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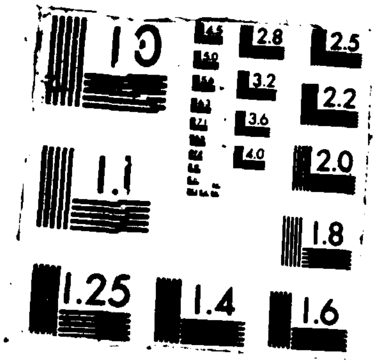
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Distribution of Matrix Homopolymer in Block Copolymers of Spherical Morphology

by

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DISTRIBUTION OF MATRIX HOMOPOLYMER IN BLOCK COPOLYMERS OF SPHERICAL MORPHOLOGY

by

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ABSTRACT

Samples made by blending deuterated polystyrene S_d of three different molecular weights with a polystyrene-polybutadiene block copolymer SB were studied with small-angle scattering techniques using x-rays (SAXS) and neutrons (SANS). The SANS results were sensitive both to the amount of added homopolymer S_d and to its chain length. Anomalously high SANS intensities and the absence of an intraparticle scattering maximum are consistent with the exclusion of added S_d from the corona of the SB micelles, resulting in S_d enrichment of the interstitial regions.

Introduction

The study of block copolymers has proved to be a fertile area for the detailed elucidation of polymer interactions; it has been particularly fruitful in the production of information generated through the interplay between theoretical studies (see, for example, papers by Meier[1], Helfand[2], Leibler[3-5], Noolandi[6,7], and their coworkers) and experimental work, particularly small-angle scattering studies involving x-rays (SAXS) and neutrons (SANS).

One of the advantages of SANS over SAXS is the possibility of manipulating the contrast (in SANS, the nuclear scattering-length density) by selective deuteration. This technique was exploited in previous studies[8,9] by synthesizing a polystyrene-polybutadiene diblock with the polybutadiene segment deuterated (SB_d) to enhance the contrast between the spherical polybutadiene microdomains and the polystyrene matrix; the SANS signal was increased by a factor of 27, allowing detection of Debye-Scherrer powder peaks characteristic of cubic packing of the B_d domains[8] and accurate assessment of sphere size and interfacial thickness for a number of samples of differing molecular weight[9]. In another experiment[10], deuterated polystyrene-polybutadiene diblocks SB_d were blended with a normal (hydrogenous) diblock SB in such a way that the scattering-length densities of the S and B phases were matched, eliminating (inter- and intradomain) structural scattering and thus (presumably) leaving scattering from isolated B_d chains as the dominant scattering mechanism.

The present study is a further attempt to use deuterated probe molecules to gain information about the distribution of polymer chains in a diblock system with spherical morphology -- this time in the polystyrene matrix.

Samples were prepared by adding deuterated homopolystyrene (S_d) to a solution of polystyrene-polybutadiene diblock[9] (SB1); the mixture was spin-cast and annealed to give transparent solid samples approximately 1 mm thick. These samples were then studied using SAXS and SANS scattering.

Experimental Section

Materials

The primary material used in this study was a polystyrene-polybutadiene diblock designated SB1; its synthesis and characterization are described in detail in Reference 9. The number-average molecular weights of the S and B segments are 79 and 11 kilodaltons, respectively, with narrow molecular weight distributions on both cases. When the material is cast from a solvent, microphase separation of the polybutadiene occurs; the B domains are roughly spherical, with an average radius[11] of 117 Å. The SANS pattern of the material[11] shows an interparticle interference peak at 0.0193 Å^{-1}, implying an average domain center-to-center separation of 325 Å.

Deuterated polystyrene (S_d) was obtained from Polysciences, Warrington PA, in three molecular weights: 68, 196, and 385 kilodaltons[12] ($Z \doteq 654$, 1885 and 3702). Gel-permeation chromatographic runs carried out in our laboratories gave polydispersity indices (M_w/M_n) of 1.07, 1.12, and 1.17, respectively, for these materials, which we shall henceforth refer to as S_d1, S_d2, and S_d3.

Blends of SB1 with the S_d polymers were prepared by dissolving them in toluene, then forming thin films (-0.1 mm) by a solvent spin-casting technique[13] (the films were stacked and annealed to provide specimens of suitable thickness)· Six samples were cast: a "dilute" series in which S_d of each molecular weight was added to SB1 so that 11 per cent of the polystyrene content was homopolymer, and a "concentrated" series in which the S_d fraction was 26 per cent.

Structural Analysis

Electron micrographs were obtained on a Phillips 200 electron microscope operated at 80 kV and calibrated against a diffraction grating carbon replica (21,600 lines/cm). Samples were stained with osmium tetroxide[14] and cut into sections (-400 Å thick) on an LKB ultramicrotome fitted with a freshly prepared glass knife.

Small-angle x-ray scattering (SAXS) experiments were carried out at the Rosenstiel Research Center at Brandeis University, through the courtesy of Dr. Walter C. Phillips, using an instrument developed there[15]. Photons were supplied by an Elliott rotating-anode generator operating at 35 keV with a Cu target. The beam was focused and monochromated (λ - 1.54 Å) by a double-mirror camera with Ni-coated mirrors. Beam size at the sample was -0.3 x 0.4 mm. Detection of scattered x-rays was carried out by an image intensifier placed (for this experiment) 368 mm from the sample. Samples were run for 30 min each. The isotropic two-dimensional scattering patterns were then examined, corrected for detector sensitivity, and subjected to a radial average routine.

Small-angle neutron scattering (SANS) experiments were performed on the 30-m instrument at the National Center for Small-Angle Scattering Research (NCSASR), Oak Ridge National Laboratory, employing neutrons of wavelength λ - 4.75 Å and sample-to-detector distances of 6 and 14 m. Scattering data (collected in runs of 30 min each) were corrected for background scattering and detector sensitivity, then radially averaged. Scattering intensities were reduced to absolute values by comparison with a specimen of irradiated aluminum of known R_g run under the same conditions.

Results

Electron Microscopy

Figure 1 shows representative micrographs of the 11% and 26% blends of S_d3 with SB1, designated $SB1(S_d3)_{0.11}$ and $SB1(S_d3)_{0.26}$ (compare with micrographs of unblended SB1 and SB_d1, Figs. 1 and 2 of Ref. 9). The micrographs confirm that the morphology is spherical in all cases. The 11% blend is almost as well ordered as the pure SB1, but the 26% blend looks significantly different -- the B domains are farther apart, and they seem to line up in strings, rather than retaining the isotropic packing pattern of the other two.

SAXS Analysis

Figure 2 shows the SAXS results for the 11% and 26% blends of S_d1 with SB1 (results for the S_d2 and S_d3 blends were virtually identical). The dominant features are the interparticle interference peaks around $Q = 0.02$ Å^{-1}. In the 26% blends, this peak is shifted to lower Q, reflecting the greater separation between B domains as the amount of added homopolymer is increased. Quantitatively, the peak occurs at $Q = 0.0200$ Å^{-1} for the 11% blends (implying a correlation length $d = 2\pi/Q = 313$ Å) and at 0.0180 Å^{-1} for the 26% blends ($d = 350$ Å).

Also apparent in the SAXS data (Fig. 2) is a broad peak around 0.05 Å^{-1}. We attribute this to the first maximum of the single-particle form factor[16] for the polybutadiene spheres, and we can thus calculate the average radius of these spheres as $R_B = 5.765/0.05 = 115$ Å, in close agreement with a previous estimate [11] (117 Å) for R_B in SB1.

In summary, the SAXS data are sensitive to the amount of homopolystyrene added (indicated by the position of the interparticle interference maximum), but are insensitive to its molecular weight.

SANS Analysis

Fig. 3abc shows the neutron-scattering patterns obtained from the 11% blends and Fig. 3def those from the 26% blends. The most prominent feature in these spectra is again the interparticle interference peak, located (in agreement with the SAXS data) at 0.0200 $Å^{-1}$ for the 11% blends and at 0.0180 $Å^{-1}$ for the more concentrated samples. This time, however, there are marked changes with the molecular weight of the added homopolymer S_d: the intensity at minimum Q rises as $M_w(S_d)$ increases, and it rises faster for the 26% samples than it does for the more dilute series.

In an attempt to obtain a more quantitative understanding of the scattering in these samples, we have developed a preliminary modeling scheme for the coherent scattering which incorporates three mechanisms: (1) scattering from single chains of labeled polystyrene S_d, (2) interparticle interference, and (3) intraparticle scattering from the B domains. As in our studies of SB/SB_d blends[10], the single-chain scattering was modeled with a Debye function.

$$I(Q) = \frac{2I_o}{R_g^4 Q^4} \left[R_g^2 Q^2 - 1 + \exp(-R_g^2 Q^2) \right] \qquad (1)$$

where Q is the magnitude of the momentum-transfer vector (equal to $4\pi\lambda^{-1}$ $\sin\vartheta$, where λ is the wavelength of the incident radiation and ϑ is half the scattering angle) and R_g^2 is the mean-square radius of gyration of the chain.

In modeling the effects of interparticle interference, we have used the treatment described by Kinning and Thomas[17], which utilizes the closed-form solution for the Percus-Yevick[18] correlation function developed by Wertheim[19] and Thiele[20]. This solution is based on the assumption of hard-sphere behavior for the interacting particles. The calculation is parameterized mainly in terms of the hard-sphere volume fraction η

$$\eta = \frac{4}{3}\pi R_{hs}^3\, n \tag{2}$$

where R_{hs} is the effective radius of the hard spheres and n is the number of spheres per cm^3. Auxiliary variables α, β, and γ are defined in terms of η:

$$\alpha = (1 + 2\eta)^2/(1 - \eta)^4 \tag{3}$$

$$\beta = -6\eta(1 + \eta/s)^2/(1 - 3)^4 \tag{4}$$

$$\gamma = \frac{1}{2}\eta(1 + 2\eta)^2/(1 - 3)^4 \tag{5}$$

Following Kinning and Thomas[17], we then write the interference factor

$$S(Q_1 R_{hs}) = \frac{1}{1 + 24\eta(G(A)/A)} \tag{6}$$

where $A = 2QR_{hs}$ and

$$G(A) = \frac{\alpha}{A^2}(\sin A - A\cos A) +$$

$$\frac{\beta}{A^3}(2A\sin A + (2 - A^2)\cos A - 2) +$$

$$\frac{\alpha}{A^5}(-A^4\cos A + [93A^2 - 6)\cos A + (A^3 - 6A)\sin A + 6]) \qquad (7)$$

Intraparticle scattering was handled as before[9,16], using the Bessel function $J_{3/2}$ to describe the form factor

$$f^2_{sphere}(QR_b) = \frac{9\pi}{2}\left[\frac{J_{3/2}(QR_b)}{(QR_b)^{3/2}}\right]^2 \qquad (8)$$

where R_b is taken as 117 Å, the radius of the B domains. Total scattering was then represented as

$$I(Q, R_{hs}, R_b) = I_{chain}(Q, I_o, R_g) + KS(Q, R_{hs})\, f^2_{sphere}(QR_b) + I_{inc} \qquad (9)$$

Here I_{chain} is the scattering from labeled polystyrene chains S_d, calculated from the Debye expression, Eq. 1. The factor K includes the contrast factor $(\rho_p - \rho_m)^2$, where ρ_p and ρ_m are the neutron scattering-length densities of the particle and matrix, and I_{inc} is the incoherent scattering, which for these samples was constant at 0.85 cm^{-1}.

Given the molecular weight and isotopic composition of the labeled homopolymer chains, it is possible to calculate expected values for the forward scattering I_o:

$$I_o = (a_H - a_D)^2 Z N_o \phi X(1 - X) \qquad (10)$$

Here a_H is the sum of coherent scattering lengths[21] for the normal repeat unit, a_D the corresponding sum for the deuterated repeat unit, Z the polymerization index, N_o the number of repeat units per cm^3 in the bulk, ϕ the volume fraction of polystyrene in the sample, and X the fraction of polystyrene which is labeled. Expected radii of gyration R_g are easily calculated[22] from the expression

$$R_g = (K/\Phi)^{1/3} M_w^{1/2} \qquad (11)$$

The quantity $(K/\Phi)^{1/3}$ for bulk polystyrene has been determined[23] to be 0.27. Expected values of I_o and R_g for the samples used in this study are listed in Table 1.

Fig. 3abc shows the SANS data for the 11% samples together with the results of the calculations described above. The hard-sphere diameter R_{hs}, the volume fraction η, and the contrast factor K were varied to secure agreement between calculation and experiment for the position and intensity of the interparticle interference peak at $Q = 0.02$ Å^{-1}, and the Debye parameters I_o and R_g were varied to fit the points at lowest Q and the general falloff of intensity as Q increases. Q values used in the calculations were those for which experimental points were available, and calculated spectra were run through several iterations of a Pascal 7-point smooth (in which adjacent points are averaged using the normalized coefficients of a sixth-power binomial expansion) to simulate instrumental broadening.

Inspection of Fig. 3 shows that in general, the algorithms used do a remarkably good job of accounting for the experiment. Two discrepancies, however, are immediately apparent. The first is that the observed interparticle interference peak is broader about the base than the calculated peak. We take this to imply that there are ways in which the arrangement of B domains in the matrix does not correspond to a hard-sphere distribution, and it may be that the existence of "strings" of spheres, as seen in Fig. 1, is responsible for this discrepancy. The second discrepancy is the complete absence in the observed spectra of the broad peak around 0.05 $Å^{-1}$ due to intraparticle scattering from the polybutadiene spheres, present in the calculated spectra and clearly seen in the SAXS data (Fig. 2). We will discuss this discrepancy in more detail later.

Discussion

Clustering of S chains

Values of I_o and R_g required to fit the observed spectra for the 11% samples (Table 1) are reasonably close to the expected values, but for the 26% samples, highly inflated values of these parameters are required (Fig. 4, Table 1). We attribute this (as in our earlier study[10]) to clustering of the deuterated chains, which of course would be more pronounced in the samples more concentrated in S_d. Note that for the 26% samples, the ratio (obs/calc) for R_g is close to the square root of the ratio for I_0, in accord with Equations 10 and 11.

Intraparticle Scattering

In SANS experiments, the intensity of the intraparticle scattering depends on the square of the difference between the scattering length densities of the contrasting regions. Using scattering lengths[21] for carbon and hydrogen of 0.665 x 10^{-12} and -0.374 x 10^{-12}cm and densities of 1.05g/cm^3 for polystyrene and 0.89 g/cm^3 for polybutadiene, we calculate scattering-length densities $\rho(S) = 1.414$ and $\rho(B) = 0.412$ (units are 10^{10}cm^{-2}), the difference being due to the higher C/H ratio and greater density of polystyrene. In deuterated polystyrene (S_d), the substitution of deuterium (scattering length = 0.667 x 10^{-12}cm) for hydrogen raises $\rho(S_d)$ to 6.47. Thus, when S_d homopolymer is blended with diblock SB the scattering-length density of the polystyrene matrix is increased. This is shown graphically for a typical micelle of SB1 in Fig. 4a, where scattering-length density is plotted against position with respect to the B domain (for simplicity, interfaces are represented as being sharp). In in a homogeneous polystyrene blend which is 11% S_d, ρ is raised to 1.97; if the S_d content is increased to 26%, ρ becomes 2.73 (dashed lines, Fig. 4b and 4c). However, if we assume that the added S_d is excluded from the corona, the interstitial regions are necessarily enriched in S_d. If we take the size of the corona to be the same as the hard-sphere radius determined from the Percus-Yerick model, we can calculate that for the 11% samples ($R_B = 117$, $R_{hs} = 200$ A), the volume fraction of S_d in the interstices is 0.337, and the corresponding ρ is 3.12 (Fig. 5b). For the 26% samples ($R_B = 117$, $R_{hs} = 215$ A), the interstitial fraction of S_d is 0.705-- the interstices are now mostly deuterated -- and $\rho = 4.98$ (Fig. 5c). Using the known value of ρ (B) given above the values of K (Eq. 9) required to fit the interparticle interference peak in each of the spectra can be used to deduce an apparent value of ρs. These derived values vary from 2.8 to 3.4 for the 11% S_d samples, and from 5.3 to 5.6 for the 26% samples (see Fig. 3). The striking fact is that these "observed" values far exceed the values of ρs calculated for a homogeneous dispersion of S_d in the S matrix, and are much more nearly in accord with the values of ρs derived from the assumption that homopolymer S_d is restricted to interstitial regions between the SB1 micelles (B core and S corona). An interesting additional trend is the slight reduction in ρs as $M_w(S_d)$ is increased, perhaps due to a "fuzzing" of the boundary between coronas and interstices with increasing chain length.

We now return to the question of the missing intraparticle peaks. They were expected to appear because we implicitly assumed that the S_d chains were distributed more or less evenly through the polystyrene matrix. Their absence forces us to take seriously the idea of the "hard spheres" used in the calculations described above. As has been pointed out before (see, for example, Refs. 4, 7 and 17), the B domains in an SB diblock are surrounded by a corona of the S segments attached to the phase-separated B segments; this corona separates the B domains and determines the effective hard-sphere radius used in the calculations.

Figure 4 demonstrates why the intraparticle scattering maximum appears in the SAXS spectra (where the B spheres are the only source of contrast, as in Fig. 4a) and does not appear in the SANS data, where the S-B contrast is overshadowed by the contrast between (labeled) interstitial and coronal regions which is not abrupt, as pictured in Fig. 4. This preliminary analysis assumes total exclusion of the homopolymer from the corona; a gradual depletion of homopolymer chains from regions spatially closer to the B domains is physically more reasonable. Thus, it is probable that the concept of a sigmoidal smoothing function[24] can be applied in characterizing the coronal-interstitial interface, and we intend to attempt such a characterization in a future study.

Conclusions

Addition of polystyrene homopolymer to a diblock consisting of polybutadiene spheres in a polystyrene matrix increases the average separation of the B spheres in a way which may be locally anisotropic, especially with homopolymer of longer chain length. The added homopolymer is not uniformly dispersed through the matrix, but is excluded from the S corona surrounding the B spheres and is thus forced into the interstitial regions between the micelles (B sphere plus S corona).

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Table 1.

Sample	I_0 (cm^{-1}) calculated	I_0 (cm^{-1}) observed	I_0 (cm^{-1}) ratio obs/calc	R_g (Å) calculated	R_g (Å) observed	R_g (Å) ratio obs/calc
$SB1(S_d1)_{0.11}$	22.9	35	1.53	70.4	87	1.24
$SB1(S_d2)_{0.11}$	66.0	105	1.59	119.5	130	1.09
$SB1(S_d3)_{0.11}$	129.6	120	0.93	167.5	190	1.13
$SB1(S_d1)_{0.26}$	47.4	97	2.0	70.4	100	1.42
$SB1(S_d2)_{0.26}$	136.6	600	4.4	119.5	250	2.09
$SB1(S_d3)_{0.26}$	268.2	10,000	37.0	167.5	960	5.73

FIGURE CAPTIONS

Fig. 1. Electron micrographs of polystyrene-polybutadiene diblocks. (a) SB1 blended with 11% deuterated polystyrene homopolymer. (b) SB1 blended with 26% deuterated polystyrene homopolymer. Samples have been stained with OsO_4, which preferentially darkens the polybutadiene.

Fig. 2. SAXS data for $Sbl(S_d l)_{0.11}$ (full curve, typical of 11% samples) and $SB1(S_d 1)_{0.26}$ (dashed curve, typical of 26% samples).

(a,b,c)

Fig. 3. SANS data for samples containing 11% S_d in SB1; (d,e,f) SANS data for samples containing 26% S_d in SB1. Circles represent experimental points, full lines are calculated from Eq. 9 using parameters given in the figure. Molecular weight of added homopolymer S_d (in Kilodaltons) is given as a left superscript.

Fig. 4. (a) SANS scattering-length density ρ for SB1 in the neighborhood of a B sphere. Dashed lines show increase in contrast for 11% and 26% added S_d homopolymer if the S_d is distributed uniformly through the matrix. (b) Scattering-length density for 11% added S_d. (c) Scattering-length density for 26% added S_d. In (b) and (c), hatched area shows ρ profile if homopolymer is excluded from the corona; dashed lines show ρ profile if homopolymer is uniformly distributed throughout the matrix.

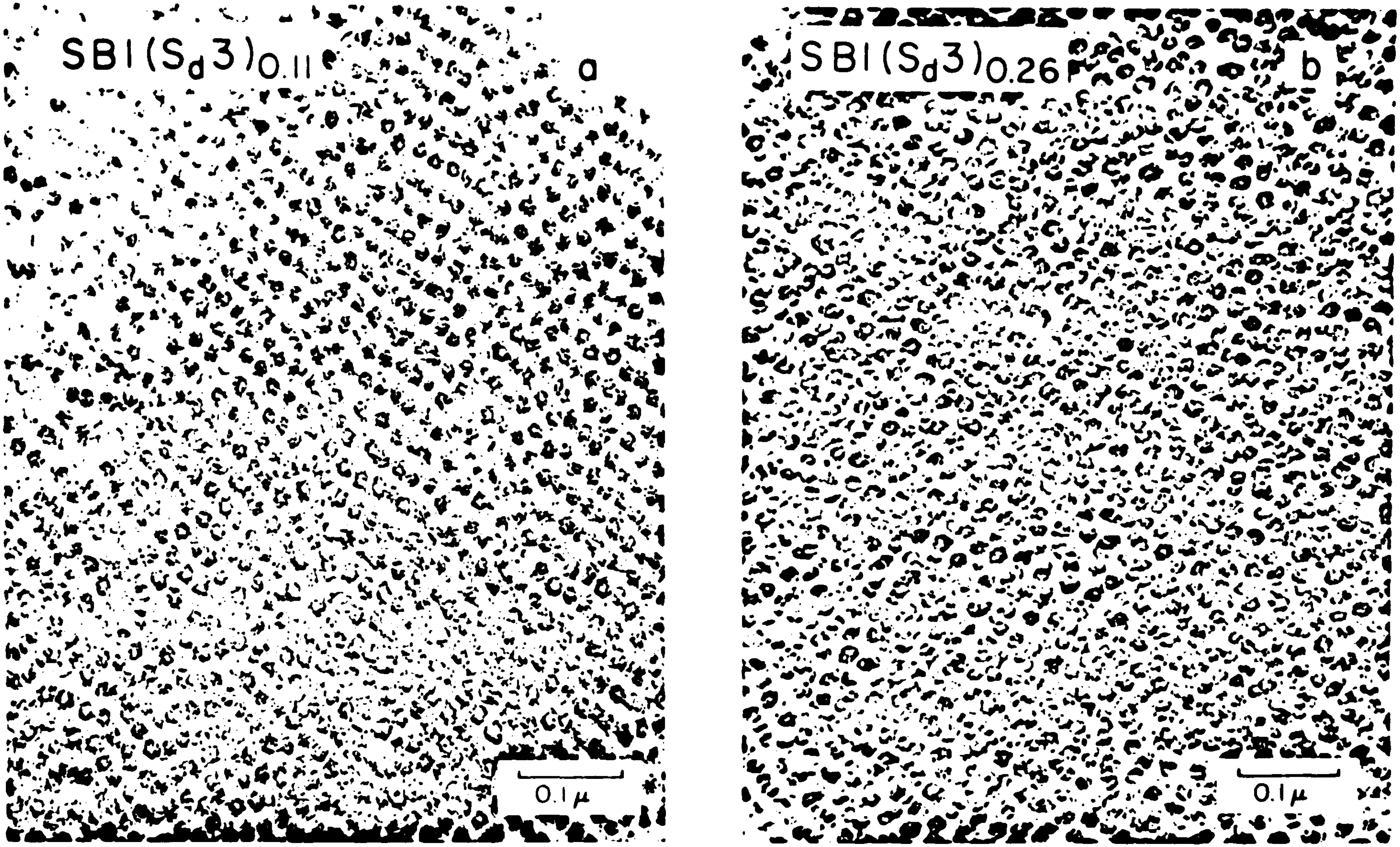

Figure 1.

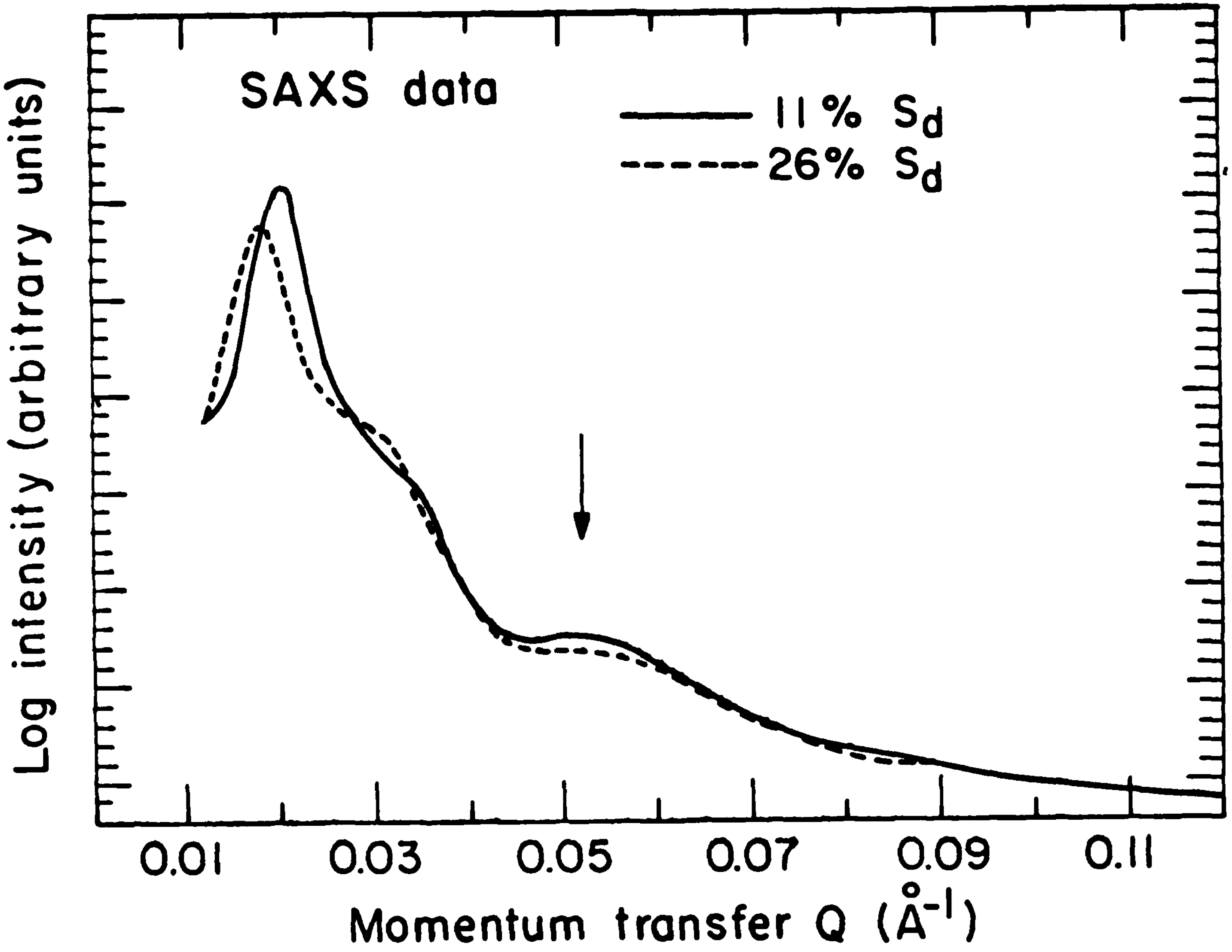
SAXS data
11% S_d
26% S_d
Log intensity (arbitrary units)
0.01
0.03
0.05
0.07
0.09
0.11
Momentum transfer Q ($\mathring{A}^{-1}$)

Figure 2.

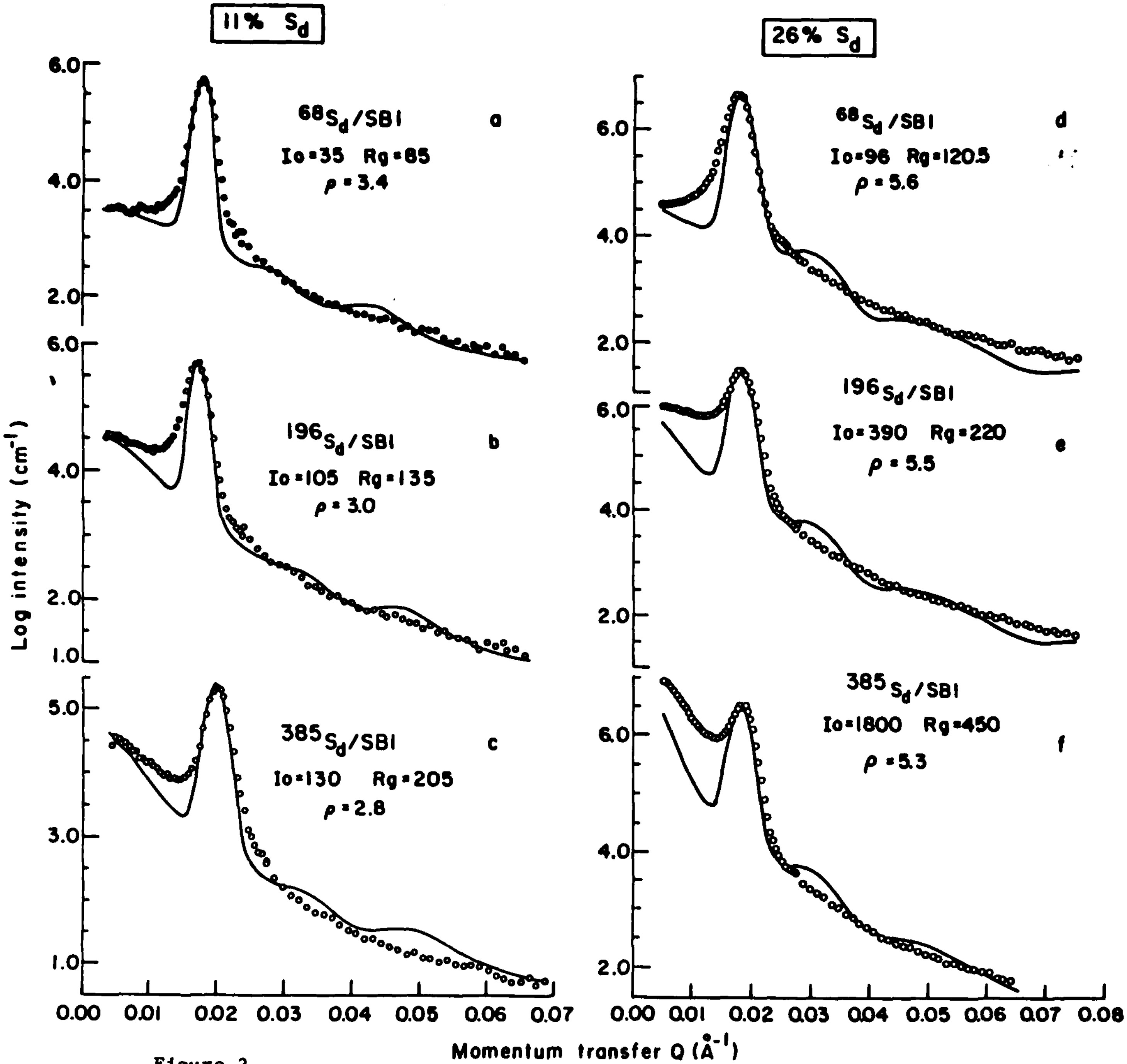
11% S_d
26% S_d
$^{68}S_d$/SBI
a
Io=35 Rg=85
ρ=3.4
$^{196}S_d$/SBI
b
Io=105 Rg=135
ρ=3.0
$^{385}S_d$/SBI
c
Io=130 Rg=205
ρ=2.8
$^{68}S_d$/SBI
d
Io=96 Rg=120.5
ρ=5.6
$^{196}S_d$/SBI
e
Io=390 Rg=220
ρ=5.5
$^{385}S_d$/SBI
f
Io=1800 Rg=450
ρ=5.3
Log intensity (cm^{-1})
6.0
4.0
2.0
1.0
5.0
3.0
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
Momentum transfer Q (Å^{-1})

Figure 3

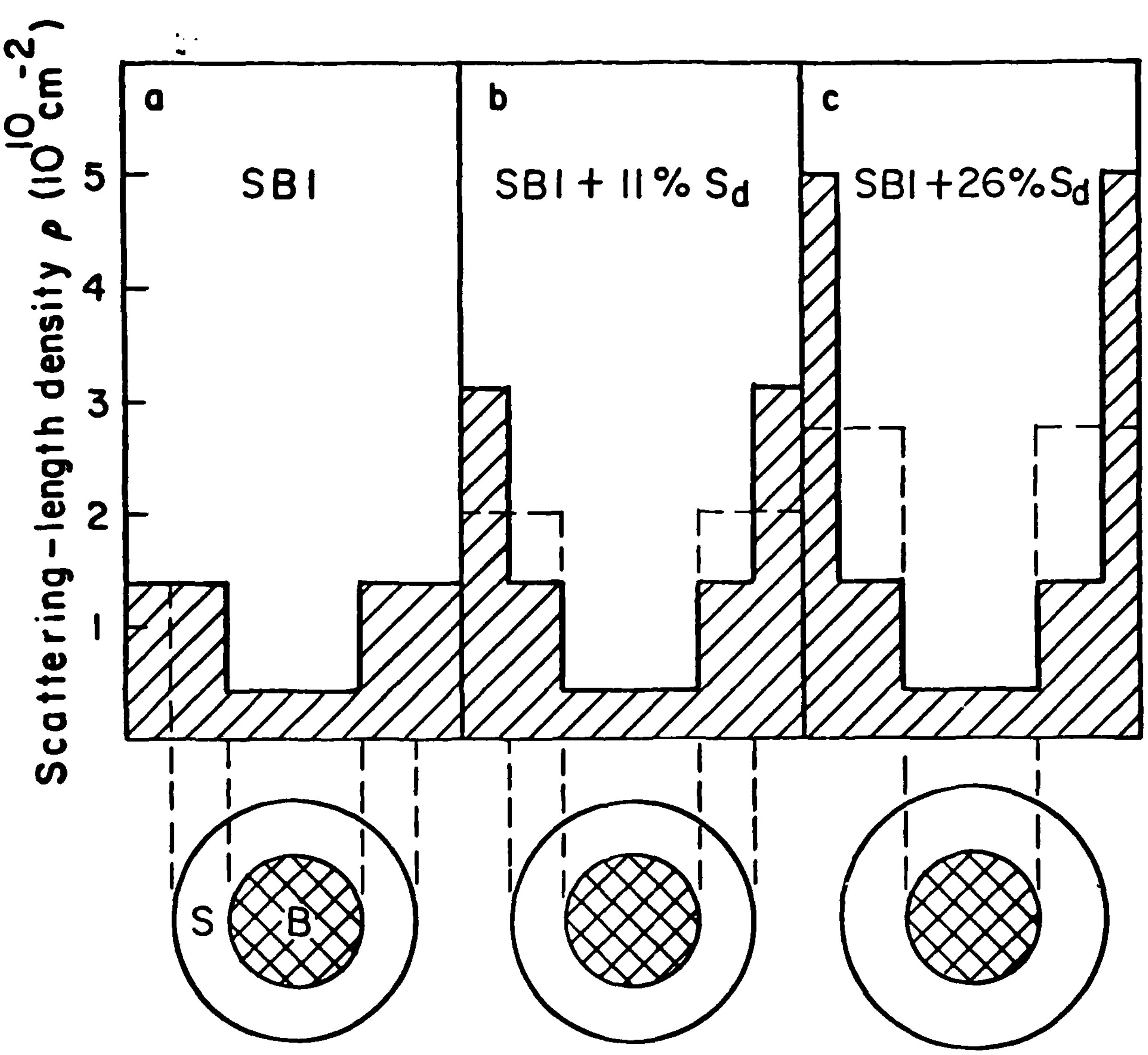
Scattering-length density ρ (10^{10} cm^{-2})
a
b
c
SBI
SBI + 11% S_d
SBI +26% S_d
5
4
3
2
1
S
B

Figure 4

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