Morphology of Styrene–Butadiene–Styrene Triblock Copolymers by a Small-Angle X-Ray-Scattering Technique

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ABSTRACT: Small-angle X-ray-scattering intensity data on styrene–butadiene–styrene block copolymers, obtained by a Kratky camera, were analyzed according to Porod's two-phase theory of small-angle X-ray scattering. One of the implications of the analysis is that the interface between the styrene and butadiene phases is sharp. Volume fractions of the two phases obtained from the experiment agree well with the values calculated from the weight composition ratio of the two phases, *i.e.*, 30/70 of styrene/butadiene. From measured characteristic chord lengths of 176 Å for the styrene and 395 Å for the butadiene phases, it was deduced that the styrene phases consist of spheres of radius 132 Å.

The morphology of styrene–butadiene–styrene block copolymers has been extensively studied, and it is now well established that the styrene phase forms domains dispersed in the butadiene matrix.[1-3] Elastomeric properties and tensile strength of the block copolymer will greatly depend on the formation and structure of the domains. The structure of these domains has been studied by electron microscopy[1-3] and by the small-angle X-ray-scattering (SAXS) technique.[4,5] Electron micrographs of solvent-cast films of S–B–S block copolymers or of microtomed sections of the bulk sample show a phase-separated domain structure in which the domains are spherical, rod-shaped or of layered form[3] depending on the molecular composition. McIntyre, *et al.*,[4] and Price, *et al.*,[5] studied those systems by a small-angle X-ray technique, but they both have assumed *a priori* a macrolattice structure in which domains form a well-defined crystallographic structure such as fcc and hcp.

We have also studied this block copolymer using SAXS techniques, but our analysis of data was based on the general two-phase theory of small-angle X-ray scattering developed mainly by Porod.[6] In this theory, no assumptions about structural regularity have been made, and each phase is assumed to be of random shape.

SAXS Theory of Two-Phase Systems

The theory of SAXS for a two-phase system has been well developed, and it is, in principle, possible to obtain a number of parameters characterizing this system.

In SAXS experiments of two-phase systems, it is assumed that the domains are sufficiently large so that electron density fluctuations on an atomic scale are negligible. Therefore, we assume that each domain has a uniform electron density. We further assume, for the moment, that the interface between phases is sharp. The small-angle X-ray scattering occurs, therefore, due to the electron density difference between the two phases.

According to the X-ray-scattering theory,[7] the intensity $I(\mathbf{h})$ scattered at angle 2θ is given by

$$I(\mathbf{h}) = I_e(\mathbf{h}) \int_V \int_V \rho(\mathbf{x}_j)\rho(\mathbf{x}_k)e^{-i\mathbf{h}(\mathbf{x}_j - \mathbf{x}_k)}\mathrm{d}\mathbf{x}_j\mathrm{d}\mathbf{x}_k \qquad (1)$$

where $\rho(\mathbf{x}_j)$ is the electron density of volume element $\mathrm{d}\mathbf{x}_j$ at $\mathbf{x}_j$. Here

$$|\mathbf{h}| = \frac{4\pi}{\lambda}\sin\theta$$

where λ is the wavelength of the X-ray, V the irradiated sample volume, and $I_e(\mathbf{h})$ the scattering intensity by an electron.

Debye, *et al.*,[8] have shown that for large angles the intensity $I(h)$ of SAXS from the two-phase system can be approximated as

$$I(h) = -\frac{8\pi I_e(h)\phi_A\phi_B(\Delta\rho)^2VG'(0)}{h^4} \qquad (2)$$

Here ϕ_A and ϕ_B are the volume fractions of phase A and phase B and $\Delta\rho$ is the electron density difference between phases. $G(r)$ is a correlation function which contains the essential structural information that can be obtained from a SAXS experiment.

In the Kratky camera geometry[9] of SAXS, slits approximating infinite height are employed which impose a distortion on the intensity pattern. In general, the observed, "slit-smeared" intensity $\tilde{I}(h)$ is expressed as[10]

$$\tilde{I}(h) = \int_0^\infty I(\sqrt{h^2 + t^2})w(t)\mathrm{d}t \qquad (3)$$

Here t is a coordinate along the direction of slit height and $w(t)$ is a weighting function of intensity I at t. Solution of the above equation requires a knowledge of the slit geometry, but various computation methods are available.[11-13] However, without "desmearing" by the computer process, the smeared intensities $\tilde{I}(h)$ can be used directly in the data analysis.

It can be shown that[6]

$$h^3\tilde{I}(h) \simeq -4\pi^2\tilde{I}_e(h)\phi_A\phi_B(\Delta\rho)^2VG'(0) \simeq \tilde{k} \qquad (4)$$

where

$$\tilde{k} = \lim_{h\to\infty} \tilde{I}(h)h^3$$

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(1) E. J. Fischer, *J. Macromol. Sci. A*, **2**, 1285 (1968).

(2) G. Kampt, M. Hoffmann, and H. Kromer, *Ber. Bunsenges. Phys. Chem.*, **74**, 851 (1970).

(3) M. Matsuo, S. Sagae, and H. Asai, *Polymer*, **10**, 79 (1969).

(4) D. McIntyre and E. Campos-Lopez, *Macromolecules*, **3**, 321 (1970).

(5) P. R. Lewis and C. Price, *Polymer*, **12**, 258 (1971).

(6) G. Porod *Kolloid-Z. Z. Polym.*, **124**, 83 (1951); **125**, 51 (1952).

(7) A. Guinier, "X-ray Diffraction," W. H. Freeman, San Francisco, Calif., 1962.

(8) P. Debye, H. R. Anderson, and H. Brumberger, *J. Appl. Phys.*, **28**, 679 (1957).

(9) O. Krathy in "Small Angle X-ray Scattering," H. Brumberger, Ed., Gordon and Breach, New York, N. Y., 1967.

(10) A. Guinier and G. Fournet, "Small Angle Scattering of X-rays," Wiley, New York, N. Y., 1956.

(11) P. Schmidt, *Acta Crystallogr.*, **19**, 938 (1965).

(12) G. R. Strobl, *Acta Crystallogr., Sect. A*, **26**, 367 (1970).

(13) J. A. Lake, *Acta Crystallogr.*, **23**, 191 (1967).

Further, we define the "smeared" invariance $\tilde{Q}$,[6] another convenient parameter in the analysis of SAXS,

$$\tilde{Q}_h = \int_0^\infty h\tilde{I}(h)\mathrm{d}h = \left(\frac{e^2}{mc^2}\right)^2 (\lambda R)^3 D \frac{1}{R^2} \sum P_s \phi_A \phi_B (\Delta\rho)^2 \tag{5}$$

where e is the electron charge, m the electron mass, c the velocity of light *in vacuo*, R the sample to detector-plane distance, D the sample thickness, and ΣP_s the energy of primary beam per unit length after being weakened by the sample. For the Kα line of the Cu target, λ 1.54 Å, and substituting the numerical value for $(e^2/mc^2)^2$, eq 5 becomes

$$\phi_A \phi_B (\Delta\rho)^2 = \frac{60\tilde{Q}_h}{RD\Sigma P_s} \tag{6}$$

The surface-to-volume ratio is[6]

$$\frac{S}{V} = \frac{16.32}{R} \frac{\tilde{k}_h}{\tilde{Q}_h} \phi_A \phi_B \ (\text{Å}^{-1}) \tag{7}$$

The average chord lengths[6] in each phase are

$$l_0(\mathrm{A}) = 4\frac{V}{S}\phi_A$$
$$l_0(\mathrm{B}) = 4\frac{V}{S}\phi_B \tag{8}$$

Experimental Section

The S-B-S block copolymer was Kraton 101 manufactured by Shell Chemical Co. This polymer consists of 30% (by weight) styrene and 70% butadiene. Molecular weights of each block are respectively 11,000-54,000-11,000.[14]

The copolymer was dissolved in benzene and precipitated to eliminate any other components that might have been added. It has been reported[5] that this polymer, when molded at ordinary conditions, is oriented radially from the center of the mold. We were able to prepare an unoriented molded sample in the following way. First the polymer was dissolved in benzene at 5% concentration by weight. It was then slowly precipitated by adding methanol. The precipitate was collected and dried *in vacuo* at room temperature. Only fine precipitate was used to mold the sample. Since thinner samples also minimize the orientation, the sample was prepared with a thickness of 0.051 cm. This thickness is only a fraction of the optimum thickness of 2-3 mm, but it did not show birefringence when observed under a polarizing microscope.

All scattering data were obtained with a Kratky small-angle X-ray camera[9] and a Siemens Kristalloflex-4 generator with a Cu target having a power of 1.4 kW. A precise description of this camera is given elsewhere.[9] The primary beam, filtered with a Ni foil, was scattered by the sample, and this scattered intensity was measured with a proportional counter through a pulse-height analyzer. The angular scan was made with a Canberra scan controller which was programmed to the desired step height. Since the counting rate was very small in the high-angle region ($2\theta \sim 3.75°$), the counting was performed for as long as 800 sec at each angular position. A necessary condition for this procedure is that the X-ray generator be extremely stable. Therefore, the stability of the generator was checked periodically, and very little deviation was detected beyond the probable statistical error. The scattering angle is expressed in m rather than in conventional 2θ. m is the distance of the counter slit in the detector plane from $2\theta = 0$ to 2θ. m is therefore related to 2θ and h in the following ways for small angles

$$2\theta \simeq m/R$$
$$h \simeq 2\pi m/\lambda R$$

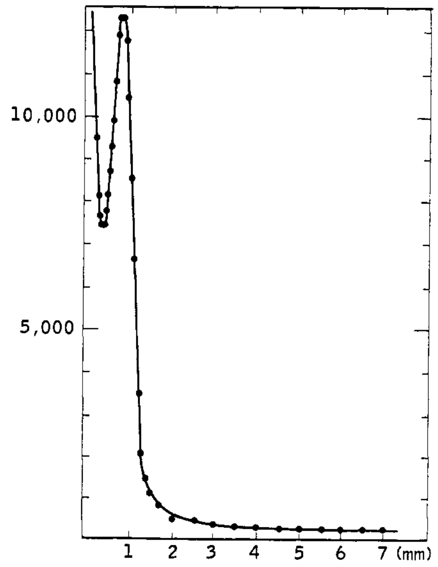

Figure 1. Scattering intensity as a function of scattering angle expressed in m.

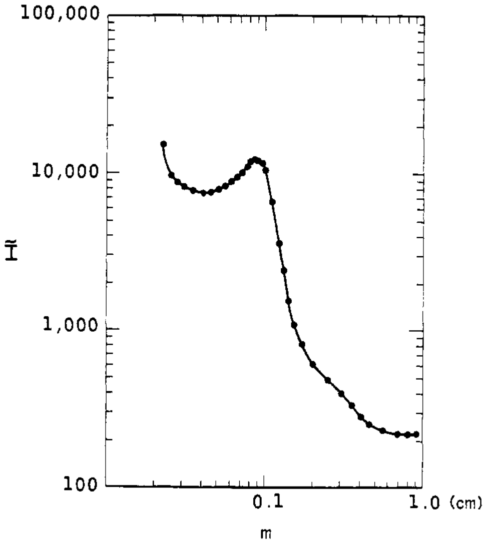

Figure 2. Plot of logarithm of observed intensity against logarithm of scattering angle expressed in m.

In further calculations, m, rather than 2θ or h, will be used to express the scattering angle.

Results and Discussion

The scattering intensity as a function of scattering angle is given in Figure 1. The logarithm of the intensity $\tilde{I}(m)$ is plotted against the logarithm of scattering angle in Figure 2. The curve does not adhere to a straight line with a tangent of -3 which should be expected from the eq 4. It has been shown[15,16] that this asymptotic behavior of scattering intensity at large angles deviates from eq 4, Porod's law. The observed intensity contains a term,[17] in general a constant, due to the electron density fluctuation within the phase and a term which arises from a finite width of boundary layer between phases. This boundary layer contains an electron density gradient. The first term is much larger than the latter term.

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(14) T. L. Smith and R. A. Dickie, *J. Polym. Sci., Part C*, **26**, 163 (1969).

(15) R. Perret and W. Ruland, *Kolloid-Z. Z. Polym.*, **247**, 835 (1971).

(16) W. O. Ruland, *J. Appl. Crystallogr.*, **4**, 70 (1971).

(17) V. Luzzati, J. Witz, and A. Micolaieff, *J. Mol. Biol.*, **3**, 367 (1961).

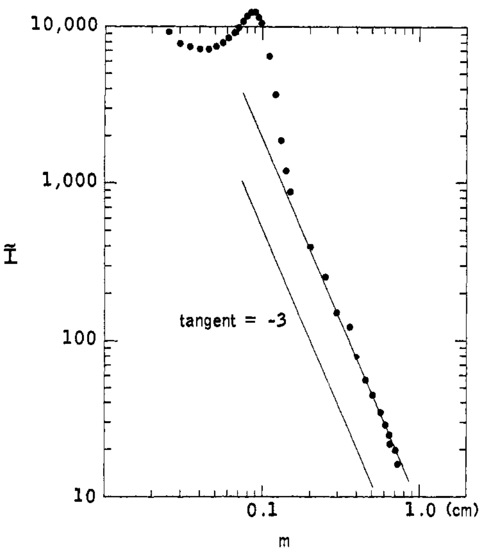

Figure 3. Plot of logarithm of calibrated intensity $\tilde{I}$ against logarithm of scattering angle expressed in *m*.

This constant term due to the electron density fluctuation can be separated by plotting $\tilde{I}(m)m^3$ against m^3. The slope of the straight line becomes this constant term, and the intercept of extrapolation of the straight line on the $\tilde{I}(m)m^3$ axis is $\tilde{k}$. In further calculations, the intensity used is that from which this constant background is subtracted. In Figure 3 is plotted the logarithm of this calibrated intensity against log *m*. This plot shows, indeed, a slope of −3 over more than half of the angular range studied. Since Figure 3 shows a straight line of tangent −3, the second correction term, due to the finite layer thickness, must be negligible. The implications of neglecting this term will be discussed later.

The primary beam intensity per unit length of the beam in the slit-height direction ΣP_s can be measured using a standard polyethylene sample kindly provided by Professor O. Kratky.[18] This standard sample was calibrated using a primary beam of known intensity. For an infinitely long primary beam, this standard sample obeys the following relation[18]

$$\frac{\tilde{I}_{c,150\text{Å}}R}{\Sigma P_c} = 0.0390 = C$$

$\tilde{I}_{c,105\text{Å}}$ is an intensity from this sample at a scattering angle corresponding to the Bragg spacing 150 Å and ΣP_c is the intensity per unit length of the primary beam after being weakened by the standard sample. Using the above relation, $\tilde{Q}(m)/\Sigma P_s$ of eq 6 becomes

$$\frac{\tilde{Q}_m}{\sum P_s} = \frac{\int_0^\infty \tilde{I}(m)m\mathrm{d}m}{\tilde{I}_{c,150\text{Å}}\dfrac{RA_s}{CA_c}}$$

A_s and A_c are the absorption factors of the sample and the standard sample, respectively.

The electron density difference between phases is calculated by assuming the density of the polystyrene phase to be 1.055 and that of polybutadiene to be 0.9. Characteristic parameters of the sample which were calculated from the scattering data are given in Table I.

TABLE I
CHARACTERISTIC PARAMETERS OF S–B–S BLOCK COPOLYMER CALCULATED FROM THE SCATTERING DATA

$\tilde{Q}_m$	93.896	S/V, Å^{-1}	7.0162×10^{-3}
ϕ_A	0.692	l_0(A), Å	394.5
ϕ_B	0.308	l_0(B), Å	175.6

The 30:70 weight ratio of polystyrene to polybutadiene in the S–B–S block copolymer studied is equivalent to a 27:73 volume ratio. This is in fairly good agreement with the volume ratio 31:69 obtained from this work. The disagreement may be due to the uncertainty in electron densities in each phase. In calculating electron densities, specific gravities of polystyrene and polybutadiene phases were assumed to be 1.055 and 0.9, respectively. Reported densities of polystyrene and polybutadiene vary, however, over a considerable range. Moreover, densities of styrene and butadiene phases in S–B–S block copolymer may not be the same with those of the homopolymers. Yet this relatively good agreement on volume ratio implies a validity of one of the assumptions of the SAXS theory, that is, the assumption of a sharp boundary between phases. This is also apparent from the fact that, as mentioned previously, the perturbation term for scattering intensity due to the finite thickness of the layer between phases appears negligible. Ruland, *et al.*,[15] have shown, from their SAXS study on solution-precipitated and bulk-crystallized polyethylene, that if the plot of $\tilde{I}m^3$ *vs.* m^3 adheres to a straight line at large angles, the interface between phases is sharp. Leary and Williams[19] have proposed a spherical model of domains having a shell in which a density gradient exists. According to them, the optimum thickness of the layer at 100° for a polymer having a molecular weight composition similar to the one studied here is about one-half of the domain radius. With an intermediate region of this size, the model of a two-phase system may no longer be useful. However, the electron micrographs show a relatively clear boundary between phases.

The electron micrographs of the thin films of S–B–S block copolymer cast from dilute solution reveal several different modes of structure. In particular, Matsuo, *et al.*,[3] observed a systematic change of structure from sphere to rod to lamella as the mole ratio is changed in S–B–S copolymer. The butadiene or styrene spheres in the micrographs are arranged in a very regular hexagonal array. But as the thickness of the film increases, this regularity appears to suffer. For the molecular composition of the S–B–S block copolymer used in this study, the electron micrographs showed a spherical structure for the polystyrene block in the thin film.

If we assume, for the moment, that the polystyrene phase is of spherical shape, from the average chord length through a sphere, one can calculate the size of the sphere. The average chord length of the styrene phase, $l_{ps} = 176.8$ Å, gives a radius $R = 132$ Å.

The approximate size of the styrene domain can also be estimated from the equilibrium chain configuration of styrene blocks. Let us assume that the random-coil configuration of the styrene block can be approximated by the unperturbed dimension of linear polystyrene with the same molecular weight. The end-to-end distance *r* of the styrene block, determined by light-scattering experiments at the Θ condition, may be given by [20]

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(18) O. Kratky, private communication.

(19) D. F. Leary and M. C. Williams, *J. Polym. Sci.*, *B*, 8, 335 (1970).

(20) E. Wada and K. Okano, *Rep. Progr. Polym. Phys. Jap.*, 7, 19 (1964).

$$\frac{\langle r^2\rangle_0^{1/2}}{M^{1/2}} \times 10^3 \simeq 700$$

For $M = 11{,}000$, $r_0 \sim 74$ Å. If we assume that the molecules extend over a region of about twice r_0, then the upper limit of the domain diameter is about 300 Å. The diameter of the domain calculated from the chord length through the styrene phase is well within this limit.

Electron micrographs have also shown that in some instances S–B–S block copolymers have a regular hexagonal arrangement. Extrapolating from the electron microscopic work on the very thin film, it is very tempting to assume that this regular array of domains is also the structure of the bulk copolymer. Lewis, *et al.*,[5] and McIntyre, *et al.*,[4] have indeed proposed a macrolattice structure of polystyrene domains from SAXS studies on the S–B–S block copolymer. In their analyses of the scattering data, they have both assumed that intensity maxima correspond to the maxima of the interparticle interference function. As pointed out, this is true only for perfect crystals and does not apply to a fluid or amorphous polymer, since "the position of intensity maxima depends in a very complex way on the structure of the arrangement of the particles and on the particular structure of each particle."[21] So before we can use the analyses of Lewis, *et al.*, and McIntyre, *et al.*, we have to establish by independent means that a three-dimensional superlattice is the structure of S–B–S block copolymer.

It has, however, been shown that this block copolymer does have a structural regularity of styrene domains when processed in a certain way. With an extruded rod of S–B–S block copolymer, Keller, *et al.*,[22] have observed a single-crystal pattern of hexagonal structure when the X-ray beam is parallel to the extrusion direction. They concluded that these patterns were caused by the hexagonal packing of very long cylinders lying parallel to the extrusion direction. But the existence of such remarkable ordering phenomena in the bulk state of an S–B–S block copolymer in which no orientation was induced has yet to be proved.

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(21) Reference 10, p 114.

(22) A. Keller, E. Pedemonte, and F. M. Willmonth, *Kolloid-Z. Z. Polym.*, **238**, 387 (1970).

Structural Evidence of Radiation-Induced Thiourea Canal Polymerization of 2,3-Disubstituted 1,3-Butadienes

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ABSTRACT: The highly 1,4-trans tactic polymerization of 2,3-dichloro-1,3-butadiene and 2,3-dimethyl-1,3-butadiene in thiourea canals by γ irradiation is supported by structural evidence based upon crystal structure analyses of the monomer–thiourea complexes, the polymer–thiourea complexes, and the resultant polymers for both the dienes. The canal polymerizations of both the dienes are analogous to each other from a structural viewpoint. The monomer–thiourea complexes are stoichiometric compounds; the mole ratio of thiourea and the monomers is 3:1. In other words, two monomers occupy the canal period of 12.5 Å. The monomers are included in the thiourea canals, which are evidently deformed from the well-known honeycomb-like hexagonal prisms. The crystals have monoclinic symmetry $P2_1/a$. The deformation of the thiourea canals is attributed to the molecular shape, size, and packing mode of the guest molecules. The packing modes of the monomers and the deformed canals are favorable for 1,4-trans tactic polymerization, and polymerization in the canals can be performed with only a slight change of the canal shape and size. The resultant polymer–thiourea complexes are nonstoichiometric compounds, but the space group is again $P2_1/a$ as in the monomer complexes. The 1,4-trans tactic polymer chains in the canals take a nearly T-S-trans-$\bar{\text{S}}$ conformation (T, trans; S and $\bar{\text{S}}$, clockwise and counterclockwise skew forms, respectively), the identity period of which is 4.80 Å.

Radiation-induced polymerization of various monomer–urea or monomer–thiourea complexes is very attractive as a unique polymerization method.[1–4] Presumably, monomers polymerize in urea or thiourea canals subject to a spatial control which may be different from steric controls by catalysts. But it is still not beyond the stage of speculation as to what the structures of the complexes are and why a special control for polymerization is possible. It should be noted that urea was reported to form molecular complexes, such as urea–oxalic acid,[5] urea–dioxane,[6] and urea–poly(ethylene oxide),[7] with entirely different structures from the well-known hexagonal canal structures of *n*-hydrocarbon–urea complexes.[8] Unfortunately, most monomer–urea or monomer–thiourea complexes which are important in polymer chemistry are unstable or do not exist at room temperature, and this seems to have prevented detailed study of this

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(1) H. Clasen, *Z. Elektochem.*, **60**, 982 (1956).

(2) I. Sakurada and K. Nanbu, *Kogyo Kagaku Zasshi*, **80**, 307 (1959).

(3) J. F. Brown, Jr., and D. M. White, *J. Amer. Chem. Soc.*, **82**, 5671 (1960).

(4) D. M. White, *ibid.*, **82**, 5678 (1960).

(5) J. H. Sturdivant, A. Schuch, and L. L. Merrit, Jr., American Crystallographic Association Meeting, Pennsylvania State University, 1950.

(6) O. Redlich, C. M. Gable, A. K. Dunlop, and R. W. Millar, *J. Amer. Chem. Soc.*, **72**, 4153 (1950).

(7) H. Tadokoro, Y. Yoshihara, Y. Chatani, and S. Murahashi, *J. Polym. Sci., Part B*, **2**, 363 (1964).

(8) A. E. Smith, *Acta Crystallogr.*, **5**, 224 (1952).