

Small-angle neutron diffraction study of block copolymer superstructure*

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The structural parameters of butadiene–styrene diblock copolymer films prepared by deposition from toluene have been studied with the aid of small-angle neutron scattering (SANS) in the temperature range from -190 up to $+210^\circ\text{C}$. The experimental scattering curves were simulated within the limits of the line-gradient model including the Debye–Waller factor, the static character of which was determined from low-temperature measurements. The structural parameters determined by SANS experiments have been compared with the parameters calculated with the help of the formulae obtained by Skoulios, Helfand and Meier. It was also observed that the system could retain information about the conditions of the superstructure formation process.

(Keywords: block copolymer; superstructure; small-angle neutron scattering; butadiene–styrene)

INTRODUCTION

Ordered supermolecular structures in block copolymers (superstructures) were first found experimentally about 30 years ago^{1,2}. Since that time block copolymers have attracted the attention of many researchers owing to their unique properties, which are connected to a great extent with the fact that a regular structure is observed only on the supermolecular scale and these systems are disordered on the molecular level. They are used as surfactants and materials for problems in medicine and microelectronics. Small-angle X-ray and neutron scattering (SAXS, SANS) techniques are the most useful for structural studies of these objects‡, as they allow one to carry out a structural study of samples with no special preparation. In this paper the SANS technique has been used to study the structural changes of styrene–butadiene diblock copolymers as a function of temperature in the range from -190 to $+210^\circ\text{C}$.

THE MODEL OF ORIENTED LAMELLAR STRUCTURE

The simple line-gradient model for the scattering length density distribution $\rho(x_D)$ of a two-phase system with period D and interphase layer thickness E (Figure 1) has

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‡ In our case the contrast between polybutadiene and polystyrene domains is of the order of $1 \times 10^{10} \text{ cm}^{-2}$ for both X-rays and neutrons. This means that structural information obtained with the aid of both these techniques is the same

been chosen for the calculation of the scattering pattern. According to this model, the small-angle scattering intensity $I(Q)$ for a lamellar structure may be written as:

$$I(Q) \simeq \left(\int G(D_L)(D_L + E)^2 F(QD_L) S(QD) dD_L \right) \times \exp(-Q^2 z^2) \quad (1)$$

where $Q = 4\pi \sin \theta / \lambda$ is the length of the scattering vector (θ is the diffraction angle, λ is the wavelength), $G(D_L)$ is the distribution function of lamellar thickness D_L , $S(QD)$ is the structural factor describing the interference between waves scattered by different lamellae, $\exp(-Q^2 z^2)$ is the Debye–Waller factor and $F(QD_L)$ is the form factor of the lamella:

$$F(QD_L) = \left(\frac{\sin[Q(D_L + E)/2]}{Q(D_L + E)/2} \right)^2 \left(\frac{\sin[QE/2]}{QE/2} \right)^2 \quad (2)$$

For $S(QD)$ the following relation has been chosen³:

$$S(QD) = \text{Re}[(1 + \tilde{F})/(1 - \tilde{F})] \quad (3)$$

where $\tilde{F} = F\{P_D(x_D)\}$ is the Fourier transform of the distribution function $P_D(x_D)$ of the deviation of the period from its average value D . For a normal distribution:

$$P_D(x_D) = \frac{1}{(2\pi\Delta^2)^{1/2}} \exp\left(-\frac{(x_D - D)^2}{2\Delta^2}\right)$$

where Δ is the dispersion of D , we have:

$$\tilde{F}(Q) = \exp(-0.5Q^2\Delta^2) \exp(-iQD) = R(Q) \exp(-iQD) \quad (4)$$

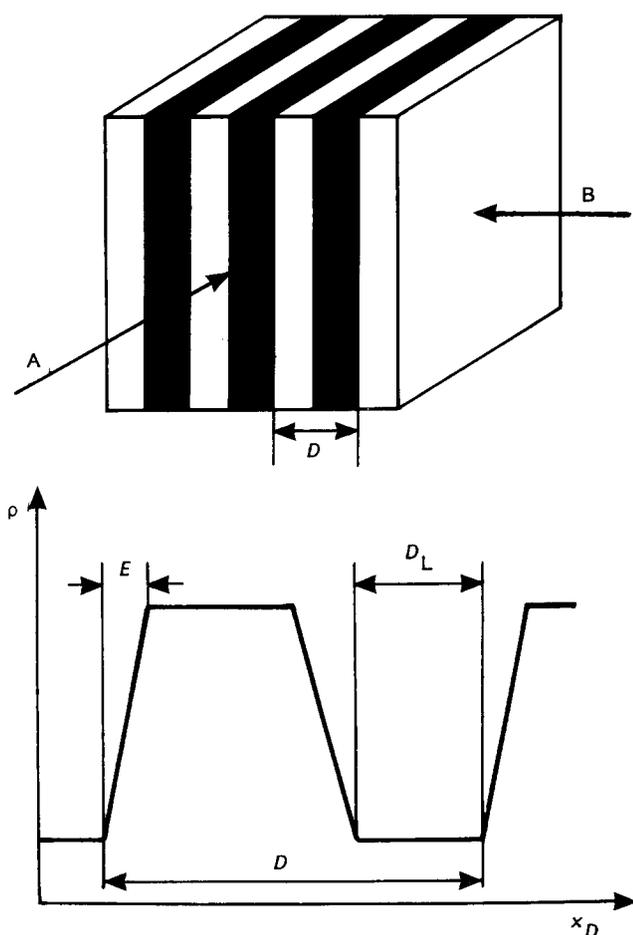


Figure 1 The model of lamellar structure and the line-gradient model of scattering length density distribution $\rho(x_D)$ in a two-phase system with interphase layers of thickness E . The orientations (A and B) of lamellae with respect to the neutron beam direction in the experiment are shown by the arrows

Then relation (3) may be rewritten taking into account (4) as:

$$S(Q) = \frac{1 - R^2}{1 + R^2 - 2R \cos(QD)} \quad (5)$$

It should be pointed out that this mathematical model describes an infinite lamellar structure without taking into consideration the fact that a real block copolymer superstructure consists of crystallites. However, as will be shown later, this assumption is valid in our case.

Thus the model of the scattering system contains five independent variables, D , $G(D_L)$, E , Δ and z . The thickness of the interphase layer E may be determined from an independent experiment using the technique offered either by Hashimoto⁴:

$$I(Q)|_{Q \rightarrow \infty} \approx \exp\left(-\frac{1}{2\pi} E^2 Q^2\right) Q^{-2} \quad (6)$$

or by Stein and Rulland^{5,6}:

$$I(Q)|_{Q \rightarrow \infty} \approx \exp[-0.144(EQ)^{1.81}] Q^{-2} \quad (7)$$

The parameter Δ may be evaluated from the Hosemann-Bagchi criterion⁷:

$$0.35/(n+1) \leq \Delta D/D \leq 0.35/n \quad (8)$$

where n is the number of diffraction maxima registered

experimentally. So the model chosen has three free variable parameters: D , $G(D_L)$ and z .

SAMPLE PREPARATION AND METHOD OF MEASUREMENTS

The samples of butadiene-styrene AB block copolymers have been synthesized at the Institute of Macromolecular Compounds, USSR Academy of Sciences, by the method of anionic polymerization. The molecular masses of the blocks were $M_{PS}^n = 5.9 \times 10^4$ and $M_{PB}^n = 5.7 \times 10^4$, with $M_w/M_n \approx 1.15$ (for a macromolecule of the diblock copolymer). The content of styrene, $\phi_{PS} = 0.51 \pm 0.02$, has been determined by the method of refractometry. The diblock copolymer macromolecules were dissolved in toluene (at a concentration of polymer of 3%), and then the solvent was evaporated for 3 days at room temperature. After that the samples were dried for 24 h in a vacuum. The dry films with a thickness of about 0.7 mm were taken off the support and cut into strips of 2 mm width and 60 mm length. These strips were packed up as a pile of size $2 \times 5 \times 60 \text{ mm}^3$.

The SANS measurements were carried out on the small-angle neutron diffractometer 'Membrana-2'⁸ in the range of scattering vectors $4 \times 10^{-3} \leq Q \leq 9 \times 10^{-2} \text{ \AA}^{-1}$. The average wavelength of the incident beam was $\bar{\lambda} = 2.3 \text{ \AA}$ and the half-width of the spectrum was $\Delta\lambda/\bar{\lambda} \approx 0.1$. The orientation of the sample depended on the situation to be studied: the A orientation (Figure 1) has been used for measurements of the equatorial reflection pattern and the B orientation for determination of the thickness of the interphase layer E . Low-temperature measurements have been performed with the help of a nitrogen cryostat, making it possible to keep the temperature of the sample, put into a tube with gaseous helium, at about -190°C . Sample heating and temperature stabilization to about $\pm 1^\circ\text{C}$ in the range from 25 to 210°C were achieved by use of a vacuum furnace. In each case the coherent component of the scattering was selected by subtracting the incoherent and instrumental backgrounds. The experimental scattering curves were compared to simulated curves corrected for the spectral and collimation distortions of the 'Membrana-2' diffractometer.

RESULTS AND DISCUSSION

First, let us estimate the degree of lamellar orientation with respect to the surface of the polystyrene-polybutadiene (PS-PB) films obtained using the expression⁹:

$$f_\alpha = (3\langle \cos^2 \alpha \rangle - 1)/2 \quad (9)$$

where α is the polar angle between the film normal and the lamella normal, f_α is the second-order orientation factor and:

$$\langle \cos^2 \alpha \rangle = \int I_{\max}(\alpha) \cos^2 \alpha \, d\alpha / \int I_{\max}(\alpha) \, d\alpha$$

The variation of the film normal orientation with respect to the incident beam direction has been experimentally achieved by azimuthal rotation of the pile of films.

In Figure 2 the diffractograms corresponding to A and B orientations of the sample are presented without the backgrounds being subtracted. One can see that the scattering intensity for A orientation in the range of the third diffraction maximum exceeds the scattering intensity for B orientation by approximately 10 times. The same

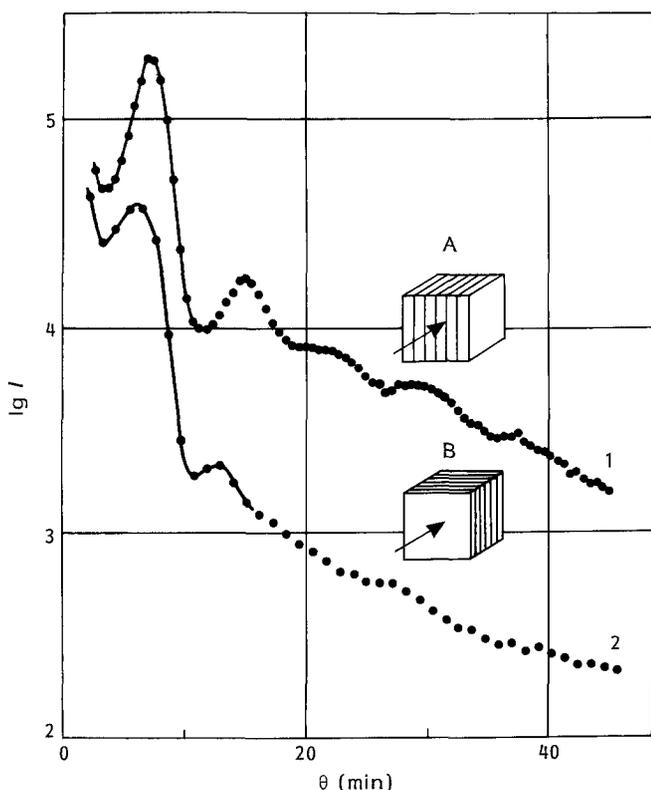


Figure 2 The scattering curves from the pile of PS-PB films: A orientation (curve 1), B orientation (curve 2). The ranges of the first maxima are shown by full curves

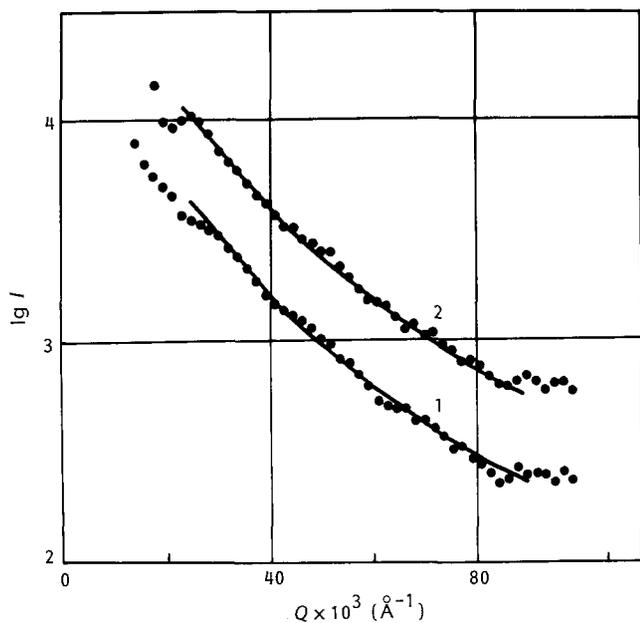


Figure 3 The scattering curves (B orientation, $Q \geq 0.02 \text{ \AA}^{-1}$) obtained for the sample at 200°C (curve 1) and 25°C (curve 2). The simulations are shown by the full curves

diffractograms have been registered for different azimuthal angles of sample rotation. After background subtraction and data processing by formula (9), the value $f_\alpha = 0.93$ has been obtained. This attests to the high degree of lamellar surface orientation parallel to the surface of the prepared films.

Now let us estimate the dimensions of crystallites using the well known relation between the relative half-width of the first diffraction maximum and the number of

lamellae in the crystallite, $\Delta Q/Q = 1/N$. This estimation performed for the first maximum of curve 1 (Figure 2), taking into account the instrumental distortions, gives the value $N = 80 \pm 25$. Thus the average dimensions of the crystallites, $ND_L \approx 40\,000 \text{ \AA}$, are much larger than the lamellar thickness, which validates the choice of the form factor (2). It can be shown that for such a number of lamellae in the crystallite the model of an infinite lattice is valid. These two facts serve as evidence for the validity of the line-gradient model in equations (1)–(5).

In Figure 3 two scattering curves registered for the B orientation of the sample in the range $0.02 \leq Q \leq 0.09 \text{ \AA}^{-1}$ at $T = 25^\circ\text{C}$ (curve 1) and at $T = 200^\circ\text{C}$ (curve 2) are presented. The interphase layer thickness E calculated here gives the value $25 \pm 3 \text{ \AA}$, which is in good accord with the value $E = 22 \pm 3 \text{ \AA}$ calculated for a lamellar styrene-butadiene block copolymer by the Helfand theory¹⁰. It should be pointed out that the value of the interphase layer thickness is independent of temperature in the range from 25 to 200°C.

Let us now discuss the main results of the present work, connected with the temperature dependence of the PS-PB lamellar structure parameters. It is worth while to begin the discussion from a consideration of the alteration of the period D in the temperature range $25 \leq T \leq 210^\circ\text{C}$ (Figure 4). One can see that the period D increases from 520 to 710 Å after heating from 25 to 130°C and then remains unchanged, not only in the range

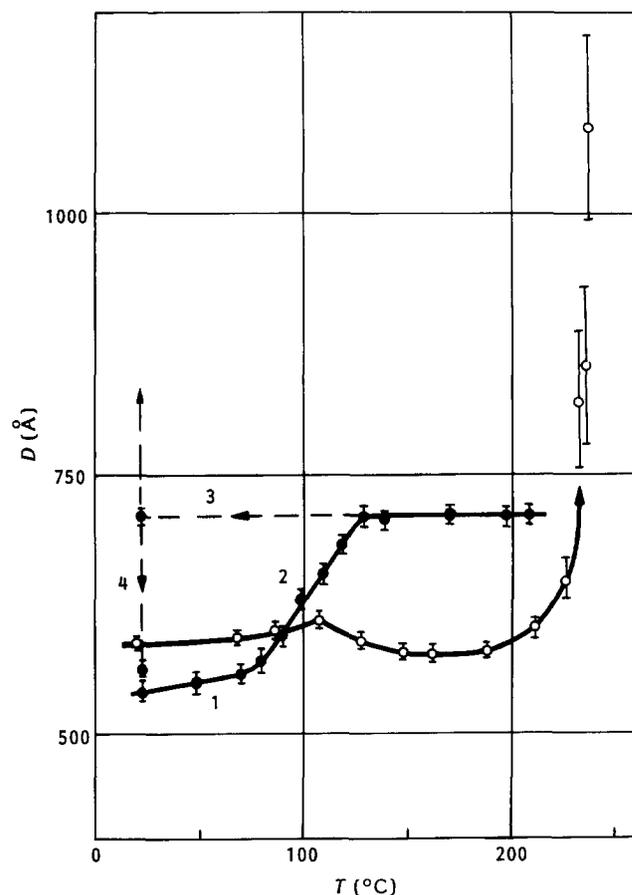


Figure 4 The temperature dependence of the superstructure period $D(T)$: (○) the data of ref. 17 for polystyrene-polyisoprene; (●) the data of the present work for polystyrene-polybutadiene. Part 1 of $D(T)$ is the region $25 \leq T \leq 75^\circ\text{C}$. Part 2 represents increasing D in the region $75 \leq T \leq 130^\circ\text{C}$. The broken line 3 shows the cooling from 210°C down to 25°C. The broken line 4 corresponds to the D change during swelling and drying

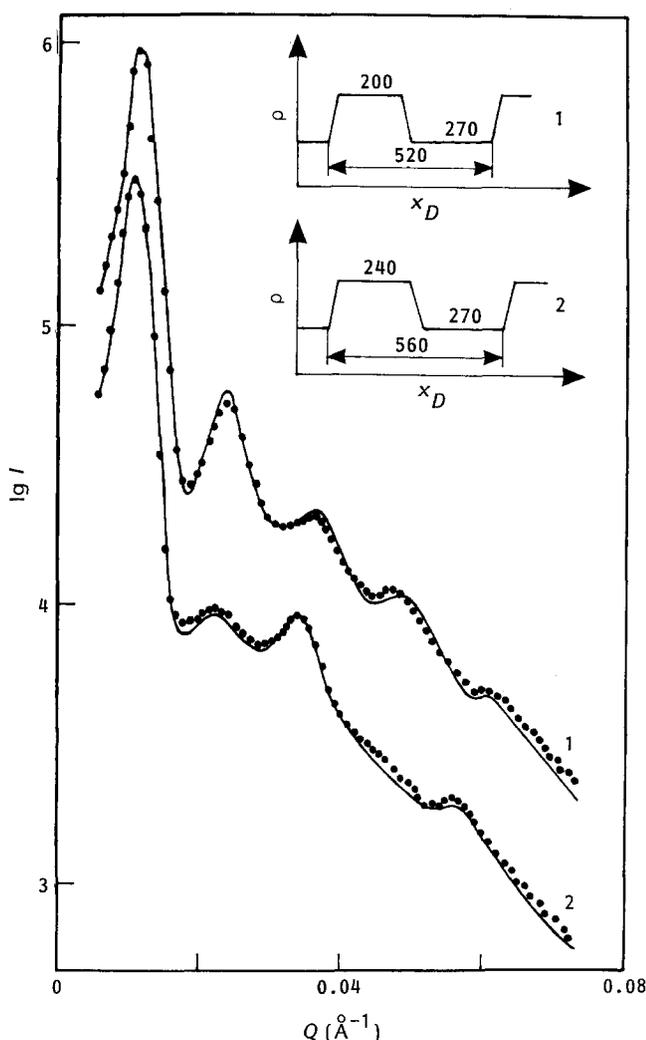


Figure 5 The scattering curves (A orientation) obtained for the sample at 25°C (curve 1) and 75°C (curve 2). The simulations are shown by the full curves. The corresponding scattering length density distribution functions $\rho(x_D)$ are given in the inset

$130 \leq T \leq 210^\circ\text{C}$ but also after cooling down to room temperature. The $D(T)$ curve in the range $25 \leq T \leq 130^\circ\text{C}$ can be divided into two linear parts with different values of $\text{grad } D(T)$: in the range $25 \leq T \leq 75^\circ\text{C}$ $\text{grad } D(T) \approx 0.8 \text{ \AA }^\circ\text{C}^{-1}$ and in the range $75 \leq T \leq 130^\circ\text{C}$ $\text{grad } D(T) \approx 2.0 \text{ \AA }^\circ\text{C}^{-1}$. Qualitative analysis of the diffractograms shows that the increase of D in the range $25 \leq T \leq 75^\circ\text{C}$ is accompanied by a decrease of the amplitude of even maxima, and at 75°C these maxima are practically completely suppressed. But after that the profiles of the scattering curves remain unchanged and further heating leads only to a change in the positions of the diffraction maxima in the range $75 \leq T \leq 130^\circ\text{C}$. Quantitative calculations of the structural parameters performed for the scattering curves from the samples at $T = 25^\circ\text{C}$ (curve 1) and at $T = 75^\circ\text{C}$ (curve 2) are presented in Figure 5. The simulated curves (full curves) have been computed with the help of the line-gradient model in equations (1)–(5). The best agreement between the experimental and simulated curves has been achieved for the following two sets of parameters:

$$E = 25 \text{ \AA}, \quad \Delta = 40 \text{ \AA}, \quad z = 20 \text{ \AA}, \quad D = 520 \text{ \AA}, \\ \bar{D}_L = 200 \text{ \AA}, \quad \delta D_L = 35 \text{ \AA}^* \quad (\text{for curve 1})$$

* Here $G(D_L)$ was set by a normal distribution

and

$$E = 25 \text{ \AA}, \quad \Delta = 40 \text{ \AA}, \quad z = 20 \text{ \AA}, \quad D = 560 \text{ \AA}, \\ \bar{D}_L = 240 \text{ \AA}, \quad \delta D_L = 35 \text{ \AA} \quad (\text{for curve 2})$$

Similar calculations have been carried out for all the diffractograms registered at the temperatures indicated in Figure 4. It must be pointed out that the set of parameters E , Δ and z are the same for all the cases; moreover, the values of E and Δ are in good agreement with these parameters calculated with the aid of formulae (6)–(8). The value of z is approximately equal to the thickness of the interphase layer E and the Debye–Waller factor is not unity. So it is interesting to elucidate the dynamic or static character of the Debye–Waller factor in our case. The scattering curve registered from the sample at $T = -190^\circ\text{C}$ shows that the profile of this curve is similar to the profile of the diffractogram from the sample at $T = 25^\circ\text{C}$. This fact makes it possible to establish the static character of the Debye–Waller factor. The period of the lamellar structure decreases with decreasing temperature and becomes $D = 496 \text{ \AA}$ (compared with the value $D = 520 \text{ \AA}$ at room temperature). The coefficient of linear expansion determined from these data is $2.4 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ and this value is typical for polymer materials.

Let us now consider the diagrams of $\rho(x_D)$ (in the inset of Figure 5) obtained for the samples at $T = 25^\circ\text{C}$ (curve 1) and $T = 75^\circ\text{C}$ (curve 2). One can conclude from these diagrams that the increase in period from $D = 520 \text{ \AA}$ at $T = 25^\circ\text{C}$ to $D = 560 \text{ \AA}$ at $T = 75^\circ\text{C}$ is achieved by increase of only one of the half-periods D_L from 200 to 240 Å, and the other one remains independent of temperature in the range $25 \leq T \leq 75^\circ\text{C}$. This fact will be discussed in detail below. Now it should be pointed out that above 75°C the mechanism causing the period to increase is changed. The increase of D from 560 Å at $T = 75^\circ\text{C}$ to 710 Å at $T = 130^\circ\text{C}$ is achieved by the simultaneous increase of both half-periods with preservation of the correlation between them.

It is known that polybutadiene macromolecules in the bulk are capable of forming a net of crosslinks under the influence of temperature. A weakly crosslinked block copolymer allows one to obtain a superstructure from a swollen sample by solvent evaporation without contact with a solid surface. This experiment was performed for the above described sample previously annealed at $T = 130^\circ\text{C}$. The sample was swollen in toluene and its volume increased approximately 20 times. After solvent evaporation the sample was dried in a vacuum for 24 h at ambient temperature. The diffractogram from the sample at $T = 25^\circ\text{C}$ is similar to the diffractogram from the sample obtained by the ordinary method of deposition and then heated up to $T = 75^\circ\text{C}$.

Let us now return to Figure 4, illustrating the dependence $D(T)$, and try to explain the structural alterations in region 1 connected with the increasing thickness of only one of the two microphase layers. The thickness of the polystyrene layer in the case of a lamellar structure may be calculated for the equilibrium state by the expression¹¹:

$$D_{\text{PS}} = D / [1 \pm \bar{v}_{\text{PB}}(1 - x_{\text{PS}}) / \bar{v}_{\text{PS}}x_{\text{PS}}] \quad (10)$$

where \bar{v}_{PB} and \bar{v}_{PS} are the specific volumes of polybutadiene ($1.087 \text{ cm}^3 \text{ g}^{-1}$) and polystyrene ($0.953 \text{ cm}^3 \text{ g}^{-1}$) blocks respectively; and $x_{\text{PS}} = 0.51 \pm 0.02$ is the volume fraction of PS in the sample. The calculation performed using

Table 1 Parameters of PS–PB system^a

Polymer	ρ_0 (10^3 mol m^{-3})	b (Å)	M_n (10^4)	z
PS	10.1	6.8	5.9	566
PB	16.5	6.3	5.7	1053

^aValues of ρ_0 and b are taken from ref. 10

formula (10) for $D = 560 \text{ Å}$ gives values of $D_{\text{PS}} = 242 \text{ Å}$ and $D_{\text{PB}} = 268 \text{ Å}$ (without taking into account the interphase thickness E), which are in very good agreement with these parameters obtained experimentally from SANS data, $D_{\text{PS}} = 240 \text{ Å}$ and $D_{\text{PB}} = 270 \text{ Å}$ (see curve 2 in the inset of Figure 5). This correlation reflects the fact that the system is coming to the equilibrium state with standard values of the specific volumes of the components as a consequence of the heating up to 75°C . As to the parameters of the lamellar structure at $T = 25^\circ\text{C}$ determined experimentally ($D = 520 \text{ Å}$, $D_{\text{PS}} = 200 \text{ Å}$, $D_{\text{PB}} = 270 \text{ Å}$), it is clear that to make a correlation of these parameters with the results of the calculation using equation (10) for $D = 520 \text{ Å}$, it is necessary to change \bar{v}_{PB} and \bar{v}_{PS} (or one of them). As D_{PB} does not change after heating from 25 to 75°C but \bar{v}_{PB} assumes its standard value ($1.087 \text{ cm}^3 \text{ g}^{-1}$) at $T = 75^\circ\text{C}$, one can conclude that the value of \bar{v}_{PB} at $T = 25^\circ\text{C}$ is less than the standard one. The calculation by formula (10) gives the value $\bar{v}_{\text{PB}} = 1.3 \text{ cm}^3 \text{ g}^{-1}$. So as a consequence of the structure formation process when the solvent has been evaporated from the solid vessel, the PS–PB film obtained has deformations. In particular, the polybutadiene microphase is found to be under the action of a volume strain with a change in \bar{v}_{PB} and the polystyrene microphase is under the action of a two-dimensional strain only without a change in \bar{v}_{PS} . These deformations can be annealed by heating up to 75°C . This hypothesis may be supported by the absence of these deformations when the film has been formed from a swollen sample by way of volume solvent evaporation without contact with a solid surface. In this case the system has come directly to the equilibrium state with the parameters $D = 560 \text{ Å}$, $D_{\text{PS}} = 240 \text{ Å}$ and $D_{\text{PB}} = 270 \text{ Å}$.

Let us now interpret the results obtained from SANS data for the sample in the temperature range $75 \leq T \leq 130^\circ\text{C}$. In this range equation (10) is valid so it is interesting to understand the physical meaning of the final state of the system at $T \geq 130^\circ\text{C}$ (see Figure 4). In order to answer this question let us estimate the value of D from the viewpoints of the thermodynamic theories of equilibrium microphase superstructures offered by Helfand^{12,13} and Meier^{14,15}.

According to Helfand, in the case when the interphase thickness E is small compared with the period D , minimization of the expression for the free-energy change leads to the following equation for the equilibrium value D_{H} :

$$2.5A_1D_{\text{H}}^{3.5} + D_{\text{H}} - A_2 = 0 \quad (11)$$

Here:

$$A_2 = \frac{2\gamma}{kT} \left(\frac{z_{\text{PS}}}{\rho_{0,\text{PS}}} + \frac{z_{\text{PB}}}{\rho_{0,\text{PB}}} \right)$$

$$A_1 = 0.141 \frac{(z_{\text{PS}}^{0.5}/b_{\text{PS}}\rho_{0,\text{PS}})^{2.5} + (z_{\text{PB}}^{0.5}/b_{\text{PB}}\rho_{0,\text{PB}})^{2.5}}{(z_{\text{PS}}/\rho_{0,\text{PS}} + z_{\text{PB}}/\rho_{0,\text{PB}})^{2.5}}$$

and

$$\gamma = kT\alpha^{0.5} \left(\frac{\beta_{\text{PS}} + \beta_{\text{PB}}}{2} + \frac{1}{6} \frac{\beta_{\text{PS}} - \beta_{\text{PB}}}{\beta_{\text{PS}} + \beta_{\text{PB}}} \right)^2$$

is the interfacial strain; $\beta_k^2 = \rho_{0,k}b_k^2/6$; b_k , $\rho_{0,k}$ are the length and the density of the statistical segment of the k th block respectively; z_k is the degree of polymerization of the k th block (where k is PS or PB); and α is the polymer–polymer interaction parameter in the system. The parameters of the system under investigation are tabulated in Table 1. In addition, from ref. 10, $\alpha = 1.63 \times 10^3 \text{ mol m}^{-3}$. For these parameters, equation (11) gives the value $D_{\text{H}} = 680 \text{ Å}$.

The Meier theory of phase separation gives the following expression for the thermodynamic equilibrium value of the superstructure period:

$$D_{\text{M}} = 2.8\alpha_s K (M/2)^{0.5} \quad (12)$$

where M is the summary number-average molecular mass of blocks A and B, α_s is the strain coefficient of chains (the value $\alpha_s = \sqrt{2}$ calculated in ref. 16 has been used), and $K = 7.5 \times 10^{-1} \text{ Å}$ is the experimental constant connected with the unperturbed dimensions of a chain whose molecular mass is M . The calculation performed with the help of (12) gives the value $D_{\text{M}} = 712 \text{ Å}$.

According to the SANS data, the period of the superstructure at $T = 130^\circ\text{C}$ is $D = 710 \text{ Å}$, and this value is in good agreement with the theoretical calculations. So one can conclude that after the annealing process the lamellar superstructure comes to thermodynamic equilibrium corresponding to the minimum of the free energy of the system.

It is interesting finally to compare the results of the present investigations with data obtained by Hadziioannou and Skoulios for a styrene–isoprene diblock copolymer¹⁷. The temperature dependence $D(T)$ has been measured for a polystyrene–polyisoprene (PS–PI) sample prepared from melting a copolymer by the method of shaking at a temperature of 130°C . The $D(T)$ curve for PS–PI in the temperature range $25 \leq T \leq 240^\circ\text{C}$ is presented in Figure 4. We do not discuss here the increase of D at $T \geq 210^\circ\text{C}$ because this temperature range has not been studied by us. But in the range $25 \leq T \leq 200^\circ\text{C}$ the behaviour of the PS–PI system prepared by the shaking method does not correspond to the behaviour of the PS–PB superstructure prepared by the method of deposition from a solvent. The absence of a strong increase of period D near the transition temperature of styrene from the glassy state to the highly elastic state ($\approx 100^\circ\text{C}$) observed in ref. 17 is connected in our opinion with the method of sample preparation. The PS–PI superstructure has been prepared under equilibrium conditions, so that the annealing process does not exert a major influence on the structural parameters.

REFERENCES

- Skoulios, A., Finaz, G. and Parrod, J. *C.R. Acad. Sci. Paris* 1960, **251**, 739
- Skoulios, A. and Finaz, G. *C.R. Acad. Sci. Paris* 1961, **252**, 3467
- Vonk, C. G. in 'Small-Angle X-Ray Scattering' (Eds. O. Glatter and O. Kratky), Academic Press, London, 1982
- Hashimoto, T., Shibayama, M. and Kawai, H. *Macromolecules* 1980, **13**, 1237
- Siemann, V. and Ruland, W. *Colloid Polym. Sci.* 1982, **260**, 999

- 6 Koberstein, J. T., Morra, B. and Stein, R. *J. Appl. Crystallogr.* 1980, **13**, 34
- 7 Hosemann, R. and Bagchi, S. N. 'Direct Analysis of Diffraction by Matter', North-Holland, Amsterdam, 1962
- 8 Agamalyan, M. M., Drabkin, G. M., Svergun, D. I. and Feigin, L. A., Preprint LNPI-1599, Leningrad Nuclear Physics Institute, 1990
- 9 Shibayama, M. and Hashimoto, T. *Macromolecules* 1986, **19**, 740
- 10 Bates, F. S., Berney, C. V. and Cohen, R. E. *Macromolecules* 1983, **16**, 1101
- 11 Skoulios, A. in 'Advances in Liquid Crystals' (Ed. G. H. Brown), Academic Press, New York, 1975
- 12 Helfand, E. *Polym. Sci. Technol.* 1974, **4**, 141
- 13 Helfand, E. and Wasserman, Z. R. *Polym. Eng. Sci.* 1977, **17**, 582
- 14 Meier, D. J. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* 1970, **11**, 400
- 15 Meier, D. J. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* 1974, **15**, 171
- 16 Hashimoto, T., Todo, A., Itoi, H. and Kawai, H. *Macromolecules* 1977, **10**, 377
- 17 Hadziioannou, G. and Skoulios, A. *Polymer* 1980, **21**, 845