Configurational studies of microphase-separated diblock copolymers in the solid state

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Microphase separation occurs in block copolymers due to thermodynamic incompatibility between the blocks and is responsible for the formation of periodic microstructures, or domains, which are on the same size scale as the root-mean-square end-to-end distance of the domain-forming block ($\langle r_k^2\rangle^{1/2}$). Experimental evidence has shown that $\langle r_k^2\rangle^{1/2}$ deviates significantly from its unperturbed analogue ($\langle r_k^2\rangle_0^{1/2}$), implying that each block in a microphase-separated block copolymer is either expanded or contracted owing to the presence of the other block. In this work, expansion coefficients for each block and for the entire copolymer molecule are predicted as functions of both molar composition and molecular weight in poly(styrene–butadiene) diblock copolymers exhibiting lamellar morphology with modified versions of the Leary–Henderson–Williams thermodynamic theory. A comparison of predictions obtained for each of these model variations, which reflect the extent of block interdependence, is also provided.

(Keywords: block copolymers; chain statistics; microphase separation; polymeric microstructure; polymer thermodynamics)

INTRODUCTION

Thermodynamic incompatibility between the blocks of a block copolymer results in microphase separation, a well documented phase transition responsible for the formation of a periodic microstructure. In the solid (or melt) state, this microstructure consists of either dispersed domains of one block in a continuous matrix of the other or co-continuous lamellae (the latter illustrated in *Figure 1*), depending primarily on the composition of the copolymer molecule. The microphases in these materials are on the same size scale as the end-to-end distance of the domain-forming block (typically tens of nanometres) owing to the covalent bonding between the blocks. Because of the influential role of the resulting microstructure on bulk thermomechanical properties, thermodynamic models, based on either the strong-segregation[1–7] or weak-interaction limits[8–10] have been developed to provide accurate predictions of both microstructural dimensions and system energetics.

Since a conceptual understanding of the behaviour of these copolymers can be readily extended to related systems (e.g. microemulsions[11]), other models have been independently proposed for the sole purpose of discerning the chain conformation of linear block copolymer molecules in a variety of solvent conditions. Tanaka and coworkers[12,13] have performed extensive Monte Carlo simulations, along with light-scattering experiments, to elucidate the configurational properties of the blocks in dilute solution. Recent theoretical efforts by Douglas and Freed[14] and McMullen *et al.*[15] utilize renormalization group methods to discern the apparent radii of gyration and block expansion coefficients of diblock copolymers with varying degrees of molecular interactions in dilute solution.

Interest in block copolymer chain conformation is not, however, restricted to the limiting case of a dilute (or theta) solution. Small-angle neutron scattering (SANS)[16–18] has been used effectively to determine the perturbed radius of gyration of deuterated blocks in microphase-separated copolymers in the solid state. Both theoretical considerations and experimental evidence seem to indicate that the blocks of these copolymers (whether in the solution or solid state) deviate appreciably from the random-coil behaviour exhibited by their homopolymer analogues of similar molecular weight. In terms of block configurations, this means that each block is either contracted or expanded along the lamellar normal (the x direction of *Figure 1*).

The objective of the present work is to apply modified versions of the Leary–Henderson–Williams (LHW) thermodynamic theory to the prediction of block configurations in solid-state diblock copolymers possessing lamellar morphology and composed of polystyrene (PS) and polybutadiene (PB) blocks. Unlike block expansion coefficients obtained from light-scattering theory, those predicted here, provided as functions of both molar composition and molecular weight, correspond to the conditions of thermodynamic equilibrium in the strong-segregation limit.

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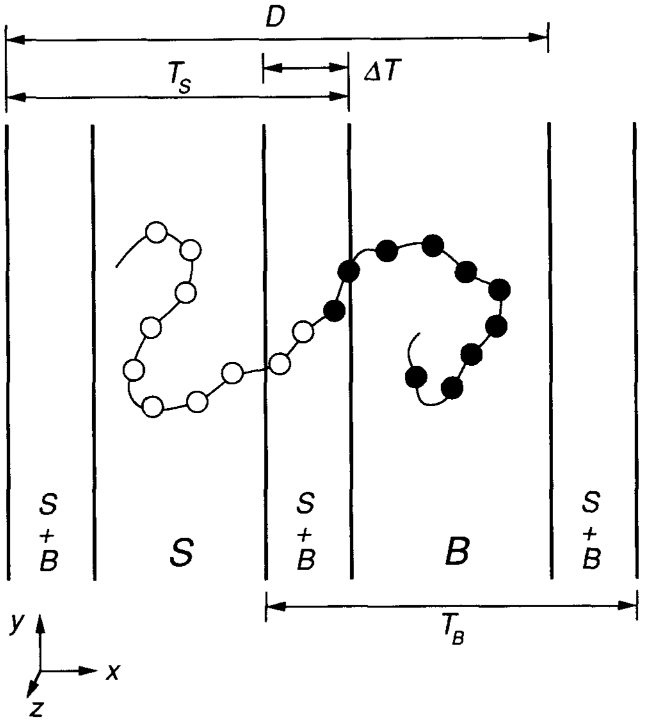

Figure 1 Schematic illustration of the lamellar morphology in a microphase-separated poly(styrene–butadiene) diblock copolymer. The microphases are denoted S and B for the styrene and butadiene cores, respectively, and the regions labelled S + B refer to the mixed interphase

THERMODYNAMIC MODEL

Theoretical background

The original theory developed by Leary and Williams[2] for triblock copolymers and later extended by Henderson and Williams[6] for diblock copolymers rests on the premise that a copolymer system tends to seek a state of equilibrium. The molar Gibbs free-energy function (G) corresponding to this equilibrated condition for a system of monodisperse molecules is given by:

$$\Delta G \rightarrow \Delta G_{\min} = (\Delta H - T\Delta S)_{\min} \tag{1}$$

where ΔG is defined by:

$$\Delta G \equiv G_{\text{struc}} - G_{\text{homog}} \tag{2}$$

and the subscripts 'struc' and 'homog' refer to the structured (microphase-separated) copolymer and its homogeneous analogue, respectively, at the same conditions of temperature, molar composition, molecular weight and molecular architecture. The sign of $\Delta G_{\min}$ reveals the preferred state of the copolymer under the prescribed conditions: if negative, the system is microphase-separated; and if positive, the system favours homogeneity. The value of the absolute temperature (T) used throughout this work is 298 K.

The molar enthalpic contribution (ΔH) to the free energy, determined from regular-solution theory, is given as:

$$\Delta H = -V\Delta\delta^2\phi_S\phi_B + \Delta V\Delta\delta^2\overline{\phi'_S\phi'_B} \tag{3}$$

where V is the molar volume (or the effective molecular weight), $\Delta\delta$ is the difference in solubility parameters between the chemically dissimilar blocks, ϕ is the volume-fraction composition of each component, and the subscripts S and B refer to the styrene and butadiene blocks, respectively. The first term in equation (3) gives the enthalpy of complete phase separation in a copolymer system. This expression is subsequently corrected for the heat of mixing that results from the interphase, the residually mixed region existing between the microphases upon microphase separation. Consequently, ΔV in equation (3) is the molar volume of the resultant interphase, and $\overline{\phi'_S\phi'_B}$ is the interphase composition product, which requires detailed information about the interphase along the lamellar normal:

$$\overline{\phi'_S\phi'_B} = \int_0^1 \left[\phi'_S(x^*)\phi'_B(x^*) + \frac{t_D^2}{6\Delta T^2}\left(\frac{\mathrm{d}\phi'_S(x^*)}{\mathrm{d}x^*}\right)^2\right]\mathrm{d}x^* \tag{4}$$

where x^* is the dimensionless interphase distance normalized with respect to the interphase thickness, ΔT. The function $\phi'_S(x^*)$ $[=1-\phi'_B(x^*)]$ is the interphase composition profile of styrene varying as a function of x^* from unity at the S side to zero at the B side and is provided elsewhere[7]. The Debye molecular interaction parameter (t_D) is equal to approximately 0.6 nm in condensed matter[19].

By defining f as the interphase volume fraction ($\equiv \Delta V/V$), equation (3) can be rewritten in its more familiar form:

$$\Delta H = -V\Delta\delta^2(\phi_S\phi_B - f\overline{\phi'_S\phi'_B}) \tag{5}$$

Expressions for f can be derived from one-dimensional material balances and are strongly dependent on morphology. For lamellae, f is given by[6]:

$$f = \frac{2\beta\phi_S}{1 - 2\beta\overline{\phi'_B}} = \frac{2\phi_B\beta T_S}{T_B - 2\overline{\phi'_S}\beta T_S} \tag{6}$$

where β is the dimensionless interphase thickness:

$$\beta = \Delta T/T_S \tag{7}$$

The microstructural dimension T_S, shown in *Figure 1*, is the domain space in which an S block is forced to reside and is equal to the demixed core of the S microphase and the two adjoining interphases. The total butadiene volumetric content within the interphase ($\overline{\phi'_B}$) in equation (6) is determined from:

$$\overline{\phi'_B} = 1 - \overline{\phi'_S} = 1 - \int_0^1 \phi'_S(x^*)\,\mathrm{d}x^* \tag{8}$$

The molar entropy (ΔS) in equation (1) is sensitive to both molecular architecture and morphology and consists of three contributions:

$$\Delta S = \Delta S_I + \Delta S_S + \Delta S_B \tag{9}$$

where the first term arises from confinement of the interphase junction to ΔT, and the ΔS_k (k = S or B) terms reflect the change in entropy, with respect to the homogeneous analogue, that occurs when the kth block is forced to reside in a predesignated location in microdomain space (i.e. T_k, presented in *Figure 1* for k = S and B). Previous probability arguments[6] for the interfacial entropy in a diblock copolymer have resulted in:

$$\Delta S_I = R\ln f \tag{10}$$

where R is the gas constant.

The ΔS_k terms in equation (9) are derived from random-flight chain statistics and elasticity theory and are written as:

$$\Delta S_k = \Delta S_k^{(1)} + \Delta S_k^{(2)} \tag{11}$$

The first contribution ($\Delta S_k^{(1)}$) deals with the probability of each block occupying the appropriate (restricted) configuration, as described above, rather than a random one. Based on the exact random-walk solution of the diffusion equation[2], the probability of either block in a diblock copolymer occupying its predesignated domain region is given by an infinite summation, which may be accurately approximated[6] by:

$$P_k \approx \frac{4}{\pi} \exp\left(\frac{-\pi^2 \langle r_k^2 \rangle}{6T_k^2}\right) \sin\left(\frac{\pi \Delta T}{2T_k}\right) \tag{12}$$

Here, $\langle r_k^2 \rangle^{1/2}$ is the *perturbed* root-mean-square (r.m.s.) end-to-end distance of the kth block along the lamellar normal and is described in detail below. The corresponding change in entropy arising from this probability is:

$$\Delta S_k^{(1)} = R \ln P_k \tag{13}$$

The second contribution to these block entropic terms ($\Delta S_k^{(2)}$) takes into account the fact that, owing to the confinement of the blocks in domain space, the end-to-end distance of the kth block in a microphase-separated block copolymer will not, in general, equal that of the unconfined kth homopolymer of equal molecular weight. Thus, a block expansion parameter α_k is introduced to reflect the extent of block deformation in one dimension (i.e. the x axis of *Figure 1*) and is defined by:

$$\alpha_k^2 \equiv \langle r_k^2 \rangle / \langle r_k^2 \rangle_0 \tag{14}$$

where $\langle r_k^2 \rangle_0^{1/2}$ is the *unperturbed* r.m.s. end-to-end distance of the kth block and is evaluated from:

$$\langle r_k^2 \rangle_0^{1/2} = K_k M_k^{1/2} \tag{15}$$

Here, K_k is the Kuhn segment length and M_k is the molecular weight of the kth block. For a chain with one end fixed (at the block junction), the form of the elastic contribution to the entropy is[6]:

$$\Delta S_k^{(2)} = -\tfrac{3}{2} R(\alpha_k^2 - 1 - \ln \alpha_k^2) \tag{16}$$

It should be borne in mind that the expressions provided here pertain to the lamellar morphology in diblock copolymers only. Extension of these principles to a triblock architecture or to spherical/cylindrical morphologies is straightforward, requiring the use of relationships provided elsewhere[2].

Model variations

Case 1. In the original version of the LHW theory (designated here as case 1)[2,6,7], a second dimensionless parameter (Γ) is introduced to scale the size of the S domain with the *unperturbed* end-to-end distance of the S block, that is:

$$\Gamma \equiv T_S^2 / \langle r_k^2 \rangle_0 \tag{17}$$

By varying both β (from equation (7)) and Γ, a minimum in ΔG is obtained at some β^* and Γ^*, and the microstructural dimensions corresponding to this equilibrium condition are deduced from the magnitudes of β^* and Γ^*. Since theoretical considerations regarding the approach to uniform core density[19] dictate that $T_S^2 = 2\langle r_k^2 \rangle$, Γ is given in terms of α_S by:

$$\Gamma = 2\alpha_S^2 \tag{18}$$

Based on the conservation of block junctions in the interphase, an expression directly relating α_B to α_S has been proposed by Meier[19]:

$$\alpha_B = \alpha_S \xi (M_B/M_S)^{1/2} \tag{19}^*$$

where ξ depends only on physical properties:

$$\xi = \rho_S K_S / \rho_B K_B \tag{20}$$

and ρ_k (k = S or B) is the mass density of the kth block. Due to the magnitudes of the homopolymer characteristics (provided elsewhere[2,6,7]), $\xi \approx 1$ in these SB copolymers.

Case 2. In the first modification of the LHW theory (denoted as case 2), the restriction placed on α_B by equation (19) is relaxed by the introduction of a third parameter, namely Γ_B. The purpose of Γ_B is to decouple the $\alpha_B(\alpha_S)$ relationship, thereby permitting the B block to assume a configuration independent of the S block. For clarity, Γ as defined by equation (17) will henceforth be referred to as Γ_S. The definition of Γ_B in case 2 is similar to that of Γ_S:

$$\Gamma_B^{(2)} = T_B^2 / \langle r_B^2 \rangle_0 \tag{21}$$

where the superscript (2) refers to case 2. To obtain values of α_B without overspecifying the system or violating material balances, the argument for uniform core density[19] is again invoked, this time with regard to the B domain. Thus, $T_B^2 = 2\langle r_B^2 \rangle$ and:

$$\Gamma_B^{(2)} = 2\alpha_B^2 \tag{22}$$

One subsequent difference between cases 1 and 2 is that owing to the definition of Γ_B and its relationship to α_B, it is unnecessary to use the material balances of equation (6) to determine T_B in case 2.

Case 3. The second alteration to the LHW theory (case 3) is similar in appearance to case 2 in that a third varying parameter ($\Gamma_B^{(3)}$) also permits relaxation of equation (19). However, this parameter is defined differently than in case 2:

$$\Gamma_B^{(3)} = T_B^2 / \langle r_B^2 \rangle \tag{23}$$

Here, $\langle r_B^2 \rangle$ is the *perturbed* end-to-end distance of the B block. The definition of Γ_S remains the same as before (equation (17)). In terms of α_B, which is defined by equation (14), equation (23) can be rewritten as:

$$\Gamma_B^{(3)} = T_B^2 / \alpha_B^2 \langle r_B^2 \rangle_0 \tag{24}$$

where, unlike in case 2, T_B is determined from the material balance constraints of equation (6), which when rearranged yields:

$$T_B = 2\beta T_S(\overline{\phi'_S} + \phi_B/f) \tag{25}$$

The corresponding value of α_B is subsequently obtained from equation (24). The approach to uniform core density in the B microphase is *not* applied to case 3.

RESULTS AND DISCUSSION

Effect of molar composition

To facilitate comparison among the predictions obtained from the three model cases described earlier, several conventions will be adopted throughout the remainder of this section. The first is that the molecular

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* This corrects an error in an earlier publication[6] in which ξ was omitted from this relationship

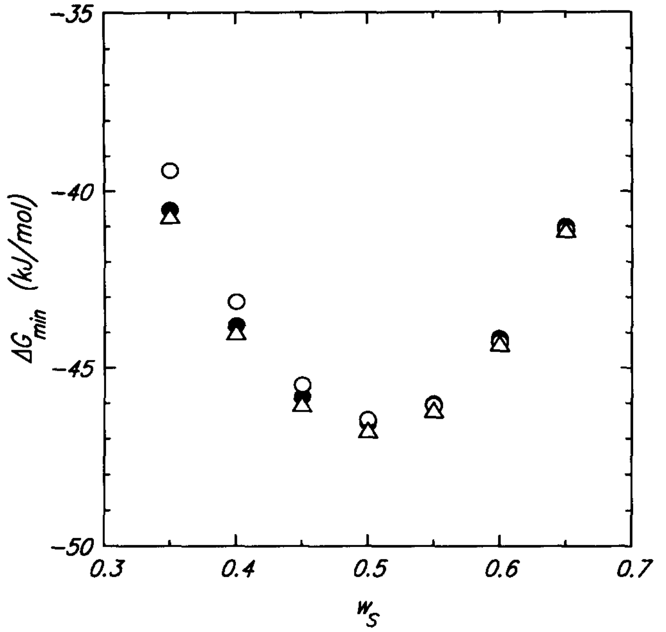

Figure 2 Functional relationship of $\Delta G_{min}(w_S)$ over the composition range $0.35 \leqslant w_S \leqslant 0.65$, which corresponds approximately to the lamellar morphology. Predictions from case 1 (○), case 2 (●) and case 3 (△) are of similar magnitude, with the greatest variation indicating that $\Delta G_{min}^{(3)} < \Delta G_{min}^{(2)} < \Delta G_{min}^{(1)}$ at low w_S. The molecular weight (M) is 10^5 g mol^{-1}, and the absolute temperature is 298 K

weight is held constant at 10^5 g mol^{-1}. The second is that the symbol definitions provided in the caption of *Figure 2* will be retained in all of the subsequent figures.

Since the system energetics of block copolymers are strongly dependent on material characteristics, we begin the model predictions with $\Delta G_{min}(w_S)$, where w_S $(= 1 - w_B)$ is the weight-fraction composition of the S block and is restricted to the range $0.35 \leqslant w_S \leqslant 0.65$ for the lamellar morphology. This functional relationship is provided in *Figure 2*. Two features are immediately apparent from this figure: (1) ΔG_{min} is negative over the entire specified composition spectrum, indicating that a microphase-separated state is thermodynamically favoured in copolymers possessing these material characteristics; and (2) ΔG_{min} reaches a global minimum near the equimolar composition, which suggests that this composition constitutes the most energetically favoured state (in agreement with other theoretical predictions[6,8]). There is little deviation among the predictions for ΔG_{min} obtained from the three model cases, especially when $w_S \geqslant 0.5$. However, for $w_S < 0.5$, $\Delta G_{min}^{(3)} < \Delta G_{min}^{(2)} < \Delta G_{min}^{(1)}$, where the superscripts again refer to the case number. According to this observation, the theoretical formalism of case 3 yields the lowest free-energy minima, implying that the two blocks deform in an independent fashion (described earlier).

Before the block expansion coefficients are presented, it is useful to examine first the function α_B/α_S *versus* w_B/w_S. In case 1, this ratio is directly obtained from equation (19), which can be rearranged to yield:

$$\ln(\alpha_B/\alpha_S) = \ln \xi + \tfrac{1}{2}\ln(w_B/w_S) \qquad (26)$$

where M_k ($k =$ S or B) in equation (19) is replaced by $w_k M$, and M is the molecular weight of the copolymer molecule. By plotting α_B/α_S *versus* w_B/w_S on double-logarithmic axes, the slope of the resulting straight line for case 1 should clearly be 1/2. This result is confirmed in *Figure 3*. Predictions acquired from cases 2 and 3 are less sensitive to w_B/w_S, with case 2 values being the least dependent on composition. The slope of $\ln(\alpha_B/\alpha_S)$ *versus* $\ln(w_B/w_S)$ is found to be about 0.14 for case 3 predictions. One interesting feature of *Figure 3* is that values obtained from case 3 agree more closely with those from case 2 at low w_S and with case 1 values at high w_S; this trend appears in subsequent functional relationships as well.

Detailed presentation of the block expansion coefficients (α_k) is facilitated here by defining the deviation from random behaviour ($\delta\alpha_k$) as:

$$\delta\alpha_k = \frac{\langle r_k^2\rangle^{1/2} - \langle r_k^2\rangle_0^{1/2}}{\langle r_k^2\rangle_0^{1/2}} = \alpha_k - 1 \qquad (27)$$

The functional relationships of $\delta\alpha_S(w_S)$ and $\delta\alpha_B(w_S)$ are depicted in *Figures 4a* and *4b*, respectively. It is of interest to note that predicted $\delta\alpha_S^{(1)}$ in *Figure 4a* are seen to exhibit negative deviation from random behaviour (i.e. $\delta\alpha_S < 0$) at low w_S, but positive deviation over most of the composition range. Both $\delta\alpha_S^{(2)}$ and $\delta\alpha_S^{(3)}$ are positive, indicating that the S block is predicted to be expanded along the lamellar normal over the entire range $0.35 \leqslant w_S \leqslant 0.65$, with the mean value ($\langle\delta\alpha_S\rangle$) equal to approximately $+0.18$. *Figure 4b* demonstrates that the B block behaves in a similar, but opposite, fashion as the S block. That is, whereas the S block tends to deviate positively from random behaviour, the B block appears to prefer a contracted configuration, with $\delta\alpha_B < 0$. In fact, only case 1 predicts that $\delta\alpha_B > 0$ at low w_S. Predictions from cases 2 and 3 show little composition dependence in $\delta\alpha_B(w_S)$, resulting in a $\langle\delta\alpha_B\rangle \approx -0.18$. Since there is no evidence that the expansion parameters should exhibit dramatic variation over the course of $0.35 \leqslant w_S \leqslant 0.65$ (as demonstrated by case 1 predictions), it appears that the predictions obtained from cases 2 and 3 are in closer agreement with *a priori* expectations. Thus, as implied from predictions of ΔG_{min}, the blocks residing outside the

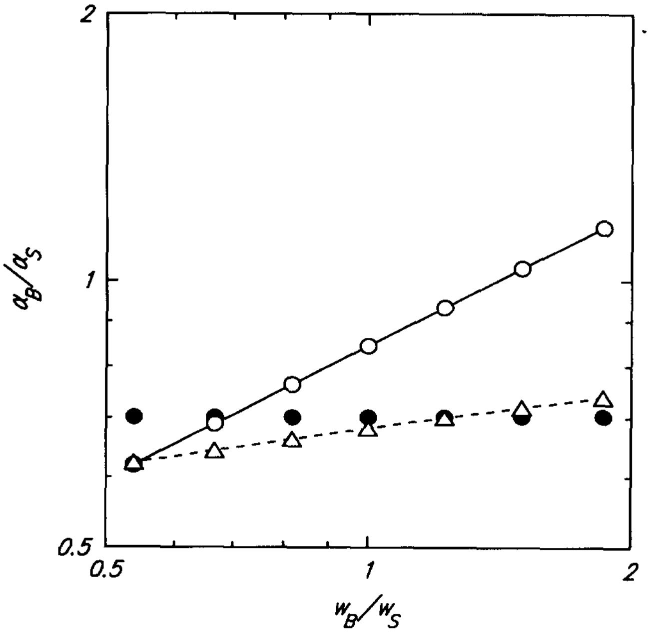

Figure 3 Double-logarithmic representation of α_B/α_S *versus* w_B/w_S predicted over the composition range $0.35 \leqslant w_S \leqslant 0.65$. Case 1 predictions (connected by the full line) obey the analytical expression given in equation (26) and possess a slope of 1/2; while case 3 values (connected by the broken line) have a slope of 0.14. Case 2 results are almost independent of w_B/w_S, remaining constant at approximately 0.7

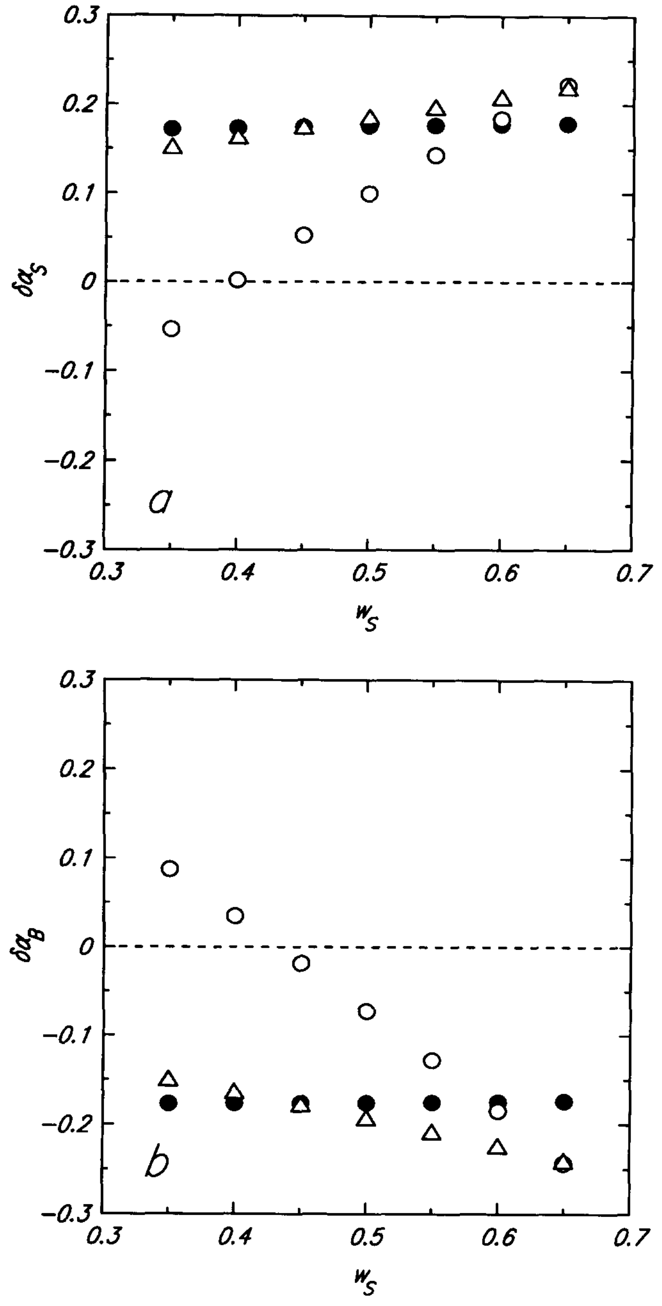

Figure 4 Deviations in the (a) S block and (b) B block expansion coefficients as functions of w_S. The broken line indicates random (Gaussian) behaviour, above which a block is predicted to be expanded and below which a block is predicted to prefer a contracted configuration. It is clear that the S block generally prefers an expanded conformation, with $\langle\delta\alpha_S\rangle \approx +0.18$, whereas the B block is generally contracted ($\langle\delta\alpha_B\rangle \approx -0.18$). Predicted $\delta\alpha_k^{(2)}$ and $\delta\alpha_k^{(3)}$ ($k = \mathrm{S}$ or B) are not strongly dependent on w_S; values of $\delta\alpha_k^{(1)}$ are sensitive to w_S and indicate random S and B block behaviour ($\delta\alpha = 0$) at $w_S = 0.40$ and 0.43, respectively

interphase region are predicted to behave as *independent* segments that are constricted to a particular region of domain space.

The predictions presented in *Figure 4* clearly demonstrate that expansion of the S block along the axis normal to the lamellae is energetically favoured, while the B block is contracted to a similar extent. (It must be borne in mind that these observations reflect the *overall*, or average, block configurations and do not address the issue of local strain along the block backbone.) Experimental observations[16] support the expanded S block along the lamellar normal in the solid state. Documented chain configurations are given in terms of the three-dimensional block radius of gyration (R_k), which may be obtained from:

$$R_k^2 = \int\int\int \rho_k(x, y, z)(x^2 + y^2 + z^2)\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \quad (28)$$

where $\rho_k(x, y, z)$ is the kth segment density expressed as a function of spatial position. Hasegawa *et al.*[16] have shown that in a microphase-separated block copolymer exhibiting a lamellar morphology, equation (28) can be rewritten as:

$$R_k^2 = 2R_{kyz}^2 + R_{kx}^2 \quad (29)$$

where the subscripts denote the coordinate axes, with the first (yz) referring to those orthogonal to the x axis in *Figure 1*. The corresponding S-block expansion coefficients, based on R_S rather than on $\langle r_S^2\rangle_0^{1/2}$, are reported to be 0.67–0.78 in the yz directions[16,20] and 1.14 in the x direction[16] of a styrene–isoprene (SI) copolymer possessing $w_S = 0.52$ and $M = 77\,600\ \mathrm{g\,mol^{-1}}$ and exhibiting lamellae. Consequently, from these data, it appears that expansion of the S blocks along the x axis, as demonstrated in *Figure 4a*, is compensated by contraction of the same blocks in the longitudinal directions (the yz plane) of the S lamellae. This implication is not readily verifiable with the present LHW theory, which only considers one-dimensional material restrictions along the lamellar normal.

The predictions for $\delta\alpha_B$ shown in *Figure 4b* also suggest that the opposite is generally true in the B lamellae; that is, the blocks are squeezed in the lateral (x) direction and are expanded along the longitudinal (yz) axes. Comparison of this predicted trend with reported data is difficult at best owing to the scarcity of relevant data available in the literature. Efforts by Bates *et al.*[17] indicate that the B blocks in an SB copolymer possessing dispersed spheres of butadiene in a continuous styrene matrix are arranged in a random (Gaussian) conformation. Miller *et al.*[18] have also shown that the soft block of a polyether–polyurethane segmented (multiblock) copolymer is extended along the lamellar normal. These data, although limited, suggest that the configuration of the soft block depends on factors such as degree of chemical dissimilarity, resultant morphology and molecular architecture. While no data have been reported regarding the configuration of the soft block in styrene–diene diblock copolymers exhibiting lamellae, the trend displayed in *Figure 4b* is certainly amenable to experimental verification.

Although theories based on two-parameter (TP) model perturbation[12,13] or on renormalization group (RG) methods[14,15] have been proposed to elucidate block configurations in diblock copolymers, it must be remembered that these models correspond to copolymers in (dilute) solution. Accordingly, parallelisms between predictions presented here and those obtained by the TP and RG models should be drawn with caution. To begin, comparisons will be made between predictions put forth here and those acquired with the TP model[12,13] only, due to the shared assumption that excluded-volume effects are negligible in the unperturbed (theta) state. In the limit of a vanishing block interaction parameter ($\zeta = 0$), the TP model predicts $\delta\alpha_S = \delta\alpha_B \approx 0.04$. It must be remembered that this apparent symmetry occurs only

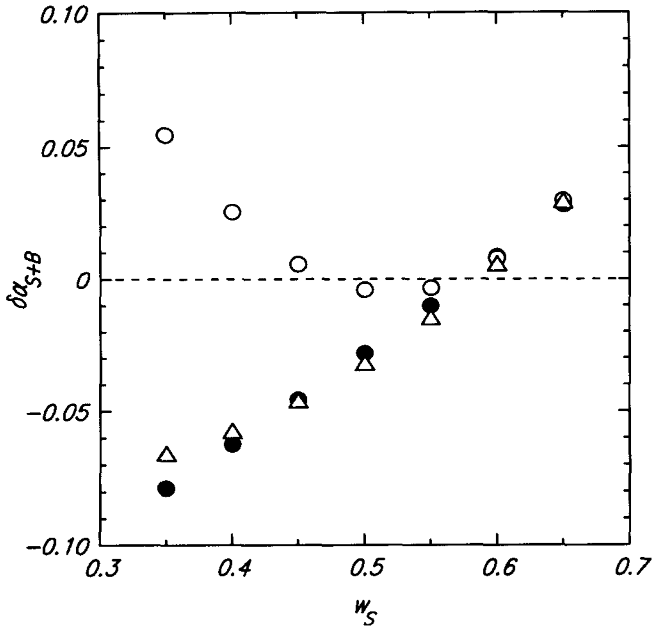

Figure 5 Deviation in the molecular expansion coefficient ($\delta\alpha_{S+B}$). Case 1 predictions demonstrate that $\delta\alpha^{(1)}_{S+B}$ oscillate around $\delta\alpha = 0$, while both $\delta\alpha^{(2)}_{S+B}$ and $\delta\alpha^{(3)}_{S+B}$ increase from negative to positive values along w_S

when the copolymer possesses a nearly equimolar composition and when $\zeta = 0$; changes in these conditions result in asymmetric $\delta\alpha_k$.

In the case when $\delta\alpha_S = \delta\alpha_B$, as predicted by the TP model above, it is apparent that the deviation in the overall molecular expansion coefficient ($\delta\alpha_{S+B}$), defined by:

$$\delta\alpha_{S+B} = \left(\frac{\sum_k \langle r_k^2 \rangle}{\sum_k \langle r_k^2 \rangle_0}\right)^{1/2} - 1 = \left(\frac{\sum_k \alpha_k^2 K_k^2 w_k}{\sum_k K_k^2 w_k}\right)^{1/2} - 1 \quad (30)$$

must always be positive. Predicted $\delta\alpha_{S+B}(w_S)$ using the LHW theory are presented in *Figure 5* and, again depending on which case is employed, $\delta\alpha_{S+B}$ can be less than *or* greater than zero. Case 1 predictions indicate a positive deviation at low w_S, which becomes negative near the equimolar composition and returns to being positive at high w_S. Both $\delta\alpha^{(2)}_{S+B}$ and $\delta\alpha^{(3)}_{S+B}$ increase monotonically from -0.08 at $w_S = 0.35$ to $+0.03$ at $w_S = 0.65$. Negative deviation in $\delta\alpha_{S+B}$, as predicted here, has been reported by Hasegawa *et al.*[16] who found that $\delta\alpha_{S+B}$ (which is defined in terms of the block radii of gyration rather than end-to-end distances) was equal to -0.08 in the same SI copolymer described earlier. Thus, the configurational behaviour of the blocks and copolymer molecules in solution, as modelled by TP and RG methods, differs significantly from that in the solid state.

Effect of molecular weight

Just as in the last section, we adopt a few conventions here to facilitate comparisons. As the molecular weight (M) is now allowed to vary, a composition is arbitrarily chosen ($w_S = 0.60$) and held constant. Secondly, in the interest of brevity, some figures will be combined in this section, thereby requiring symbols different from those used before. These new symbols, valid for *Figure 6* only, are defined in the caption of that figure.

Since application of the LHW theory to block characteristics is only valid in microphase-separated copolymers (in the strong-segregation limit), a brief description of the function $\Delta G_{\min}(M)$, which is provided in detail elsewhere[21], is worthwhile. Although this relationship is not duplicated here, suffice it to say that $\Delta G_{\min}$ is predicted to become more negative with increasing M. Thus, microphase separation becomes increasingly more thermodynamically favoured in copolymers with increasing chain length. Since computations yield $\Delta G_{\min}(M = 50\,000) = -16.5$ kJ mol^{-1} in all three model cases presented here, microphase separation is indeed preferred in copolymers with $w_S = 0.60$ from 50 000 to 500 000 g mol^{-1}, and predictions of block configurations from the LHW theory are valid over this molecular-weight range.

Values of $\delta\alpha_k$ (k = S or B), as defined by equation (27), are presented as a function of M in *Figure 6*. In all three cases, predicted $\delta\alpha_S$ are greater than zero and possess values near $+0.2$, while $\delta\alpha_B < 0$ and reach values of similar magnitude (i.e. $\delta\alpha_B \approx -0.2$). All three cases exhibit a clear dependence on M. While both $\delta\alpha^{(1)}_S$ and $\delta\alpha^{(1)}_B$ increase with M, predictions of $\delta\alpha^{(2)}_k$ and $\delta\alpha^{(3)}_k$ appear to be symmetric about $\delta\alpha = 0$ (i.e. $\delta\alpha_S \approx -\delta\alpha_B$ in cases 2 and 3 only). Although one might expect *a priori* that the blocks in a long-chain, microphase-separated copolymer would tend to behave in a fashion similar to their unperturbed homopolymer analogues, the predictions of *Figure 6* indicate otherwise; namely, that the blocks deviate from random-coil behaviour more in high-molecular-weight materials, in agreement with TP simulations[12].

The overall molecular expansion coefficient ($\delta\alpha_{S+B}$) is provided as a function of M in *Figure 7*. As expected from the behaviour of $\delta\alpha^{(1)}_S$ and $\delta\alpha^{(1)}_B$ in *Figure 6*, $\delta\alpha^{(1)}_{S+B}$ is observed to increase over the entire M range. The apparent symmetry of $\delta\alpha_k$ from cases 2 and 3 in *Figure 6* is actually biased in favour of $\delta\alpha_S$ (>0), thereby

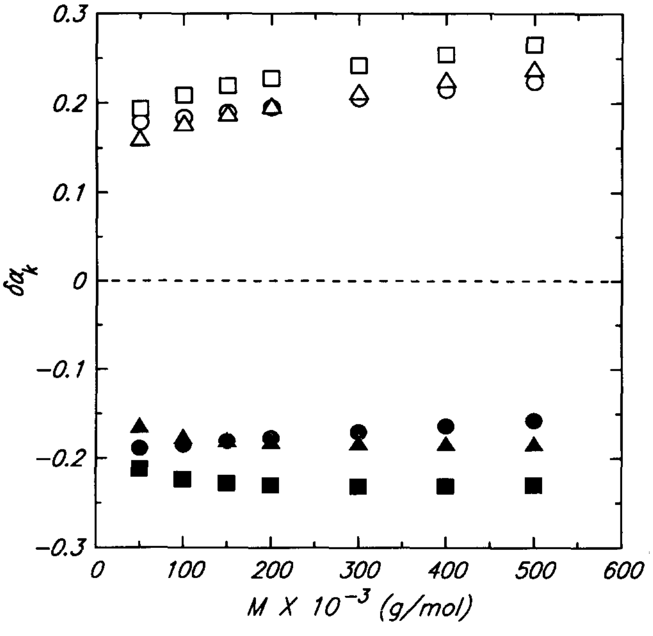

Figure 6 The functional relationship of $\delta\alpha_k(M)$ for $w_S = 0.60$ and over the range $50\,000 \leqslant M \leqslant 500\,000$, wherein $\Delta G_{\min} < 0$. Case 1 predictions are denoted by circles, case 2 by triangles and case 3 by squares. The type of block (i.e. S or B) is determined from the convention that open symbols refer to the S block and closed symbols correspond to the B block. Except for $\delta\alpha^{(1)}_B$, all predictions indicate that the extent of block deviation from random behaviour (broken line) increases with M

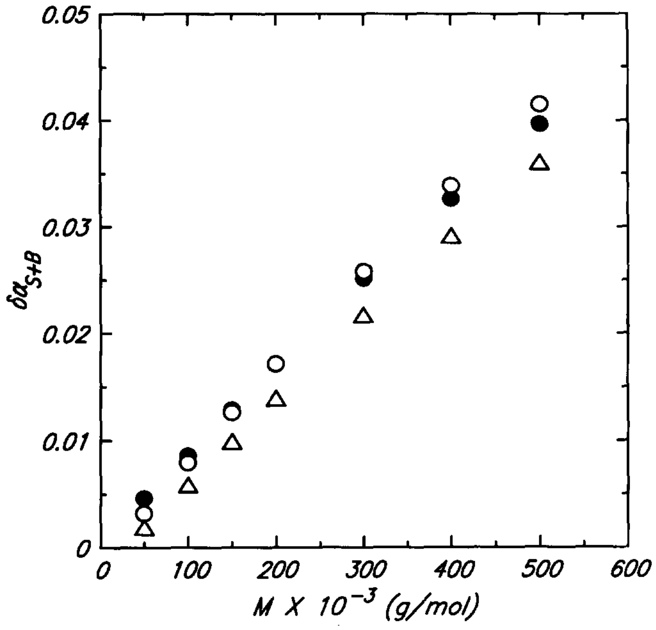

Figure 7 Plot of $\delta\alpha_{S+B}$ presented as a function of molecular weight. According to predictions from all three cases, which do not exhibit substantial variation, $\delta\alpha_{S+B}$ is seen to increase with increasing M, implying that long copolymer molecules are stretched more along the lamellar normal than short ones (of equal molar composition and molecular architecture). The symbols are the same as those described in *Figure 2*

resulting in $\delta\alpha_{S+B}$ that are also positive and increasing with M. Therefore, in all three cases, $\delta\alpha_{S+B}$ is a monotonically increasing function of M, suggesting that a long copolymer molecule is stretched more than its short-chain analogue.

CONCLUSIONS

Block configurations along the lamellar normal in microphase-separated diblock copolymers have been predicted with three model variations of the Leary–Henderson–Williams (LHW) thermodynamic theory in the strong-segregation limit. Case 1 utilizes the original theoretical formalism, based on two varying parameters and material–property relationships, one of the more crucial of which relates the expansion coefficients of the two blocks via the block lengths. In the model variations, this particular relationship is relaxed in favour of the introduction of a third varying parameter, which, although defined differently in cases 2 and 3, allows each block to assume a configuration independent of the other.

Calculated free-energy minima, almost invariant among the three cases, indicate that the model copolymers are all microphase-separated at the conditions of interest. Values of $\Delta G_{\min}$ suggest that case 3 predictions correspond to the most energetically favoured condition, which implies that the blocks residing outside the interphase behave almost independently of each other. Deviations in the expansion coefficients from random-coil behaviour have been predicted for each block and for the entire copolymer molecule as functions of molar composition and molecular weight. These deviations suggest that the S block generally prefers an expanded configuration along the lamellar normal, while the B block is generally contracted in the same direction, over the composition range $0.35 \leqslant w_S \leqslant 0.65$. According to the theory, the copolymer molecules can be either expanded or contracted, depending on w_S. If the theoretical formalisms of cases 2 and 3 come closest to representing physical reality (based on arguments presented earlier), then it appears that the molecular expansion coefficient increases monotonically with w_S. Predictions of $\delta\alpha_k(M)$ show that the blocks become increasingly removed from random behaviour as M increases, while $\delta\alpha_{S+B}(M)$ is also found to increase over the M spectrum $50\,000 \leqslant M \leqslant 500\,000$.

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