Small-Angle X-ray Scattering from Block Copolymers as an Ideal Model System for a Pseudo Two-Phase Solid Texture

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The microdomain structure of polystyrene–polysoprene A–B type block copolymers was analysed by small-angle X-ray scattering (SAXS) as an ideal model system for a pseudo two-phase solid structure. The structure was analysed in terms of spatial distribution, size, and the interfaceal structure of the dispersed domains of one component (A segments) in the matrix of the other (B segments). The SAXS analyses were performed with two collimating systems, a Rigaku Denki camera (essentially a four-slit system with the addition of Soller slits) and a Kratky camera, which had widely different slit-length and slit-width weighting functions and was used to investigate instrumental effects, especially the role of the Soller slits in the obtaining of reliable desmeared intensity data in the tail of the SAXS curve. Comparison of the results indicated that the Soller slits facilitate the accurate evaluation of the interfaceal thickness from the desmeared intensity data in the tail. The accuracy of the infinite slit-height approximation and the effect of truncating the higher-order terms in \( I_k \) (the intensity associated with the interphase) on the estimated interfaceal thickness are discussed. The infinite slit-height approximation leads to values 25–35% smaller than the exact value (23 Å), and the truncation also leads to a value of the interfaceal thickness smaller (19 Å) than the value (23 Å) based on the full analysis. The value obtained is in good agreement with the values predicted from the theoretical-mechanical theories of block copolymers in bulk.

I. Introduction

Block copolymers composed of incompatible and noncrystallizable A and B polymer segments form a typical pseudo two-phase texture in the solid state, which is well known as the microdomain structure (Molau, 1970). The domain structure is formed as a consequence of the microphase separation of the A and B segments in solidification processes. There are five fundamental microdomain structures: a sphere and A rod dispersed in a matrix of B, their phase-inverted structures and the alternating lamellar structure (Inoue, Soen, Hashimoto & Kawai, 1969). It has been established that the shape of the domain primarily depends upon the fractional composition of A segments in the copolymers and that size of the dispersed domain and the interdomain distance (typically 100 to 1000 Å) depend upon the molecular weight.

Fig. 1 shows a schematic representation of relative segment density variations, \( \Psi_A \) and \( \Psi_B \), across the microdomain. Since the polymeric solid is incompressible, the conformations of the chain molecules A and B in the domain space are those which give rise to uniform overall segment density, as shown in Fig. 1. It was suggested (Meier, 1973; Helfand, 1975; Hashimoto, Nagatoshi, Todo, Hasegawa & Kawai, 1974; Hashimoto, Todo, Itoi & Kawai, 1977) that there exists an interfaceal region of finite thickness \( \Delta R \) (designated hereafter as the interphase) in which the chemical junction points of A and B are located and a partial mixing of the incompatible chain segments occurs.

The physics controlling the morphology of the domain structure, such as equilibrium size, shape and interfaceal thickness, has been described as a function of molecular and thermodynamic parameters (Meier, 1969, 1973, 1974; Helfand, 1975; Helfand & Wasserman, 1976). Moreover, the osmium-staining method developed by Kato (1967) enables one to stain selectively the rubber (polysoprene, polybutadine, etc.) phase having unsaturated double bonds and to observe clearly the domain structure under transmission electron microscopy. Thus the microdomain structure of block copolymers may be regarded as an ideal model structure on which to study physical properties of heterogeneous solid texture.

Since the molecular origin of the domain structure is well understood, the block copolymer would give an ideal model substance for the study of SAXS theory and technique. In this article, the domain structure of a particular block copolymer is analyzed in terms of both the spatial distribution and size of the dispersed domains and its interfaceal structure. The analysis of the interfaceal thickness is based upon the systematic deviation from the Porod’s rule of the SAXS intensity in the tail. Also investigated are the possibility of analyzing the interfaceal thickness on the basis of the desmeared curve in the tail and the role of the Soller slits on the analysis and on the accuracy of the final results.

II. Test specimens

Polystyrene and polysoprene diblock copolymers designated as SI-3 in a previous paper (Todo, Uno, Miyoshi, Hashimoto & Kawai, 1977) were used. They have a narrow
molecular weight distribution (total number-average molecular weight 20.2 × 10^4) and a fractional composition of 13% polyisoprene by weight.

The copolymers were cast into films about 0.2 mm thick by pouring ca 5% toluene solution on to a glass plate and evaporating the solvent very gradually over more than a week at about 30°C. The film specimens thus formed were further dried for several days under a high vacuum of ca 10^-6 mm Hg.

The domain structure was investigated under transmission electron microscopy by using the osmium tetroxide staining technique. The results indicated that the styrene-rich copolymers have a microdomain structure with the polyisoprene spheres dispersed in a matrix of polystyrene segments. The size of the domains is quite uniform and the interdomain distance is quite regular owing to the narrow molecular weight distribution, giving rise to the many scattering maxima due to intra- and interparticle interference, as shown later.

III. Theoretical background

Scattering intensity \( I(s) \) from the microdomain structure is given by (Hosemann & Bagchi, 1962),

\[
I(s) = N(\langle f(s)^2 \rangle - \langle f(s) \rangle^2) + (1/v) \langle f(s) \rangle^2 [S(s)]^2,
\]

where \( s = (2 \sin \theta) / \lambda, \) \( N \) is the number of particles (the spherical domains) and \( v \) the volume occupied by each particle. The functions \( f(s), Z(s) \) and \( S(s) \) are the scattering amplitude, the lattice factor and the shape amplitude of a particle, the lattice factor and the shape amplitude of the paracrystalline macrolattice. The asterisk designates a three-dimensional convolution operation.

For a spherical particle of radius \( R, f(s) \) is given by

\[
f(s) = (\rho_1 - \rho_2) \sqrt{3} \Phi(U), ~ U = 2\pi R s,
\]

\[
\Phi(U) = (3/U^3) \sin(U - U \cos U), ~ V = 4\pi R^3 / 3, \tag{3}
\]

where \( \rho_1 \) and \( \rho_2 \) are the electron densities of the particle and its surrounding medium. The intensity from an isolated particle, \( f^2(s) \), exhibits a series of scattering maxima (at the scattering angle \( 2\theta_{m,i} \) for the \( i \)th maximum) due to intra-particle interference:

\[
4\pi(R/\lambda) \sin \theta_{m,i} = \begin{cases} 5.765, & \text{for } i = 1 \\ 9.10, & \text{for } i = 2 \\ 12.3, & \text{for } i = 3 \end{cases}
\]

It was shown (Todo et al., 1977) that the angles \( 2\theta_{m,i} \) are hardly affected by the small portion of the interphase, so that equation (4) can be applied to evaluate the dispersed domain size even for a particle with a small fraction of the interphase.

The lattice factor \( Z(s) \) is associated with regularity in spatial arrangement of the particles and gives rise to scattering maxima due to interparticle interference, as shown later. For disordered systems, \( Z(s) \) approaches unity at large \( s \).

The functions \( g(r) \) and \( h(r) \) are the electron density variation of the ideal two-phase system and the smoothing function related to the interphase respectively. \( g(r) \) is the convolution square or autocorrelation of \( g \), and \( F[g^2] \) is the three-dimensional Fourier transformation of the function,

\[
F[g^2] = \int g(r) \exp (2\pi i s \cdot r) dr.
\]

For an isotropic and ideal two-phase system,

\[
I_d(s) = (\text{const.}) s^{-4}
\]

according to Porod's (1951, 1952) rule.

The scattering \( I_d(s) \) arising from the domain-boundary interphase is given by (Ruland, 1971)

\[
I_d(s) = \exp (-4\pi^2 \sigma^2 s^2)
\]

\[
= 1 - 4\pi^2 \sigma^2 s^2 + O[(\pi \sigma s)^4]
\]

for a sigmoidal density variation at the interphase, i.e.

\[
h(z) = (2\pi \sigma^2)^{-1/2} \exp (-z^2/2\sigma^2),
\]

where \( \sigma \) is a parameter related to the density variation at the interphase. Therefore, if the interfacial thickness is small compared with \( R, \) it follows that

\[
I_d(s) \approx (\text{const.}) s^{-4} \left[ 1 - 4\pi^2 \sigma^2 s^2 \right].
\]

Thus a plot of the type \( s^2 I_d(s) \) vs \( s^{-2} \) gives an approximated value of \( \sigma. \) The exact value of \( \sigma \) is obtained by a full analysis of (10),

\[
\ln s^2 I_d(s) = (\text{const.}) - 4\pi^2 \sigma^2 s^2.
\]

For the spherical domain having a trapezoidal density variation at the interphase of thickness \( \Delta R = 2\sqrt[3]{3} \sigma, \) the domain structure was investigated under transmission electron microscopy by using the osmium tetroxide staining technique. The measured intensity distributions were corrected for air scattering and absorption before further analysis.

IV. Collimation correction

The measured intensity distribution \( I_{obs} \) is smeared as a result of collimation errors in slit height and slit width. It is related to the true intensity \( I(s) \) by Fredholm's integral equation of the first kind (see for an example, Guinier & Fournet, 1955),

\[
I_{obs}(s) = \int W(t)W_u(u)I([s - u]^2 + t^2)^{1/2} du.
\]

Therefore the estimation of \( I(s) \) from \( I_{obs} \) involves (i) evaluation of \( W_t \) and \( W_u \), the effective slit-length and slit-width weighting functions, and (ii) the desmearing procedure to solve \( I(s) \) from the integral equation.

IV. 1 Experimental conditions

The SAXS intensity distribution was measured with the two systems, Rigaku and Kratky. In both cases the intensity was measured by a scintillation counter with a pulse-height analyser. Ni-filtered Cu Kα radiation was used as an incident X-ray source. The measured intensity distributions were corrected for air scattering and absorption before further analysis.

In the Rigaku system, a rotating-anode X-ray generator
(Rotaflex Ru-200 PL) (operated at 40 kV and 200 mA) was used as an incident X-ray source. The intensity was measured on a conventional low-angle X-ray goniometer (no. 2202, Rigaku Denki). Fig. 2 shows the set-up of the Rigaku collimating system, which is a four-slit system together with Soller slits. The size of the focal spot is the size on the target in projection.

In the Kratky system, a Philips broad-focus X-ray tube with a copper target (operated at 45 kV and 35 mA) was used as an X-ray source. The operational conditions have been described in detail elsewhere (Hamada, Hayashi & Nakajima, 1975; Hayashi, Hamada & Nakajima, 1977). The collimating system is as follows; the length-limiting device and the counter slit are 18 and 10 mm, respectively, in length and are placed at 190 and 440 mm, respectively, from the focal spot of 12 mm in length. The sample plane is at 225 mm from the focal spot.

IV. 2 The weighting functions of the systems

The weighting functions of the two collimating systems were obtained by numerical calculations with the equations derived by Hendricks & Schmidt (1967, 1973). When the Soller slits are used it should be noted that \( w_s \) and \( -w_s \) in equation (4) of Hendricks & Schmidt (1967) should be modified by \( x_u \) and \( x_s \), respectively and that \( -l_c \) and \( l_c \) in equation (5) of Hendricks & Schmidt (1967) should be modified by \( x_u' \) and \( x_s' \), respectively, where the quantities \( x_u \) and \( x_s \) correspond to \( x_u' \) and \( x_s' \). The detailed procedure of evaluating the weighting function will be described elsewhere (Todo, 1978).

The calculated results are shown in curves (1) and (3) for the slit-length weighting function \( W_w(u) \) (Fig. 3a) and in curve (1) for the slit-width weighting function \( W_w(u) \) (Fig. 3b), where the curves (1) and (3) are those for the Rigaku and of the Kratky collimating systems respectively. In these calculations the intensity of the focal spot and the sensitivity of the detector are assumed to be uniform.

![Fig. 2. The Rigaku Denki collimation system for the small-angle X-ray scattering experiment.](image)

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![Fig. 3. (a) The slit-length, \( W_w(u) \) and (b) the slit-width, \( W_w(u) \) weighting functions. The curves (1) and (2) are the calculated and measured weighting functions for the Rigaku collimation system, and curves (3) and (4) are the respective weighting functions for the Kratky collimating system.](image)

Fig. 3. (a) The slit-length, \( W_w(u) \) and (b) the slit-width, \( W_w(u) \) weighting functions. The curves (1) and (2) are the calculated and measured weighting functions for the Rigaku collimation system, and curves (3) and (4) are the respective weighting functions for the Kratky collimating system.

The calculated weighting function was experimentally verified as follows. In the case of the Rigaku collimating system the direct measurement of \( W_w(u) \) is impossible, so the calculated result was verified in alternative ways. Since \( W_w(u) \) was calculated with the same computer program and parameters as those used for the calculation of \( W_w(u) \), the verification may be performed indirectly by comparing the measured and calculated \( W_w(u) \). The measured \( W_w(u) \), which is shown as curve (2) of Fig. 3b is in good agreement with the calculated result. For further confirmation of the treatment, especially of the treatment involving the Soller slits, the intensity distribution along the slit-length direction immediately after the fourth slit (point B in Fig. 2) was measured and compared with the calculated intensity distribution. The intensity distribution was measured by a microdensitometric scan of the photographs taken at the position B. A good agreement between the calculated and measured functions was obtained, verifying again the principles, the computer program and the parameters of the collimation system. Measurements of the focal-spot size and its intensity uniformity were performed by measuring the intensity distribution in the slit-length direction at the sample plane (i.e. at the point A).

In the Kratky collimating system \( W_w(u) \) was directly measured (curve 4 in Fig. 3a) by the method described in detail by Todo (1978). Again a good agreement between the calculated and measured curves was obtained.

IV. 3 Desmearing procedure

Two types of desmearing procedure were studied, since the various desmearing procedures have never been tested and compared for a common experimental specimen. These include the iterative methods developed by Lake (1967) and Glatter (1974), and the two methods developed by Schmidt (Schmidt & Hight, 1960; Schmidt, 1965). The detailed comparisons of the desmearing procedures will be fully discussed elsewhere (Todo, 1978).

At small scattering angles (typically less than 60° in 2θ for the particular test specimen in Fig. 4) almost complete agreement between various desmeared curves was obtained in terms of the peak heights, widths and intensities, except for minor variations in the intensity profile at the scattering minima, where the amplification of the statistical fluctuation of the photon counting is relatively large and the rate of convergence in the iterative methods is slow. On the other hand, at large scattering angles where the intensity profile is related to the interfacial structure of the two-phase system, the situation is substantially different. In general, the desmearing of the slowly varying (with 2θ) intensity profile of low intensity with high statistical fluctuations makes the amplification of the statistical errors so serious that the desmeared intensity cannot be used for further analyses.

In this regard the only correction which is of practical use is the type of the desmearing developed by Glatter (1974), which includes the smoothing of the correction factor and the first trial function to suppress the amplification of the errors. In this article, we have used an iterative method with an intensive and empirical smoothing program for the correction factor and for the first trial function for the desmearing in the SAXS curve in the tail, both functions being smoothed by successive approximation of the data points by polynomials with a least-squares fit (Todo, 1978).

An another important problem in the desmearing of the tail of the SAXS curve is the reduction of the errors arising from the termination effect, since the data can be measured...
only over a limited angular range. The termination effect was kept small by the approximation and extrapolation of the data points over a fairly large angular range in the tail to a polynomial by a least-squares fit. The uncertainty involved in the extrapolation should be greatly reduced by decreasing the width of the slit-length weighting function with Soller slits.

IV. 4 Comparison of the desmeared curves

The desmeared curves constructed for the two collimating systems were compared on the same specimen, SI-3. Fig. 4 shows the smeared ($I_{obs}$) and desmeared ($I_{obs}$) SAXS intensity distributions of the specimen measured with the Rigaku system (solid circles) and with the Kratky system (open circles). The corresponding curves at even higher scattering angles are shown in Fig. 5. It should be noted that intensity in the ordinate is not in absolute units.

The desmeasuring of the two types of curve for both slit-width and slit-length collimation errors was performed by the common iterative method described above.

The smeared curve measured with the Kratky system shows more diffuse intensity distribution than that from the Rigaku system. Despite the differences, the desmeared curves are shown to be essentially identical, and especially complete agreement is obtained at the peak positions; the scattering maxima arising from the interparticle interference appear at the scattering angles $2\theta = 15.6', 22.1', 27.0', \text{and } 31.2'$. The maximum at $2\theta = 15.6'$ is attributed to regularity in the nearest-neighbour distance $D$ between the spherical domains. The distance $D$, calculated from Bragg’s equation $(2D \sin \theta = \lambda)$, is $339$ Å, which is in good agreement with the distance observed with electron microscopy. The maxima at $2\theta = 22.1', 27.0', \text{and } 31.2'$ correspond to the maxima arising from distances $D/2$, $D/3$ and $D/2$ respectively, which suggests that the domains are arranged in an ordered cubic lattice.

The broad scattering maximum at $2\theta = 50.4'$ is due to a scattering maximum from an isolated spherical domain. The radius $R$ calculated by using equation (4) is $96$ Å, which is also in good agreement with the radius observed with electron microscopy.

The two desmeared curves also agree quite well in terms of the relative peak heights and peak widths. A slight deviation between the two curves is seen at the large-angle tail (at $2\theta > 80'$). The desmeared curves at these scattering angles definitely involve extrapolation of the data points beyond measurable or measured angles. Since the slit-length weighting function for the Kratky system is much wider than that for the Rigaku system, it requires more extensive extrapolation. Hence the desmeared curve in the tail obtained with the Kratky system involves greater uncertainty. This demonstrates an important advantage of using Soller slits.

The smeared and desmeared curves for the large-scattering-angle tails obtained from the two systems may be more clearly compared with the linear plots shown in Fig. 5, in which the original smeared data $I_{obs}$ (solid circles), the desmeared curves $I_{obs}$ (broken lines) and the assumed background scattering (solid lines) are shown. The curves shown in the top and bottom halves of the figure correspond to the results obtained with Rigaku and Kratky collimating systems respectively. At large scattering angles, $2\theta > 2.5'$, the measured scattering curve $I_{obs}$ from the Rigaku system becomes nearly identical to the desmeared curve $I_{obs}$, indicating that the weighting function is narrow enough to give no smearing effect for the intensity distribution under consideration. There is, however, a substantial difference between the measured and desmeared curves for the Kratky system because of

![Fig. 4. The smeared ($I_{obs}$) and desmeared ($I_{obs}$) SAXS intensity distributions for the SI-3 specimen measured with the Rigaku Denki system (solid circles) and with the Kratky camera system (open circles).](image)

![Fig. 5. Smeared intensity distributions (solid circles, $I_{obs}$) and desmeared intensity distributions (dotted lines, $I_{obs}$) measured by the Rigaku Denki (the curves in the upper half) and Kratky camera (the curves in the lower half) systems at large scattering angles, and assumed background intensity distributions (solid lines) for the SI-3 specimens.](image)

**Table 1. The analysed domain properties for the SI-3 specimen**
The values in and outside the parentheses were obtained from the Kratky and the Rigaku cameras respectively.

<table>
<thead>
<tr>
<th>Inter-domain distance</th>
<th>Radius of domain</th>
<th>Interfacial thickness $\Delta R$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$ (Å)*</td>
<td>$R$ (Å)*</td>
<td>$\Delta R_0$ †</td>
</tr>
<tr>
<td>339</td>
<td>96</td>
<td>15±1</td>
</tr>
<tr>
<td>(339)</td>
<td>(96)</td>
<td>(17±1)</td>
</tr>
</tbody>
</table>

* Values obtained from the desmeared curves.
† Values obtained from the smeared curves on the basis of the infinite slit-height approximation.
‡ Values obtained with the approximated equation (13) and by using equation (15). The value of $\sigma$ is equal to $5.5±0.6$ Å.
§ Values obtained with the exact equation (14) and by using equation (15). The value of $\sigma$ is equal to $6.6±0.6$ Å.
the broad distribution of the weighting function. Thus the background subtraction may be made more reliable by inserting the Soller slits.

Table 1 summarizes the instrumental effect in terms of the estimated interdomain distance, domain radius and interfacial thickness for the SI-3 specimen. The results obtained from the two systems are shown to be in good agreement.

V. Estimation of the interfacial thickness

In this section we will consider the accuracy of (i) the infinite slit-height approximation and (ii) truncating the higher-order terms of $I_b$ (equations 10 and 11) for both the Rigaku and Kratky systems in estimating the interfacial thickness $\Delta R$.

V.1 Infinite slit-height approximation

For a narrow-interphase approximation, $I_b$ is truncated at the second term and the scattered intensity in the tail is given by (13). If the slit height is infinite, it follows that (see, for example, Guinier & Fournet, 1995)

$$\tilde{I}(s) = (\text{const.}) s^{-3} [1 - 8\pi^2 \sigma^2 s^2].$$

Therefore the plot of $s^2 \tilde{I}(s) vs s^{-2}$, as in Fig. 6, gives the values $\sigma$ and $\Delta R$ from the slope and intercept at $s^{-2} = 0$. In order to obtain $\tilde{I}(s) = (I_{\text{obs}} - I_b)$, the measured intensity $I_{\text{obs}}$ was corrected for the background scattering $I_b$ due to thermal density fluctuations and to amorphous scattering. The background scattering intensity $I_b$ was empirically approximated by

$$I_b = a(2\theta)^n + b,$$

as shown in Fig. 5 (solid lines), in a manner similar to Vonk's (1973) procedure. The estimated interfacial thickness $\Delta R_{\text{x}}$ under the infinite slit-height approximation is shown in Table 1.

The interfacial thickness $\Delta R_{\text{app}}$, was more rigorously evaluated, without assuming the infinite slit-height approximation, from the desmeared curve shown in Fig. 5 (dotted lines) and by using the narrow-interphase approximation, i.e. equation (13). Again the desmeared intensity $I_{\text{obs}}$ was corrected for background scattering $I_b$ of the type,

$$I_b = a'(2\theta)^n + b',$$

as shown by the solid lines in Fig. 5. The plot of $s^2 \tilde{I}(s) vs s^{-2}$ with the corrected intensity $I(s)$ (Fig. 6) gave the interfacial thickness $\Delta R_{\text{app}}$, as in Table 1. It should be noted (i) that the infinite slit-height approximation generally gives a narrower interfacial thickness and (ii) that the approximation fits better the Kratky system which has a broader weighting function than the Rigaku system. The FWHM of $W_t(u')$ is 9.2° for the Kratky collimation system and 2.1° for the Rigaku system.

V.2 Accuracy of the narrow-interphase approximation

In this section we calculate an exact value of $\sigma$ from the desmeared curve based upon the exact equation (14) and an exact interfacial thickness $\Delta R_{\text{exact}}$ by using equation (15). Again the desmeared intensity $I_{\text{obs}}$ is corrected for the background scattering $I_b$. Then the plot of $\ln s^4 I(s) vs s^2$, as in Fig. 7, gives the exact value of $\sigma$ = 6.6 ± 0.6 Å and therefore $\Delta R_{\text{exact}}$ (= 23 ± 2 Å) (Table 1). The exact analysis gives a larger value (23 Å) of the interfacial thickness than the value 19 Å (corresponding to $\sigma$ = 5.5 Å) based upon the narrow-interphase approximation.

It should be noted that the final result for interfacial thickness is rather insensitive to the manner of the background subtraction, with a variation in the final result of less than 10% of the average value.

VI. Conclusion

The advantage of using Soller slits to obtain reliable desmeared intensity data in the tail of the SAXS curve and thus an accurate interfacial thickness has been demonstrated. The reduction of the width of the slit-length weighting function with Soller slits reduces the uncertainty involved in the extrapolation of data points beyond the measurable angles and the serious amplification of statistical errors in photon counting. The disadvantage of using the Soller slits may be realized in decreased scattered intensity and in complication of the calculation and experimental verification of the slit-length weighting function. The former disadvantage was overcome by using a high incident X-ray flux (from a 12 kW rotating anode generator), and the latter by a method described in detail in the text.

The accuracy of the finite slit-height approximation, which is widely used in evaluating the interfacial thickness, was experimentally tested. The results indicated that the approximation generally gives a smaller estimation of the interfacial thickness than the exact evaluation, leading to about 35 and 25% smaller values for the Rigaku and Kratky

![Fig. 6](image)

Fig. 6. The plots of $sI vs s^{-2}$ and $s^2I vs s^{-2}$ for the evaluation of the interfacial thickness $\Delta R$, based upon the approximate equations (13) or (17) for the SI-3 specimens.

![Fig. 7](image)

Fig. 7. The plot of $\ln s^4 I vs s^2$ for the evaluation of the interfacial thickness $\Delta R_{\text{exact}}$, based upon the exact equation (14) for the SI-3 specimens.
systems respectively. Accuracy in truncating the higher-order terms of $I_n$ in equation (11) (i.e. the narrow-interphase approximation) was also checked experimentally. The results indicated that the approximation again gives a smaller estimation (about 15% smaller) of the interfacial thickness than the estimation based upon the exact equation. These results are summarized in Table 1.

The $\Delta R$ value ($23 \pm 2 \text{ Å}$) is almost identical to that of the lamellar microdomain previously studied (Hashimoto et al., 1977). The estimated values are also in good agreement with the values predicted by the statistical-mechanical theories of block copolymers.

In previous analyses (Todo et al., 1977) the domain-boundary thickness of a series of block copolymers having spherical domain structure was analysed on the basis of the measured data and the infinite slit-height approximation. The value of $\Delta R$ for the SI-3 specimen was previously estimated to be 21 Å, slightly larger than the value obtained in this article ($15 \pm 1 \text{ Å}$). This may be attributed to the minor contribution of the Bremsstrahlung radiation in the tail of the SAXS curves due to improper use of the pulse-height analyser. In the previous analyses it was suggested that the value corresponding to $\Delta R_{\text{app}}$ can be evaluated by comparing the smeared theoretical scattering intensity with the weighting function used in the experiment and the measured intensity corrected for the background scattering. This method seems to bear repeating for further studies, since the method is free from the problem of the amplification of the statistical errors produced by the desmearing.

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