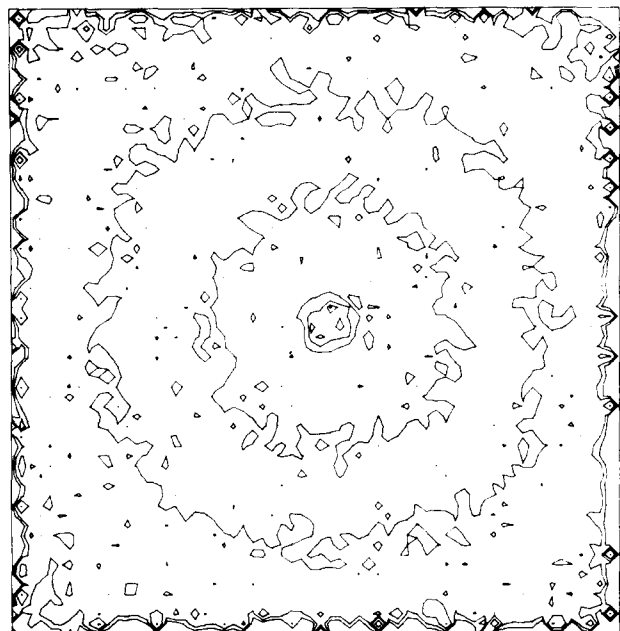


Figure 1 Two-dimensional scattering from 10.4% PSD molecules ( $M_w = 77\,400$ ) in PSH matrix ( $M_w = 75\,000$ )

$$P_1(K) + N Q_{11}(K) = 0 \quad (2)$$

and similar equations may be written for a system consisting of a pure unlabelled component 2 with only a change of subscripts. If two polymers are blended together in such a fashion that  $X_1$  equals the mole fraction of component 1,  $X_2$  is the mole fraction of component 2 and  $N$  is the total number of molecules per unit volume, the resulting scattering is now given by:

$$I(K) = X_1 N a_1^2 P_1(K) + X_1^2 a_1^2 N^2 Q_{11}(K) + X_2 N a_2^2 P_2(K) + X_2^2 a_2^2 N^2 Q_{22}(K) + 2X_1 X_2 N^2 a_1 a_2 Q_{12}(K) \quad (3)$$

In general the intrachain functions  $P_i(K)$  and interchain functions  $Q_{ij}(K)$  in equation (3) are different for a blend of dissimilar components. However, in the case where the components of the blend differ only in that the molecules of one component are isotopically labelled, we may simplify equation (3) as follows. Assuming that deuteration of the hydrogenous molecule has a negligible effect on the monomer-monomer interaction, the average configuration of a labelled molecule does not differ from that of an unlabelled molecule and hence we may write:

$$P_1(K) = P_2(K) = P(K) \quad (4)$$

and

$$Q_{11}(K) = Q_{22}(K) = Q_{12}(K) = Q(K) \quad (5)$$

Since both labelled and unlabelled molecules have the same molecular weight, equation (2) is valid independent of the subscript:

$$Q(K) = -P(K)/N \quad (6)$$

Substituting equation (6) into equation (3) and simplifying

yields the final result for the scattering

$$I(K) = X_1 X_2 (a_1 - a_2)^2 N P(K) \quad (7)$$

This shows that the form of the scattering curve in this case is governed only by the single chain form factor  $P(K)$ . The mole fraction of each component will modulate the scattered intensity with the maximum coherent scattering of the blend occurring at a 50–50 mixture of the two components. The analogy between this result and the Laue monatomic scattering from binary alloys is apparent.

Our result differs from that of Akcasu *et al.*<sup>10</sup> in that we have assumed at the outset that density fluctuation scattering is small and hence the scattering from a fully labelled sample is negligible compared with that from a blend of labelled and unlabelled molecules. While this assumption has been verified for amorphous polystyrene (see below), it does not hold for semicrystalline polymers or phase segregated blends where significant scattering from the two phase structure occurs. For these systems, a correction must be made by subtracting a term proportional to the coherent scattering from a fully labelled blend as pointed out by Akcasu *et al.*<sup>10</sup>.

## EXPERIMENTAL

Hydrogenated and deuterated atactic polystyrene were obtained from Polymer Laboratories of Shrewsbury, England. The molecular weight,  $M_w$ , of the hydrogenated and deuterated samples were 75000 and 77400, respectively, with polydispersities of 1.03 and 1.09, respectively. Samples were prepared by dissolving each component in boiling chlorobenzene and reprecipitating into excess methanol. The polymer was vacuum dried and pressed into a disc-shaped pellet, 0.13 cm thick. Samples containing 5, 10, 20, 30, 40, and 50 mol % deuteropolystyrene (PSD) in hydrogenated polystyrene (PSH) were prepared in addition to pure PSH and PSD blanks.

The neutron experiments were performed on the new 30 m SANS facility<sup>14,15</sup> at the National Center for Small Angle Scattering Research (Oak Ridge National Laboratory). The incident beam, of wavelength  $\lambda = 4.74 \text{ \AA}$  ( $\Delta\lambda/\lambda = 6\%$ ), was collimated by a source slit ( $1.8 \times 1.8 \text{ cm}$ ) and a sample slit (0.9 cm diameter) separated by a distance of 10 m. The area detector ( $64 \times 64 \text{ cm}^2$ ), with  $1 \text{ cm}^2$  element size, mounted on rails inside a 20 m vacuum flight path, was positioned at a distance of 10 m from the sample. The samples were typically measured for 2700 s and after correcting for instrumental backgrounds, incoherent scattering, and sample transmission, the scattered intensities were normalized to a constant sample thickness. Samples of both pure PSD and PSH were also measured to check that no voids or scattering heterogeneities were present and to provide a basis for subtracting incoherent scattering, arising principally from  $^1\text{H}$  nuclei. A typical two-dimensional contour plot of a blend is shown in Figure 1.

## RESULTS AND DISCUSSION

Debye<sup>16,17</sup> has shown that the single chain scattering function for a Gaussian random coil is given as:

$$P(K) = \frac{2}{u^2} (e^{-u} - 1 + u) \quad (8)$$

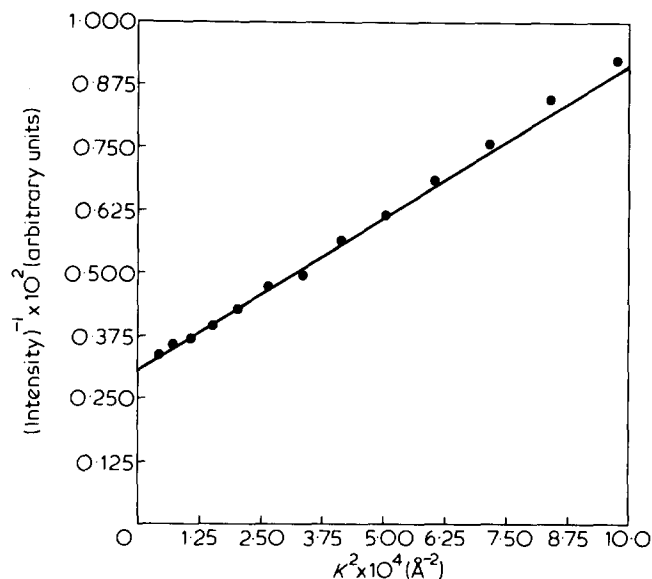


Figure 2  $I^{-1}(K)$  vs.  $K^2$  for PSD molecules in sample containing 10.4 wt % PSD in PSH

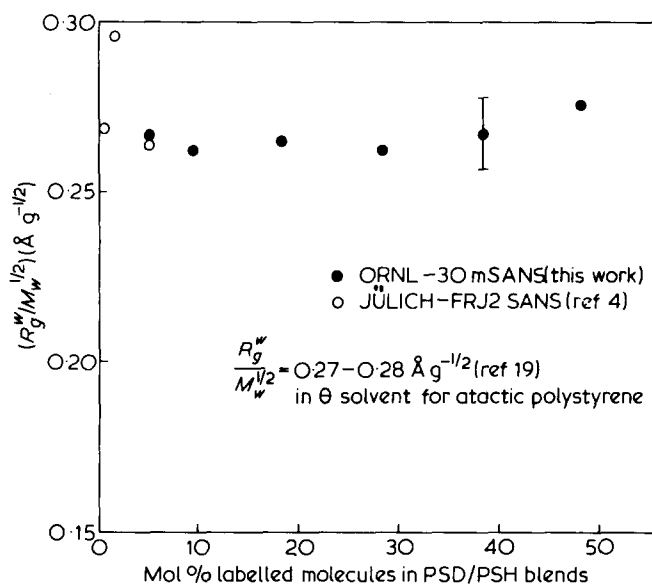


Figure 3 Variation of  $R_g^w/M_w^{1/2}$  with concentration of labelled molecules for PSD/PSH blends

where  $u = K^2 \langle R_g^2 \rangle$  and  $\langle R_g^2 \rangle$  is the mean square radius of gyration. For  $K^2 \langle R_g^2 \rangle \ll 1$ , the radius of gyration can be obtained from the slope of the plot of  $I(K)^{-1}$  vs.  $K^2$ .

Figure 2 shows a typical plot of  $I(K)^{-1}$  vs.  $K^2$  from which (z-averaged) values of the radius of gyration were obtained. Small polydispersity corrections<sup>18</sup> were applied to give weight-averaged radii,  $R_g^w$ .

Figure 3 shows the plot of  $R_g^w/M_w^{1/2}$  vs. concentration of the tagged chain. The average value of  $0.266 \text{ Å g}^{-1/2}$  is in excellent agreement with previous measurements made at low concentrations<sup>2-4</sup> and with the value for polystyrene in a  $\theta$ -solvent<sup>19</sup>. No concentration dependence was observed.

Figure 4 shows the normalized forward scattering (extrapolated to  $2\theta = 0$ ), vs. concentration of the labelled chains. A straight line could be drawn through all the points, indicating that the intensity of the scattering is simply dependent on the mole fraction of the labelled chains (see equation 7). Extensive studies of labelled

polystyrene blends<sup>2-4</sup> have shown that these systems do not exhibit anomalous forward scattering associated with segregation of the labelled species<sup>5,8</sup>, and for this reason accurate absolute calibration of the intensity was not attempted. However, an approximate internal calibration, performed with respect to the  $^1\text{H}$  incoherent scattering from the PSH blank, demonstrated that the molecular weights calculated from the forward scattering are of the correct order of magnitude, as expected for statistically distributed labelled molecules.

These results indicate that provided the molecular weight of the parent and labelled molecules are the same and their distributions are narrow, the single chain form factor of the polymer in bulk may be obtained from a scattering measurement at a single concentration for any concentration of labelled molecules. The theory given above has therefore been confirmed for well-defined polystyrenes over the range of concentration of 5–50 mol% deuterated polystyrene. For the special case of matched parent and labelled molecules, the radius of gyration is independent of the concentration of labelled molecules and there is no need to restrict SANS measurements to dilute concentrations of labelled molecules or to extrapolate to zero concentration, thus permitting a significant gain of scattering intensity for weakly scattering systems\*. While the maximum coherent scattering occurs at a 50:50 mixture of the two components, it may be advisable to work at a somewhat lower ratio of PSH in PSD to maximize the ratio of coherent to incoherent scattering.

\* During the course of this work we have become aware of complementary high concentration SANS work on polystyrene by C. Tangari *et al.* (University of Michigan) and F. Boue *et al.* (Laboratoire Leon Brillouin, Saclay). Similar conclusions were reached on methods to extract single chain form factors at high concentrations of labelled polymer.

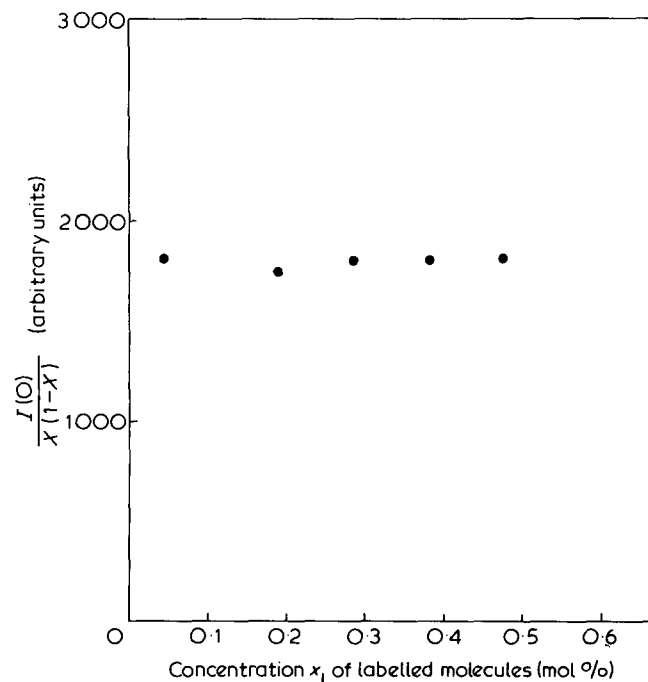


Figure 4 Variation of  $I(0)$  with concentration of labelled molecules in PSD/PSH blends

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