A small angle neutron scattering investigation of block copolymers of styrene and isoprene in the solid state

Randal W. Richards and James L. Thomason
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK

(*Received* 19 *June* 1980; *revised* 20 *October* 1980)

Block copolymers of styrene and isoprene have been synthesized using anionic initiation, the weight fraction range of styrene covered being 0.20–0.85. The solid state structure has been examined by electron microscopy and small angle neutron scattering, for two copolymers small angle X-ray scattering measurements have also been made. From the neutron scattering measurements it has been possible to determine the structural arrangement of the domains, the domain morphology and size, the mean square radius of the styrene block in the domain and the interfacial layer thickness. The results have been compared with theoretical models of domain structure and the general theoretical features seem to be confirmed.

Block copolymers of styrene and a diene have been investigated for about 15 years[1] and are of commercial interest in their use as adhesives, synthetic rubber and impact resistant plastics. The major characteristic of these materials is the phenomena of microphase separation which takes place in the solid state[2,3]. Earlier investigations have shown that this separation results in domains of one of the blocks being dispersed in a matrix formed by the other. The morphology, i.e. the geometric form, of the domains is chiefly controlled by the composition of the copolymer (moulding conditions also play an important role) and three morphological units have been identified — spheres, cylinders and lamellae[4]. Experimental investigations of these materials has used electron microscopy[2,3,5] as the main technique although small angle X-ray scattering[5,6–9] (SAXS) has also been used especially by Kawai *et al.*[10] A notable result of these investigations was the identification of long range ordering between the domains, i.e. a *para* crystalline structure was formed.

Theories of domain formation[11,12] using statistical thermodynamics have been developed simultaneously with the experimental work. In particular, the work of Meier[13–15] has produced formulae relating domain parameters to block dimensions and the thermodynamic interaction between the two components of the copolymer. An important result of such theories has been the prediction of an interfacial layer[16] surrounding the domains where the two components are partially mixed and the estimation of its thickness. The existence of the interfacial region is still under speculation, however, results of SAXS[10,17] and dynamic mechanical analysis[18,19] of block copolymers substantiate its existence to some extent.

Small angle neutron scattering (SANS) is one of the newer techniques used to examine polymer structure[20]. It has been particularly successful in investigating, at a molecular level, polymer states which were previously unexaminable, e.g. the solid state and concentrated solutions[21,22]. In this paper we report initial results on the application of this technique in the study of the solid state structure of block copolymers of styrene and isoprene cast from toluene solution. Facets of the structure we investigated are: the interdomain distance and domain organization over a range of copolymer composition, and for one copolymer the domain morphology and size is reported together with the interfacial thickness and block dimensions in the domain.

EXPERIMENTAL

Copolymer preparation

Di-block (SI) and tri-block (SIS) copolymers of styrene (S) and isoprene (I) were prepared by anionic polymerization of the rigorously dried monomers in benzene. For this, a special reaction flask was used which had grease free taps and all operations were performed under high vacuum (circa 1.33×10^{-4} N m^{-2}). Sequential addition of monomers was used to prepare the copolymers since n-butyl lithium was the initiator. Samples of the polymer produced at each stage were retained for future analysis, the final product being 'killed' by addition of a small amount of degassed methanol. 15–20 g of hydrogenous copolymer were prepared at a time by this technique.

Copolymers with deuterated styrene blocks (DSI or DSIS) were prepared on a much smaller scale, typical amounts of copolymer being 0.5–1.0 g. Extreme care was taken in excluding impurities since quantitative initiation of ~0.25 g portions of deuterated styrene was required. The small scale of these preparations militated against taking samples at each stage of the polymerization.

After precipitation and drying, both hydrogenous and deuterated copolymers were analysed by gel permeation chromatography (g.p.c.) to determine the molecular weight distribution $\bar{M}_w/\bar{M}_n$. The composition of the copolymers was determined by u.v. absorption in spectroscopic grade chloroform using the characteristic polys-

0032–3861/81/050581–09$02.00

Table 1

Co-polymer	$10^{-4}\bar{M}_n$	$\bar{M}_w/\bar{M}_n{}^a$	Weight fraction of styrene, W_s	$10^{-4}\bar{M}_n{}^a$ of styrene block
SI 1	3.05	1.07	0.203	0.93
SI 2	7.01	1.15	0.355	3.21
SI 4	17.81	1.06	0.73	8.65
SI 5	29.25	1.39	0.85	23.20
SIS 1	3.32	1.17	0.153	0.78(x2)
SIS 2	6.48	1.07	0.413	1.45(x2)
DSI 1	9.15[a]	1.06	0.312	1.73

[a] From g.p.c.

tyrene absorption wavelength of 262 nm. Infra-red spectra of the copolymers showed the isoprene microstructure was predominantly *cis* 1,4.

Hydrogenous copolymers were also characterized by membrane osmometry to determine the number average molecular weight ($\bar{M}_n$) absolutely. This could not be used for the deuterated copolymers, due to the small amounts prepared. Consequently the agreement of g.p.c. molecular weights with their hydrogenous counterparts in conjunction with the composition was used as a criterion for the success of replicating the hydrogenous copolymers. Copolymer molecular weights by g.p.c. did not agree with the absolute values of $\bar{M}_n$. However, agreement between these two values was excellent for the polystyrene blocks. Contamination of the final product was usually slight and confined to trace amounts of adventitously 'killed' polystyrene. For the deuterated copolymers, the presence of this small amount of polystyrene enabled us to determined the deuterated styrene block molecular weight.

The results of this characterization scheme for the copolymers discussed here are given in *Table 1*.

Electron microscopy

Ultra-thin films of the block copolymers were cast from solutions in toluene by dropping 1 μl of the solution (circa 0.1% w/v copolymer) on to an electron microscope support grid of 200 mesh and allowing the solvent to evaporate. The films were stained by osmium tetroxide and transmission electron micrographs (*TEM*) obtained on a Phillips EM200 electron microscope located in the department of Metallurgy in the University.

Small angle X-ray scattering (*SAXS*)

As a comparison small angle X-ray measurements were made on two of the copolymers, SIS2 and SI4. These measurements were made by the courtesy of Dr. C. Price, Manchester University, on a Rigaku-Denki small angle X-ray camera. Photographic detection was used, the sample to film distance being 25 cm with Ni filtered Cu K_α incident radiation. The exposed negatives were subsequently analysed using a Joyce–Loebl double beam recording microdensitometer Mk III C.

Small angle neutron scattering (*SANS*). Approximately 1 mm thick samples of the copolymers were prepared by casting from toluene solution on to optical quality quartz discs. The toluene was evaporated off slowly at room temperature for 1 week, final traces being removed under vacuum for two days. Samples were not subsequently thermally annealed since these copolymers are particularly prone to degradation. Discs were then mounted in cylindrical brass cells and SANS measurements made at room temperature.

The range of scattering vector, Q, ($=(4\pi/\lambda)\sin(\theta/2)$, where λ = neutron wavelength, θ = scattering angle) investigated was particularly wide, $0.3 \leqslant 10^2 Q(\text{Å}^{-1}) \leqslant 15$. This range of Q was obtained by using two small angle neutron diffractometers with overlapping Q ranges. For $0.3 \leqslant 10^2 Q(\text{Å}^{-1}) \leqslant 4.5$, the D11 diffractometer at the Institut Laue–Langevin, Grenoble, France[23] was used; measurements in the range $2.6 \leqslant 10^2 Q(\text{Å}^{-1}) \leqslant 15$ were made on the AERE Harwell, UK[24] small angle diffractometer. All data was normalized to the neutron scattering from a 2 mm thick water standard which gives an essentially flat isotropic scattered intensity over the range of Q investigated.

RESULTS

Electron microscopy

Typical electron micrographs of four of the copolymers are shown in *Figure 1*. There is evidence of microphase separation in all of the micrographs and the morphology is dependent on the styrene weight fraction. The long range ordering of the domains observed by other workers[2,4,5] is not apparent. However, the electron micrographs are of sufficient quality to make estimates of the average interdomain separation and domain size which we discuss below.

Small angle X-ray scattering. A smoothed microdensitometer plot for SI4 is shown in *Figure 2*, only one diffraction maxima is evident but the increase in density at smaller distances from the beam centre is, we believe, due to the presence of another maximum beyond the range of the camera used. This supposition is confirmed on comparing the inter domain distance, d_{int}, calculated from this maxima with that obtained from SANS diffraction patterns. From SAXS we obtain $d_{\text{int}} = 500$ Å which is almost half that from SANS and would be expected for a second order reflection from a lamellar structure (see below).

For copolymer SIS2, only one clear diffraction maximum was apparent in the microdensitometer profile. From its position the value of d_{int} calculated is 327 Å which compares well with the value obtained below from SANS.

Small angle neutron scattering

SANS measurements have been used to determine four features of the solid state structure of the copolymers.

(1) The interdomain distance and long range ordering of the domains.

(2) The domain morphology and size.

(3) The dimensions of the styrene blocks in the domains.

(4) The thickness of the interfacial layer surrounding the domain.

Items 2, 3 and 4 are reported for SI 1 and DSI 1 alone in this paper.

For randomly oriented scattering centres the scattered neutron intensity $I(\tilde{Q})$ at a scattering vector $\tilde{Q}$, is given by the general equation[25,26].

$$I(\tilde{Q}) = K(\rho_p - \rho_m)^2[\langle F_p^2(\tilde{Q})\rangle - \langle F_p(\tilde{Q})\rangle^2 + \langle F_p(\tilde{Q})\rangle^2 A_i(Q)] \tag{1}$$

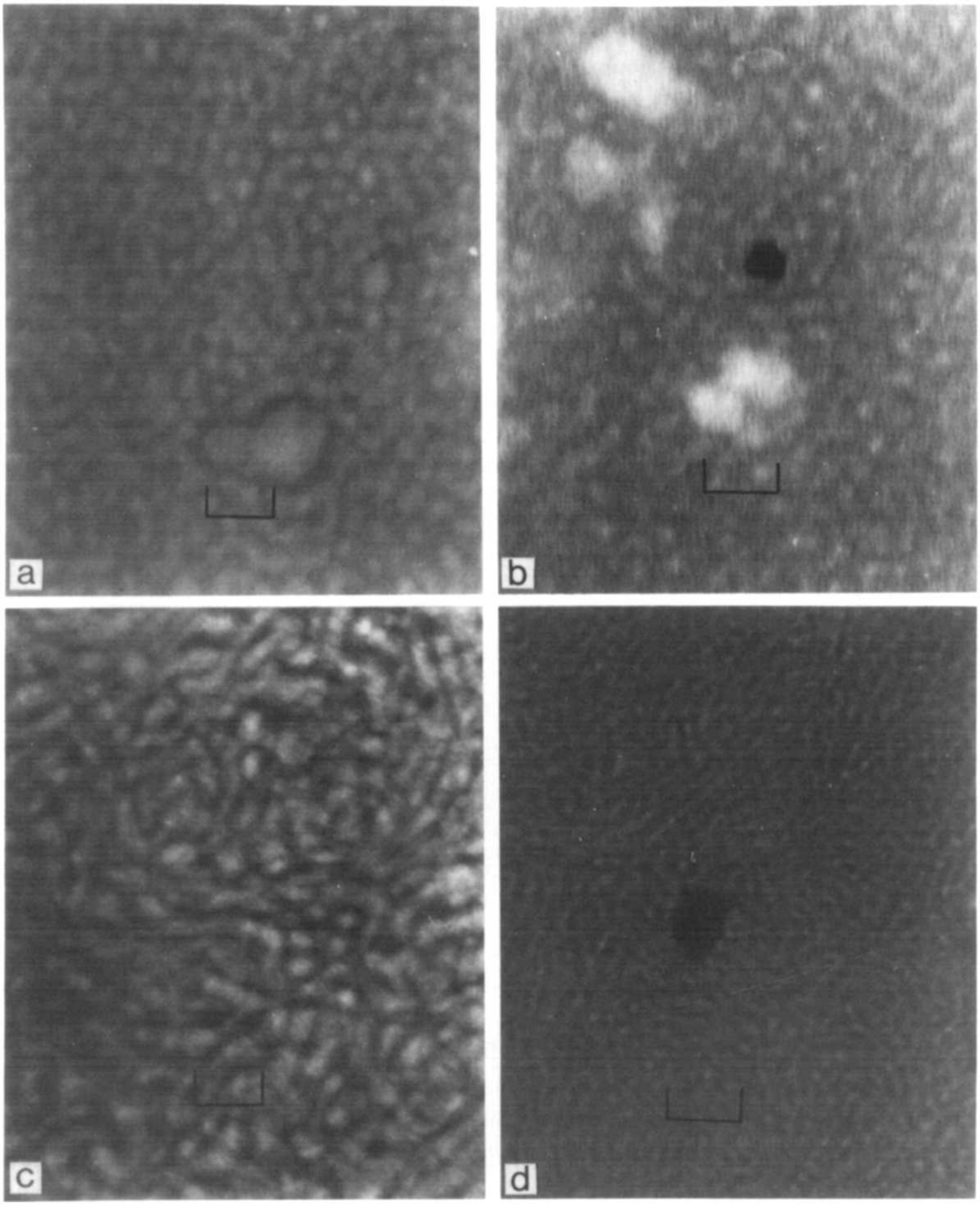

Figure 1 Electron micrographs of solution cast films of styrene-isoprene block copolymers. a, SI 1; b, SIS 1; c, SI 2; d, SIS 2. Scale marker = 0.1 μ (1000 Å)

In equation 1, K is a constant which will include such factors as neutron source 'brightness', thickness of sample and detector efficiency.

ρ_i is the scattering length density of the particle, p, and the matrix in which it is dispersed, m.

$F_p(\tilde{Q})$ is the single particle form factor and $\tilde{Q}$ denotes a vector quantity.

$A_i(Q)$ is the interparticle interference function.

For scattering particles which are reasonably uniform in shape and size, $\langle F_p^2(\tilde{Q})\rangle \simeq \langle F_p(\tilde{Q})\rangle^2$ (exact cancellation is obtained for spherical particles)[25].

Consequently, equation 1 reduces to

$$I(\tilde{Q}) = K(\rho_p - \rho_m)^2 \langle F_p(\tilde{Q})\rangle^2 A_i(Q) \qquad (2)$$

At large values of Q, the interparticle interference function reduces to 1, at lower values a series of discrete peaks in $I(\tilde{Q})$ as a function of Q will be apparent for particles which are arranged in a 'pseudo-crystalline' lattice. These peaks should be apparent even where $(\rho_p - \rho_m)^2$, the contrast factor, is very small. However, scattering due to the particle form factor, $F_p(\tilde{Q})$, will depend markedly on the contrast factor since it pertains to an isolated particle. The contrast factor may be accentuated by using deuterated polymers, *Table 2* gives values of the coherent scattering length, b, of styrene, isoprene and deuterated styrene together with their scattering length density, which is defined as $\rho = b/V_s$, where V_s is the volume of the scattering particle (the monomer units in

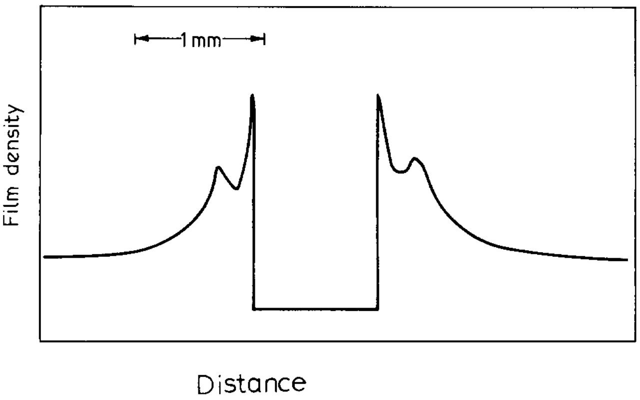

Figure 2 Microdensitometer plot from small angle X-ray scattering photograph of SI 4

the polymer). From this Table it is apparent that the contrast factor for the combination of deuterated styrene with isoprene is nearly thirty times that of the hydrogenous styrene–isoprene combination. Hence by judicious use of deuterated styrene blocks the scattering due to the form factor may be enhanced. The results for points 1–4 are presented below.

Table 2

Scattering particle	$10^{12}b$ (cm)	$10^{-10}\rho$ (cm cm^{-3})
Styrene	2.328	1.416
Isoprene	0.333	0.289
Deuterated styrene	10.66	6.302

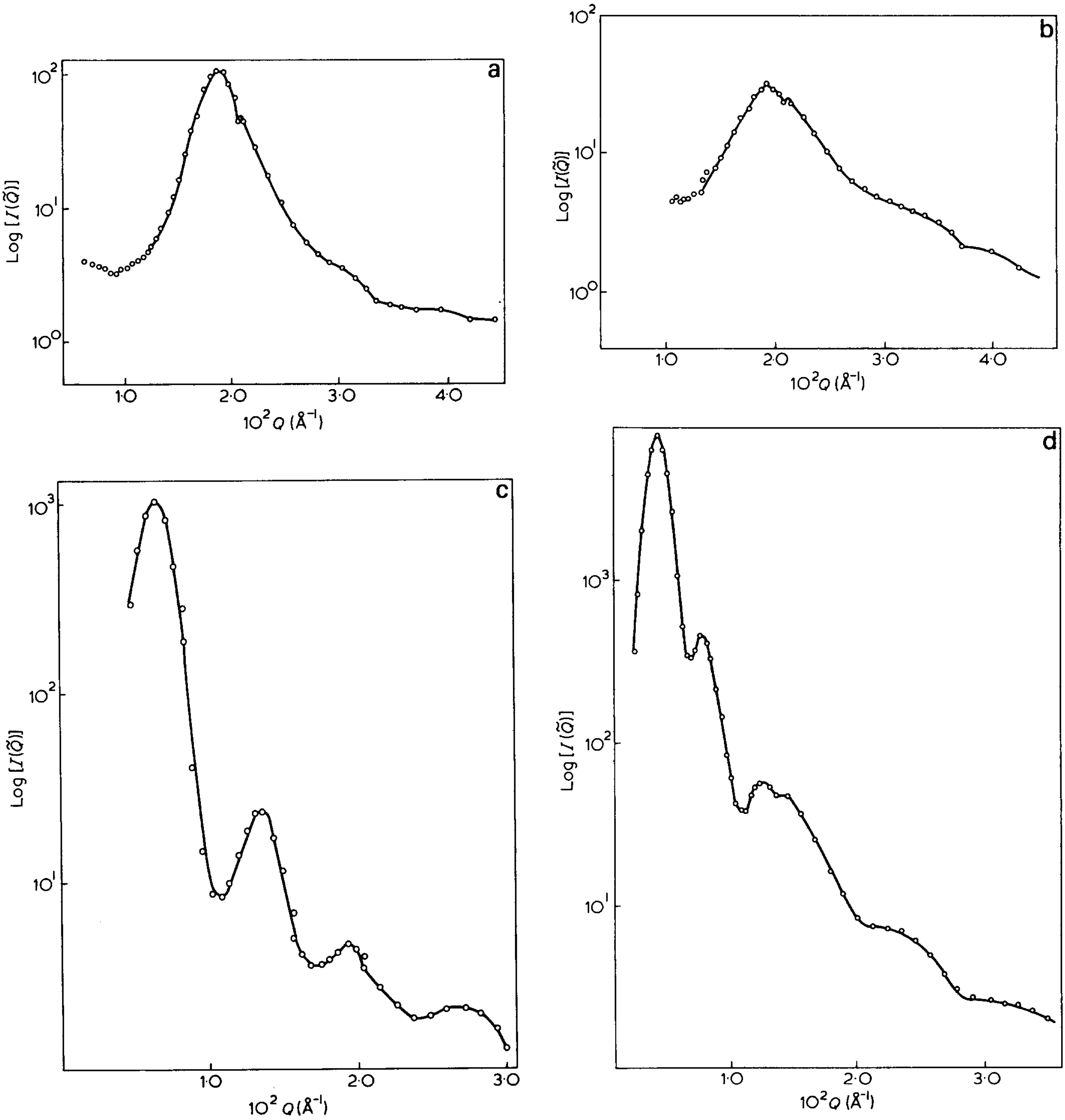

Figure 3 Water normalized neutron scattering profiles for styrene–isoprene block copolymers. a, SI 1; b, SIS 1; c, SI 4; d, SI 5

Table 3

Copolymer	d_{int} (Å)	d_1/d_1	d_2/d_1	d_3/d_1	d_4/d_1	d_5/d_1	d_6/d_1
SI 1	338	1	0.87	0.62	0.39		
SI 2	576	1	0.52	0.39	0.29		
SI 4	952	1	0.49	0.34	0.24	0.19	0.17
SI 5	1366	1	0.58	0.39	0.31	0.191	0.14
SIS 1	324	1	0.87	0.56	0.49		
SIS 2	307	1	0.65	0.51			
DSI 1	383	1	0.84	0.59			

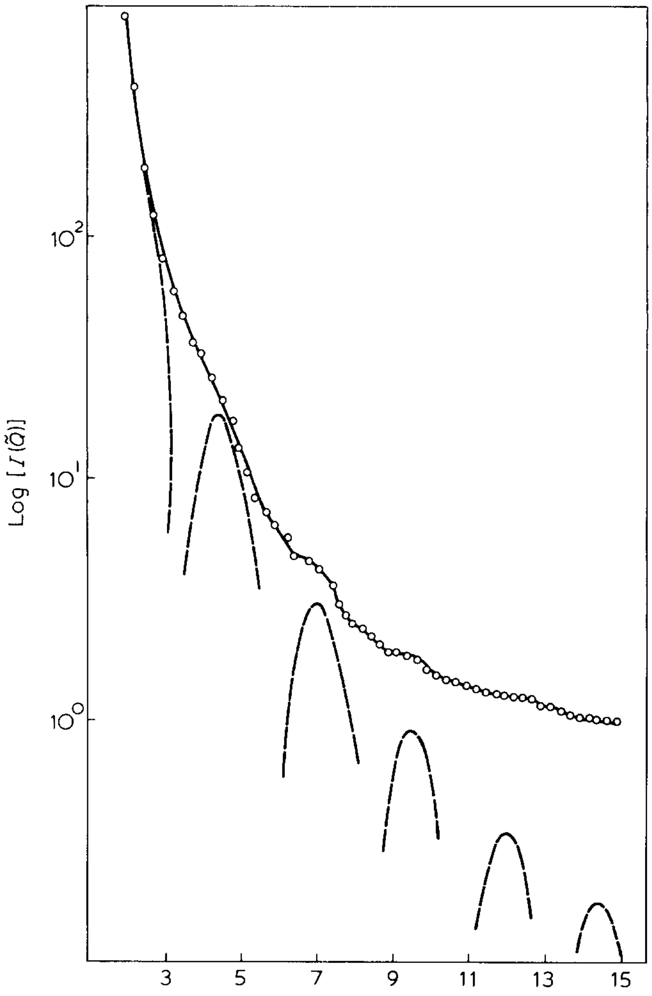

Figure 4 Water normalized neutron scattering intensity for DSI 1 at high Q (— — — —) = Bessel function for an isolated hard sphere of radius 130 Å

Interdomain distance and domain ordering. Typical water normalized SANS envelopes for some of the hydrogenous copolymers in the Q range $0 < 10^2 Q(\text{Å}^{-1}) \leqslant 4.5$ are shown in *Figure 3*. All have one peak of large intensity and several subsidiary peaks of lesser amplitude, the resolution of these subsidiary peaks being less than that of the main peak. The line connecting the points is drawn as a guide to the eye.

A value for d_{int} was obtained from the Q value of the first maximum, Q_{max}, using Bragg's law, i.e.

$$d_{int} = \frac{2\pi}{Q_{max}}$$

These values together with the ratio of the spacings from subsidiary peaks to that of the first maximum, d_n/d_1, are given in *Table 3*.

(2) *Domain morphology and size.* For DSI 1, the scattered neutron intensity, normalized to water, for $3 \leqslant 10^2 Q(\text{Å}^{-1}) \leqslant 15$ is shown in *Figure 4*. Damped oscillations are apparent superimposed on the general decay in $I(\tilde{Q})$ as a function of Q. Form factors for isolated hard spheres or cylinders result in such damped oscillations[27–29], for an isolated hard sphere, the model most appropriate for DSI 1, the form factor is given by equation 3:

$$\langle F_p(\tilde{Q})\rangle^2 = \frac{9\pi J_{3/2}(QR_s)}{2\ (QR_s)} \tag{3}$$

where $J_{3/2}(x)$ is a spherical Bessel function of order 3/2. The theoretical curve for a sphere of radius 130 Å has been included in *Figure 4*. The coincidence between the maxima of the theoretical and experimental curves is sufficiently good for us to have some confidence in this value of the domain radius, R_s.

(3) *Styrene block dimensions in the spherical domains.* To determine the z average mean square radius of gyration ($\langle s^2\rangle_z$) of the styrene block, a mixture of DSI 1 and SI 1, such that DSI 1 was 4% (w/w) of the mixture, was dissolved in toluene and films for SANS measurements cast directly from this solution. As a 'background' sample an identical film of hydrogenous SI 1 was used. The excess scattered neutron intensity due to the presence of DSI 1 was obtained by subtracting the 'background' scattered intensity from that of the doped copolymer.

In this situation, the form factor in equation 2 is given by the Guinier equation[26]:

$$\langle F(\tilde{Q})\rangle^2 = \exp(-Q^2\langle s^2\rangle_z/3) \tag{4}$$

from which:

$$I(\tilde{Q}) = K(\rho_p - \rho_m)^2 \exp(-Q^2\langle s^2\rangle_z/3)$$

Assuming that interparticle interference is absent this may be rearranged to give:

$$\frac{KC(\rho_p - \rho_m)^2}{I(Q)} = \frac{1}{M_w}\left(1 + \frac{\langle s^2\rangle_z}{3}Q^2\right) \tag{5}$$

Excess scattered neutron intensities are plotted accordingly to equation 5 in *Figure 5*, using the scattering vector range $3.6 \leqslant 10^2 Q(\text{Å}^{-1}) \leqslant 7.28$. This range of scattering vector was chosen since it was removed from the region of the main Bragg peak but the intensity of scattering was sufficient to give good counting statistics. From *Figure 7*, the mean square radius of gyration obtained is $1.59 \pm 0.2 \times 10^3$ Å^2.

From the intercept of *Figure 7* it is possible to calculate a value for the molecular weight of the styrene block. This calls for an absolute calibration of the neutron diffractometer and the method we have used is detailed in the appendix. By this means we obtain a molecular weight (M_w) of $2.6 \pm 0.3 \times 104$ for the deuterated styrene block of DSI 1. This is in excellent agreement with the g.p.c. molecular weight of 2.1×10^4. The agreement between the two values implies that the deuterated copolymer is dispersed randomly throughout the domains and is not aggregated.

(4) *Thickness of the interfacial layer*. When Q is greater than the reciprocal of the shortest dimension of the scattering particle, then the intensity of scattering should follow the Porod approximation, i.e., a Q^{-4} dependence[27]. Thus, for the case of spherical domains this approximation may be used to estimate the surface area of the sphere. The decrease in $I(Q)$ for SI 1 over the range $8 \leqslant 10^2 Q(\text{Å}^{-1}) \leqslant 15$, which is well within the range where the Porod approximation is valid, does not follow such a behaviour and the exponent in a $\log I(\tilde{Q}) - \log(\tilde{Q})$ plot is not an integral value. Two causes for such deviations have been proposed by Ruland[30]: (1) a finite region where the scattering length density changes, or (2) fluctuations of the scattering length density in the two phases. The former is more feasible for block copolymers with microphase separation. The means by which the thickness of the interfacial layer may be obtained from small angle scattering data have recently been reviewed by Koberstein *et al.*[31] Equation 6 relates $I(Q)$ in the Porod region to the interfacial thickness, t, for a trapezoidal or expanded sigmoidal scattering length density change across the interface.

$$(Q)/2\pi^4 I(Q) = K^*(1 - [\pi^2 t^2 (Q/2\pi)^2]/3) \qquad (6)$$

Data for DSI 1 are plotted according to this equation in *Figure 6*, from the slope and intercept we obtain $t = 29 \pm 3$Å. The oscillations on this Figure are due to the maxima of the Bessel function scattering from the spherical domains.

DISCUSSION

Table 4 gives the characteristic ratios for simple regular arrangements of domains with respect to each other[32], notice being taken of the characteristic absences[33]. By comparing *Tables 3* and *4*, it is seen that SI 4 corresponds to a lamellar arrangement of alternating styrene and isoprene domains. However, SI 5 is in best agreement with a two dimensionally close packed arrangement of cylinders, although certain diffraction maxima (in this case the 20, 22, 31 and 40 reflections) are absent.

Electron micrographs of solution cast films show circular isoprene domains dispersed in a polystyrene matrix. Unfortunately, the electron micrographs do not show a regular arrangement of domains. We believe this is due to the preparation method of the ultra-thin films. Such small quantities of solution are used that evaporation

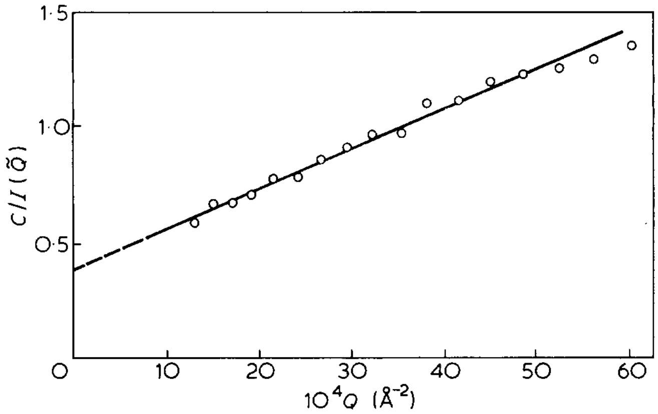

Figure 5 Zimm type plot of scattered neutron intensity for DSI 1 (4% w/w) in SI 1

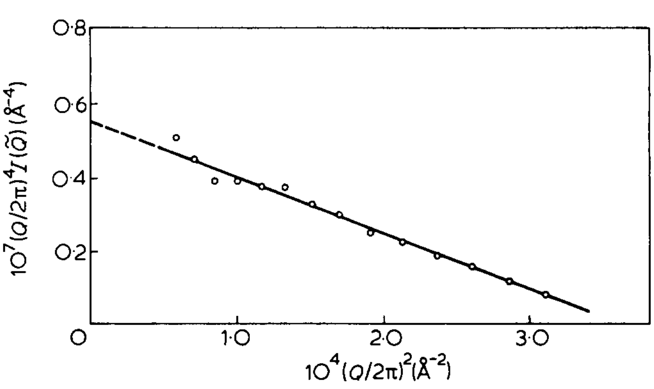

Figure 6 Plot of $(Q/2\pi)^2\, I(\tilde{Q})$ as a function of $(Q/2\pi)^{-2}$ to determine the interfacial thickness, t, of SI 1

Table 4

Simple cubic (*sc*)	d_{hkl}/d_{100} hkl	1 100	0.707 110	0.577 111	0.5 200	0.447 210	0.408 211	0.353 220	0.333 221
Face-centred cubic (*fcc*)	d_{hkl}/d_{111} hkl	1 111	0.866 200	0.613 220	0.521 311	0.500 222	0.434 400	0.379 331	0.387 420
Body-centred cubic (*bcc*)	d_{hkl}/d_{110} hkl	1 110	0.707 200	0.577 211	0.5 220	0.408 222	0.377 321	0.353 400	0.333 330
Hexagonally close packed cylinders (*hpc*)	d_{hk}/d_{10} hk	1 10	0.577 11	0.500 20	0.378 21	0.333 30	0.289 22	0.270 31	0.250 40
Lamellae (*l*)	d_n/d_1 n	1 1	0.5 2	0.333 3	0.25 4	0.2 5	0.167 6	0.143 7	0.125 8

takes place quickly and there is insufficient time for ordering to be achieved. In spite of this lack of order, the average centre-to-centre separation of the domains estimated from the electron micrographs is 1190 Å, in fair agreement with d_{int} obtained from SANS data. It appears that copolymer SI 5 has an hexagonally close packed array of cylinders, with a separation distance of ~1370 Å normal to the surface of the sample. In the absence of electron micrographs normal to the surface of the sample this assignment cannot be directly confirmed, this is also true for SI 4 since other workers have shown that lamellae are parallel to the film surface[34]. We hope to confirm these structures by future electron microscopy on specimens obtained by ultra-microtoming slices from the samples used for SANS work. However, the SANS data are sufficiently good for us to be confident of the proposed structures. Also the composition of SI 4 and SI 5 are such that lamellar and hexagonally packed structures, respectively, could be expected[4].

For copolymers SI 2 and SIS 2 assignment of structural arrangement is not easy. Comparison of *Tables 3* and *4* indicates that either a face centred cubic array of polystyrene spheres or a hexagonally packed array of styrene cylinders would be the closest descriptions of the solid state structure. Indeed, close examination of the electron micrographs (*Figure 1*), shows a series of connected polystyrene spheres. The composition of these copolymers falls within the range where a change in solid state structure may be expected[2], and there may be a mixture of the face centred cubic and hexagonally packed structures present in the material.

For SIS 1, a face centred cubic structure is most suitable from comparison of *Tables 3* and *4*. The second diffraction maximum is broad and may be a combination of the 220 and 311 reflections. From the electron micrograph the average domain separation is ~460 Å, in poor agreement with the value of d_{int} from SANS results.

With regard to SI 1 and DSI 1, comparison of experimental and theoretical characteristic ratios indicates that a face centred cubic structure is the most suitable. DSI 1, surprisingly, has fewer diffraction maxima than the hydrogenous polymer. Due to the increased contrast when the styrene blocks are fully deuterated we would have expected that weak diffraction maxima would be more apparent. This is not observed and may be due to the increased contribution of void scattering which becomes evident when the deuterated polymer content is increased, this void scattering would effectively mask the weaker subsidiary maxima. Apart from this there are several diffraction maxima absent from SI 1; they are the 311, 222 and 400 reflections. SAX studies of similar copolymers are similar in that certain diffraction maxima are missing from the scattering envelope[6]. An explanation has been proposed to account for these absences: the maxima in the interparticle interference function, $A_i(Q)$ coincide with a minima of the particle form factor. We do not believe that this is the full explanation, although it is a contributing factor, it being more likely that the three missing reflections have merged into one broad peak which cannot be discerned from the general background. From the electron micrographs the average centre-to-centre distance between the styrene domains is estimated to be 370 Å, which is excellent confirmation of the SANS value of 338 Å. For DSI 1 the interdomain distance from electron micrographs is 420 Å, also in excellent agreement with the SANS value of 383 Å. Also, for DSI 1 the diameter of the spherical domains estimated from electron micrographs is 230 Å, in fair agreement with the value of 260 Å obtained by SANS. This SANS value is a 'hard sphere' value since it has been obtained by fitting (qualitatively) a hard sphere form factor to the experimental data. The breadth of the maxima in *Figure 4* and the finite value of the interfacial thickness show that the domains are not hard spheres. A check on the veracity of the proposed face centred cubic structure and the domain diameter may be obtained via a calculation of the volume fraction, φ_s, of polystyrene in the copolymer. For a face centred cubic structure:

$$\varphi_s = 0.74\left\{\frac{2R_s}{d_{\text{int}}}\right\}^3 \tag{7}$$

Using the SANS values of R_s and d_{int} φ_s is calculated to be 0.232, assuming that the densities of polystyrene and polyisoprene in the block copolymers is the same as their respective homopolymers, then the weight fraction obtained by u.v. analysis corresponds to a volume fraction of polystyrene of 0.295. Considering that these two values of the volume fraction are obtained by two independent methods, the agreement is very good. Also, we have used a hard sphere radius for the domains, but it is apparent that some of the polystyrene is in the interface and this may explain the slight discrepancy between the two values.

Much theoretical work has been concentrated on the existence of an interfacial region around the domains. In this interfacial region junctions are located between the two block sequences, and partial mixing of the two species takes place. Evidence for this interfacial region is not yet strong even though its existence is considered to be crucial in explaining some dynamic mechanical properties of this type of block copolymer[18,19,35]. The interfacial thickness is dependent on the copolymer molecular weight, composition and the thermodynamic interaction between the two block lengths. Using solubility parameters as a first approximation for the latter parameter, Meier[15] has calculated values of the interfacial thickness and the volume fraction of copolymer intermixed, $\Delta V(t)/V$, which is a single valued function of the product of copolymer molecular weight and interaction parameter. Interfacial thickness values calculated by this theory range from 15 to 80 Å and our experimental value of 29 ± 3 Å falls well within this range. A better comparison with the theory is gained from the parameter $\Delta V(t)/V$, using the values of d_{int} and t from our SANS studies in conjunction with the proposed face centred cubic structure, we calculate that for DSI 1, $\Delta V(t)/V$ should be 0.11. From the theoretical calculations of Meier this ratio is approximately 0.16. The tolerably close agreement between the theoretical and experimentally calculated values provides some support for Meier's theory. The theoretical value of $\Delta V(t)/V$ is extremely sensitive to the value of the solubility parameters used. Using the range of solubility parameters quoted in the literature for the two homopolymers, it is possible to obtain values for $\Delta V(t)/V$ ranging from 0.08 to 0.24. The original theory relates to lamellar domains which SI 1 does not have, however it should be applicable to block copolymers of different domain structure without too much error.

Finally, there remains the radius of gyration of the styrene block of DSI 1 in the spherical domains of SI 1. A statistical thermodynamic theory has been used by Meier[14] to obtain equations relating domain dimensions to the root mean square end-to-end distance, $\langle r^2\rangle^{1/2}$, of the block making up the domain. For spherical domains, of direct interest here,

$$R_s = 1.33\langle r^2\rangle^{1/2} \tag{8}$$

The radius of the spherical domains of DSI 1 is 130 Å (from SANS) whilst that of SI 1 is estimated from electron micrographs at 116 Å; the difference is not large even though the molecular weights of the deuterated styrene blocks of DSI 1 are almost twice that of the hydrogenous blocks of SI 1. Assuming that a Gaussian segment density distribution prevails in the domains and hence $\langle r^2\rangle = 6\langle s^2\rangle$, then from the SANS determined value of $\langle s^2\rangle$ (1.59×10^3 Å^2) we obtain $R_s = 130$ Å from equation 8. This value is in good agreement with the sphere radii quoted above obtained by other methods. Although it would be attractive to conclude that Meier's predictions are supported by these figures, we feel that this would be too ambitious at this stage. There are good reasons to expect that $\langle r^2\rangle$ does not equal $6\langle s^2\rangle$ in these system, additionally the value of 130 Å for the sphere radius is subject to an error of at least ±20 Å.

For the styrene block molecular weight (2.1×10^4) used for the determination of $\langle s^2\rangle$, the unperturbed mean square radius of gyration of homopolystyrene is 1.31×10^3, by comparison with the experimental value it appears that the styrene block is slightly expanded in the domain and the expansion coefficient α, is 1.1. In view of the supermolecular ordering in the block copolymers and the consequent difficulties in subtracting the background scattering from that of the doped sample, the fact that we have obtained a not unreasonable value of $\langle s^2\rangle$ is encouraging for the similar measurements we intend to carry out on the other copolymers.

CONCLUSIONS

We have demonstrated that much more information may be obtained about the solid state structure of block copolymers using SANS than by any other single technique. More diffraction maxima are apparent in the neutron scattering profiles than in those from X-ray scattering and consequently structural assignments can be made with much less ambiguity.

By using deuterated styrene blocks it has been possible to confirm the spherical domain morphology of one of the copolymers and determine the domain size. Independent confirmation of the domain size and structural arrangement with respect to each other was obtained by the good agreement between the volume fraction calculated from these data and that from elemental analysis. Values of the interfacial thickness and mean square radius of gyration gave some support to Meier's theories of domain formation and structure of block copolymers.

ACKNOWLEDGEMENTS

We thank the Science Research Council for financial support of this project. The assistance of the technical establishment at the ILL is acknowledged, particular thanks are due to Mr. V. Rainey for assistance with the Harwell small angle diffractometer.

REFERENCES

1 Holden, G., Bishop, E. and Legge, N. *J. Polym. Sci.* (*C*) 1969, **26**, 59

2 Inoue, T., Soen, T., Hashimoto, T. and Kawai, H. *J. Polym. Sci.* (*A-2*) 1969, **7**, 1283

3 Uchida, T., Soen, T., Inoue, T. and Kawai, H. *J. Polym. Sci.* (*A-2*) 1972, **10**, 101

4 Gallot, B. R. M. *Adv. Polym. Sci.* 1978, **29**, 85

5 Lewis, P. R. and Price, C. *Polymer* 1972, **13**, 20

6 Lewis, P. R. and Price, C. *Polymer* 1971, **12**, 258

7 Price, C., Lally, T. P., Watson, A. G., Woods, D. and Chow, M. T. *Br. Polym. J.* 1972, **4**, 413

8 McIntyre, D. and Campos-Lopez, E. *Macromolecules* 1970, **3**, 322

9 Legrand, A. D., Vitale, G. G. and Legrand, D. G. *Polym. Eng. Sci.* 1977, **17**, 598

10 Todo, A., Hashimoto, T. and Kawai, H. *J. Appl. Cryst.* 1978, **11**, 558

11 Helfand, E. and Wasserman, Z. R. *Polym. Eng. Sci.* 1977, **17**, 582 (and cognate references)

12 Bendler, J. and Solc, K. *Polym. Eng. Sci.* 1977, **17**, 622

13 Meier, D. J. *J. Polym. Sci.* (*C*) 1969, **26**, 81

14 Meier, D. J. *Polymer Prepr.* 1970, **11**, 400

15 Meier, D. J. *Polymer Prepr.* 1974, **15**, 171

16 Leary, D. P. and Williams, M. C. *J. Polym. Sci.* (*B*) 1970, **8**, 149

17 Hashimoto, T., Nagatoshi, K., Todo, A., Hasegawa, H. and Kawai, H. *Macromolecules* 1974, **7**, 364

18 Shen, M. H. and Kaelble, D. H. *J. Polym. Sci.* (*B*) 1970, **8**, 149

19 Kraus, G. and Rollmann, K. W. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 1133

20 Maconnachie, A. and Richards, R. W. *Polymer* 1978, **19**, 739

21 Richards, R. W. in 'Developments in polymer characterization', (Ed J. V. Dawkins) Applied Science Publishers, 1978, Ch. 5

22 Richards, R. W., Maconnachie, A. and Allen, G. *Polymer*, to be published

23 Neutron Beam Facilities available at the HFR published by the Institute Laue–Langevin, 1977

24 'Neutron Beam Instruments at Harwell' (Eds A. H. Baston and D. H. C. Harris) HMSO 1978

25 Hosemann, R. and Bagchi, S. N. 'Direct Analysis of Diffraction by Matter', North Holland Publishing Co. Amsterdam, 1962

26 Kostorz, G. 'Treatise on Materials Science and Technology, Vol 15 Neutron Scattering', Academic Press, New York, 1979

27 Guinier, A. and Fournet, G. 'Small Angle Scattering of X-rays', Wiley, New York, 1955

28 Oster, G. and Riley, D. P. *Acta Crystallogr.* 1952, **5**, 1

29 Oster, G. and Riley, D. P. *Acta Crystallogr.* 1952, **5**, 272

30 Ruland, W. *J. Appl. Crystallogr.* 1971, **4**, 70

31 Koberstein, J. T., Morra, B. and Stein, R. S. *J. Appl. Crystallogr.* 1980, **13**, 34

32 For cubic systems. $d_{hkl}/d_{111} = [3/(h^2+k^2+l^2)]^{1/2}$ For a two dimensional array of hexagonally close packed cylinders $d_{hk}/d_{10} = [1/(h^2+hk+k^2)]^{1/2}$.

33 Barrett, C. S. 'Structure of Metals' 2nd Edn. McGraw–Hill, New York, 1953

34 Hashimoto, T., Todo, A., Itoi, H. and Kawai, H. *Macromolecules* 1977, **10**, 377

35 Aggarwal, S. L. *Polymer* 1976, **17**, 938

APPENDIX

Calculation of molecular weight of polymers from absolute scattering intensity

We assume the following conditions: incident neutron beam of intensity $I_0 n$ cm^{-2} s^{-1}.
Sample thickness, t cm; Cross sectional area of beam incident on sample, S cm^2; Total scattering cross section, σ_t; Detector efficiency, ε_d; Average nuclear density, $n_n(\equiv N/V)$; Where N is the number of nuclei in the sample volume V 'illuminated' by the beam; Incoherent scattering cross section, σ_{inc}; Differential coherent scattering cross section per atom, $d\sigma_c/d\Omega$; Solid angle in which scattered neutrons are counted, $\Delta\Omega$; The total scattered neutron intensity is, at any value of the scattering vector, $\tilde{Q}$,

$$I(\tilde{Q})=I_0St\,\exp(-n_n\sigma_t t)n_n\varepsilon_d\left\{\frac{d\sigma_c}{d\Omega}+\frac{\sigma_{inc}}{4\pi}\right\}\Delta\Omega \qquad \text{(A1)}$$

We assume that the incoherent scattering contribution ($\sigma_{inc}/4\pi$) can be subtracted, e.g., by measuring the scattered intensity from an 'undoped' sample, and hence we obtain the intensity due to coherent scattering alone.

$$I(\tilde{Q})=I_0St\,\exp(-n_n\sigma_t t)n_n\varepsilon_d\frac{d\sigma_c}{d\Omega}\Delta\Omega \qquad \text{(A2)}$$

We must determine the instrumental parameters in the combination $I_0S\varepsilon_d\Delta\Omega$. This may be obtained by using a purely incoherent scattering material since the scattered intensity is isotropic. Vanadium is such a material but generally water has been preferred due to its higher scattering power. For the calibrant material scattering incoherently,

$$I_c(\tilde{Q})=\frac{I_0S\varepsilon_d\Delta\Omega(1-T_c)}{4\pi} \qquad \text{(A3)}$$

where T_c = transmission of the calibrant i.e., ratio of intensities at $Q=0$ in the presence and absence of calibrant

$$\therefore\; I_0S\varepsilon_d\Delta\Omega=\frac{4\pi I_c(\tilde{Q})}{(1-T_c)} \qquad \text{(A4)}$$

$\therefore$ Replacing in A2

$$\therefore\; I(\tilde{Q})=\frac{4\pi I_c(\tilde{Q})}{(1-T_c)}t\,\exp(-n_n\sigma_t t)n_n\frac{d\sigma_c}{d\Omega} \qquad \text{(A5)}$$

But $\exp(-n_n\sigma_t t)$ = sample transmission T_s

$$\therefore\; I(\tilde{Q})=\frac{4\pi I_c(\tilde{Q})tT_s}{(1-T_c)}N_n\frac{d\sigma_c}{d\Omega} \qquad \text{(A6)}$$

We now use a two phase model for $(d\sigma_c/d\Omega)$, that is we have N_p particles (polymer molecules) of scattering length density ρ_p and volume V_p dispersed in a matrix of scattering length density ρ_m, thus

$$\frac{d\sigma_c}{d\Omega}=\frac{V_p^2N_p}{N}(\rho_p-\rho_m)^2\langle F_p(\tilde{Q})\rangle^2 \qquad \text{(A7)}$$

where $\langle F_p(\tilde{Q})\rangle$ is the single particle form factor so defined as to equal 1 at $Q=0$.

In A7 $N_p=c/MN_ASt$ where c = concentration in g ml^{-1}, M = molecular weight, N_A = Avogadro's Number, and $V_p=\bar{v}M/N_A$ with $\bar{v}$ = partial specific volume of the polymer molecule.

Replacing for these quantities in A7 and A6 and noting that $St=V$ we obtain

$$I(\tilde{Q})=\frac{4\pi I_c(\tilde{Q})}{(1-T_c)}tT_s\frac{\bar{v}^2M}{N_A}c(\rho_p-\rho_m)^2\langle F_p(\tilde{Q})\rangle^2$$

$$\therefore\frac{cI_c(\tilde{Q})}{I(\tilde{Q})}=\frac{(1-T_c)N_A}{4\pi tT_s\bar{v}^2M(\rho_p-\rho_m)^2\langle F_p(\tilde{Q})\rangle^2} \qquad \text{(A8)}$$

Hence on extrapolating equation (A8) to $|\tilde{Q}|=0$; $\langle F_p(\tilde{Q})\rangle^2=1$ $\therefore$ rearranging

$$\frac{1}{M}=\frac{cI_c(0)4\pi tT_s\bar{v}^2(\rho_p-\rho_m)^2}{I(0)(1-T_c)N_A} \qquad \text{(A9)}$$

All the terms on the right hand side of equation A9 are known for the sample either by experiment or by calculation and hence the molecular weight may be calculated. As in light and small angle X-ray scattering this value is a weight average molecular weight, $\bar{M}_w$. Thus, for the sample used to determine the radius of gyration of the styrene sequences in the copolymer, DSI 1 in SI 1, the following data was obtained. $c=0.012$ g ml^{-1} (concentration of deuterated polystyrene in specimen).

$I_c(0)/I(0)=0.38$, $t=0.2$ cm

$T_s=0.47$, $\bar{v}=0.94$

$(\rho_p-\rho_m)^2=3.31\times10^{21}$ cm cm^{-3}*

$T_c=0.39$

Hence,

$$1/M=\frac{0.012\times0.38\times4\pi\times0.2\times0.47\times0.94^2\times3.31\times10^{21}}{(1-0.39)N_A}$$

$$=2.64\times10^4$$

---

* For the calculation of the contrast factor $(\rho_p-\rho_m)^2$, the value of ρ_p corresponds to deuteropolystyrene, whilst ρ_m is a weighted sum of the scattering length densities for hydrogenous polystyrene and polyisoprene.