Dielectric Investigation of Bridge Fraction in Triblock/Diblock Mixed Lamella

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Introduction

Microphase-separated structure is almost indistinguishable for A−B-type diblock copolymers and A−B−A-type triblock copolymers, the latter being regarded as a head-to-head connected dimer of the former.[1−3] However, the B blocks of these copolymer chains have quite different conformations. The B block of the diblock chain has a tail-type (tethered) conformation, while the B block of the triblock chain has either a bridge-type or a loop-type conformation. The loop/bridge population ratio in the latter is expected to have significant influences on physical properties such as the relaxation modulus and mechanical toughness.[3−9] Thus, the estimation of this population ratio has been an important subject in investigation of block copolymers.

A dielectric method of this estimation was recently proposed for polystyrene−polyisoprene−polystyrene (PS−PI−PS) triblock copolymers.[8] In these copolymers, the middle PI block had the type A dipoles parallel along its backbone, and the direction of these dipoles was once inverted at the midpoint of the PI block (so that large-scale motion of this block was dielectrically detected even at $T < T_g^{PS}$).[8] The dielectric method is based on a molecular picture of a thermodynamic/kinetic similarity between the (dangling) loop and tail and a difference between the bridge and tail under the thermodynamic constraint of preserving the bulk density. For a bulk lamella system of a low-*M* PS−PI−PS copolymer prepared from slow solvent casting, the dielectric method gave an estimate of the bridge fraction, $\phi_b = 0.41$.[8] This estimate is close to the prediction of self-consistent mean-field calculation.[10,11] The dielectric method was also applied to swollen PS−PI−PS triblock copolymer networks having spherical PS domains embedded in a PI matrix solvated with *n*-tetradecane (PI-selective solvent).[9] The bridge fraction ϕ_b was found to decrease with decreasing copolymer concentration *c* (because of the unfavorable enhancement of the bridge tension with decreasing *c*), and this change of ϕ_b was well correlated with changes in the viscoelastic properties.

Although the dielectric method has a limitation due to lack of explicit consideration of knotted loops,[12−14] it gives a reasonable estimate of the bridge fraction ϕ_b for the above low-*M* PS−PI−PS copolymer systems (possibly containing just a small number of the knots[13,14]). In a well-segregated state, this fraction is essentially determined by a mixing entropy (combinatorial entropy) for distributing the middle blocks into various groups of the bridge and loop configurations and the conformational entropies of the blocks in respective groups.[11]

Concerning this thermodynamic nature of ϕ_b, we expect an interesting change in the bridge/loop distribution of the PS−PI−PS chains on blending of PS−PI−PS with its half fragment PS−PI: If the tail-type PI block of PS−PI and loop-type PI block of PS−PI−PS are thermodynamically similar (as hypothesized in the dielectric method), the blending is equivalent to addition of the loops and should shift the equilibrium distribution of the bridge-type and loop-type PS−PI−PS chains toward the bridge-rich side. This enrichment, if happens, in turn lends support to the molecular picture of the similarity between the loop and tail.

We have conducted dielectric experiments for PS−PI−PS/PS−PI lamellar blends to examine this expectation. The bridge fraction ϕ_b of the PS−PI−PS chains indeed increased on blending, as anticipated. Furthermore, this increase was close to that deduced from a self-consistent mean-field model. Details are presented in this Note.

Experimental Section

The PS−PI diblock copolymer ($M_S = 11.7 \times 10^3$, $M_I = 11.6 \times 10^3$) and PS−PI−PS triblock copolymer ($M_S = 11.7 \times 10^3$, $M_I = 23.2 \times 10^3$; dimer of PS−PI connected at the PI ends), being synthesized, purified, and characterized in the previous work,[8] were used. The PI block of PS−PI had the type A dipoles aligned in the same direction along its backbone, while the PI block of PS−PI−PS had the type A dipoles symmetrically inverted at the midpoint.

The PS−PI−PS/PS−PI blends of various PS−PI−PS weight fraction w_{SIS} (identical to the volume faction) were prepared by slow solvent casting from homogeneous toluene solutions of PS−PI−PS/PS−PI mixtures over a week at room temperature. The blend films thus obtained were thoroughly dried in a vacuum at 70 °C for a week. At this drying temperature, the PS blocks were in the glassy state. Thus, the loop/bridge population ratio in the PS−PI−PS/PS−PI films should have been essentially fixed when the microphase separation occurred during the solvent-cast process.[12−14] Since the PI blocks have fairly small M_I, the loops formed on this microphase separation in the presence of the solvent would have been in an expanded state to mainly take the dangling (unknotted) configuration.

For these blend films, dielectric measurements were conducted with a transformer bridge (1620A, QuadTech). A guarded, parallel-plate-type dielectric cell having the interelectrode gap of 0.2 mm and a vacant capacitance of 60 pF was utilized. The films of thickness ≅0.5 mm were compressed/squeezed between the electrodes in the cell to the thickness of 0.2 mm at 100 °C in a vacuum and then cooled to room temperature. This sample preparation procedure (including the magnitude of sample compression/squeezing) was similar to that adopted in the previous work.[8] Thus, our blends should have had the PS/PI lamellar structure parallel to the electrodes as similar to the structure confirmed in the previous work.[8]

The dielectric measurements were carried out at several temperatures *T* between 0 and 60 °C where the PS blocks were in the glassy state while the PI blocks were in the rubbery liquid state. The time−temperature superposition worked for the dielectric data obtained at those *T* (where the lamellar structure was frozen because of the lack of global motion of the PS blocks), and the shift factor a_T was identical to that for homo-PI. These data were reduced at a reference temperature, 40 °C.

Results and Discussion

Dielectric Data. For the PS−PI−PS/PS−PI triblock/diblock blends of various PS−PI−PS weight fraction w_{SIS}, Figure 1 shows the angular frequency (ω) dependence of the dielectric loss (ϵ'') at 40 °C. Two solid curves indicate the ϵ'' data for bulk PS−PI−PS and PS−PI

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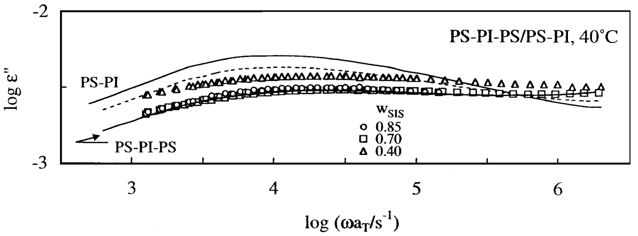

Figure 1. Dielectric loss ϵ'' of PS−PI−PS/PS−PI lamellar blends of various PS−PI−PS fraction w_{SIS} at 40 °C (symbols). The solid curves indicate the ϵ'' data of bulk PS−PI−PS and PS−PI systems, and the dotted curve shows the ϵ'' of the blend with $w_{SIS} = 0.4$ *expected* for the case of no thermodynamic interaction between the PI blocks of the triblock and diblock chains.

systems.[8] The PS/PI lamellar structure essentially parallel to the electrodes should be formed in all systems. Since the PI blocks in the PS−PI−PS system have fairly small M_I (= 23.2 × 10^3) and this system was prepared by slow solvent casting, these blocks would have hardly formed heavily knotted loops, and their motion was not significantly affected by the entanglement.

The PS block is glassy and dielectrically inert at 40 °C. Thus, the dielectric relaxation seen in Figure 1 is exclusively attributed to the global (large scale) motion of the PI blocks, as explained below. (Fast dispersion due to the segmental motion of the PI blocks emerges at high $\omega > 10^7$ s^{-1} not covered in our experiments.[14])

The PI block of the diblock copolymer has the type A dipoles without inversion. Thus, the microscopic polarization at a time t in the direction of the electric field (normal to the lamellar surface), $P_E(t)$, is proportional to the component $R_n(t)$ of the end-to-end vector of the PI block in this direction. Similarly, for the PI block of the triblock copolymer having the symmetrically inverted type A dipoles, $P_E(t)$ is proportional to $R_n'(t) = R_{n1}(t) + R_{n2}(t)$ with $R_{n1}(t)$ and $R_{n2}(t)$ being the components of two end-to-center vectors of the PI block normal to the lamellar surface. The equilibrium dielectric relaxation function $\Psi(t)$ is proportional to the autocorrelation function of $P_E(t)$ and can be written as[14−16]

$$\Psi_{SI}(t) = K\langle R_n(t)\, R_n(0)\rangle \quad \text{for diblock PS−PI} \tag{1a}$$

$$\Psi_{SIS}(t) = K\langle R_n'(t)\, R_n'(0)\rangle \quad \text{for triblock PS−PI−PS} \tag{1b}$$

Here, ⟨...⟩ indicates an average over the chains in the system, and K is a constant determined by a number density of the PI segment and the magnitude of the type A dipole per segment.[14] As noted from eq 1a, the dielectric relaxation of the PS−PI system detects the motion of the free end for the PI block tethered on the glassy PS lamella. For the dipole-inverted PI block of the PS−PI−PS triblock copolymer having both ends fixed on the PS lamella, the relaxation reflects the motion of its midpoint[17] (cf. eq 1b).

As noted in Figure 1, the bulk PS−PI and PS−PI−PS copolymers as well as their blends exhibit no terminal dielectric behavior (characterized with the proportionality $\epsilon'' \propto \omega$) in a range of $\omega > 10^3$ s^{-1} at 40 °C. For homo-PI chains having the same M as the PI blocks of these copolymers, the terminal behavior is clearly observed at those ω.[12,14] Thus, the global motion of the PI blocks (motion of the free end and/or midpoint) is significantly retarded/broadened compared to that of the homo-PI chains.

This retardation is related to the thermodynamic constraint of preserving the bulk segment density in the PI lamellar domain:[8,12,14] This constraint forces neighboring PI blocks to move in a highly cooperative way (to keep the constant segment density). Since the PI blocks have fixed ends, a given block should take significantly distorted (either flattened or stretched) conformations having small entropies to compensate a density change due to the motion of its neighbors. These cooperativity and entropic penalty naturally result in the observed retardation/broadening of the dielectric relaxation of the PI blocks.

Bridge Fraction. As seen in Figure 1, the ϵ'' value at low ω (<2 × 10^4 s^{-1}) is smaller for the bulk PS−PI−PS system than for the PS−PI system, but the slow dielectric mode distribution (observed as the shape of the ϵ'' curves at low ω) is quite similar for these systems. This dielectric similarity can be related to a similarity between the dangling loop (in the PS−PI−PS system) and tail (in the PS−PI system), as discussed previously:[8] The two-half-fragments of the loop are anchored on the same PS lamellar domain so that they always have the same end-to-end vector components $R_{n1}(t) = R_{n2}(t)$ in the direction normal to the lamellar surface (cf. eq 1b). Because of this coincidence of R_n, the loop fragments exhibit the same tension and friction and are subjected to the same entropic penalty. These tension, friction, and penalty for the loop fragment are very similar to those for a tail, suggesting the thermodynamic/kinetic similarity between the loop and tail.

In contrast, the two fragments of the bridge (in the PS−PI−PS system) anchored on the opposing PS domains do not always have the same end-to-end vector components and an increase in the entropic penalty for one fragment (due to stretching, for example) tends to be canceled by a decrease in the penalty for the other.[8] This cancellation would reduce the total penalty for the midpoint motion of the bridge-type PI block compared to that for the loop-type PI block.

The above argument leads to a molecular picture that the slow dielectric response of the PS−PI−PS system is dominated by the loops therein, and the response normalized per loop fragment is similar to the response of the tail in the PS−PI system. This picture can be formulated as a relationship between the dielectric relaxation functions $\Psi_{SIS}(t)$ and $\Psi_{SI}(t)$ of PS−PI−PS and PS−PI systems; $\Psi_{SIS}(t) = \phi_b\Psi_b(t) + \phi_l\Psi_l(t) \cong \phi_l\Psi_l(t) \cong \phi_l\Psi_{SI}(t)$ at long t where ϕ_b and ϕ_l are the bridge and loop fractions in the PS−PI−PS system and $\Psi_b(t)$ and $\Psi_l(t)$ ($\cong\Psi_{SI}(t)$) are the relaxation functions of the bridge and loop, respectively.

The above relationship is rewritten for the measured dielectric losses of the PS−PI−PS and PS−PI systems as[8]

$$\epsilon_{SIS}''(\omega) = \phi_l \epsilon_{SI}''(\omega) \quad \text{at low } \omega \tag{2}$$

An important consequence of eq 2, the coincidence of the relative dielectric mode distribution of these systems at low ω, is in accord with the experimental observation (Figure 1), and the bridge fraction estimated with eq 2, $\phi_b = 1 - [\epsilon_{SIS}''(\omega)/\epsilon_{SI}''(\omega)]_{\text{low } \omega} = 0.41$, is in close agreement with the prediction of self-consistent mean-field calculation.[11] Thus, the above argument of the similarity between the loop and tail and the difference between the bridge and tail appears to be valid for the low-M

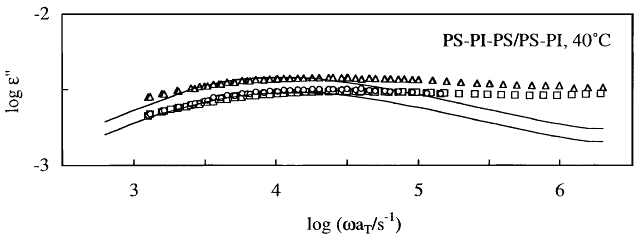

Figure 2. Comparison of the dielectric loss ϵ'' of PS−PI−PS/PS−PI lamellar blends (symbols) with the vertically shifted ϵ'' data of bulk PS−PI system (solid curves). The symbols are the same as in Figure 1.

PS−PI−PS and PS−PI systems, the former possibly containing just a small number of heavily knotted loops.

Now, we turn our attention to the PS−PI−PS/PS−PI blends. In Figure 1, the dotted curve indicates a simple average $\epsilon_{\text{ave}}'' = w_{\text{SIS}}\epsilon_{\text{SIS}}'' + (1 - w_{\text{SIS}})\epsilon_{\text{SI}}''$ for the blend with $w_{\text{SIS}} = 0.4$. If the PI blocks of the PS−PI−PS and PS−PI chains do not interact with each other and their conformation and dynamics are the same in the blend and respective bulk systems, the $\epsilon_{\text{SIS/SI}}''$ data of this blend should coincide with the ϵ_{ave}''. However, this coincidence is not observed in Figure 1. Furthermore, the $\epsilon_{\text{SIS/SI}}''$ data of the blends with $w_{\text{SIS}} \geq 0.7$ are very close to the ϵ_{SIS}'' data of bulk PS−PI−PS system. These results strongly suggest that the PS−PI−PS and PS−PI chains were mixed in lamellar domains and the PI blocks of the former thermodynamically interacted with the PI blocks of the latter to adjust their conformations (bridge/loop population ratio) when the microphase separation occurred during the sample preparation (solvent cast) process.

The argument of the similarity between the loop and tail and the difference between the bridge and tail would also apply to these blends. Then, the bridge fraction ϕ_{b} of the PS−PI−PS chains is estimated as (cf. eq 2)

$$\phi_{\text{b}} = \frac{f_{\text{b}}}{w_{\text{SIS}}}, \quad f_{\text{b}} = 1 - \left[\frac{\epsilon_{\text{SIS/SI}}''(\omega)}{\epsilon_{\text{SI}}''(\omega)}\right]_{\text{low } \omega} \tag{3}$$

Here, f_{b} is the fraction of the bridge-type chains in the whole ensemble of the PS−PI−PS and PS−PI chains where two PS−PI chains (two tails) are counted as one loop. Figure 2 examines if the blends and bulk PS−PI system exhibit the same ω dependence in their ϵ'' data at low ω as deduced from eq 3. The ϵ_{SI}'' data of the bulk PS−PI system vertically shifted by appropriate factors (solid curves) are well superposed on the $\epsilon_{\text{SIS/SI}}''$ data at low ω ($<3 \times 10^4$ s^{-1}), suggesting the validity of eq 3. Thus, we utilized eq 3 to estimate ϕ_{b} and f_{b}.

In Figure 3, the ϕ_{b} and f_{b} thus estimated are plotted against the PS−PI−PS weight fraction, w_{SIS}. f_{b} decreases just moderately with decreasing w_{SIS} to 0.4, and ϕ_{b} exhibits a corresponding increase, meaning that the bridge formation of the PS−PI−PS triblock chains is enhanced when these chains are mixed with the PS−PI diblock chains. These results are in accord with our expectation that the (dangling) loop-type PI blocks and the tail-type PI blocks are thermodynamically similar and the blending is equivalent to the addition of the loops, which in turn lends support to the dielectric method of estimating ϕ_{b} on the basis on this similarity.

Here, it is informative to examine the w_{SIS} dependencies of f_{b} and ϕ_{b} more quantitatively. For this purpose, we utilized the self-consistent mean-field model proposed by Zhulina and Halperin.[10] For the bulk triblock lamellar systems, the ZH model regards a loop-type middle block to be equivalent to two tails and formulates an average free energy per triblock chain F_{chain} under an incompressible condition. F_{chain} is given by a sum of the elastic free energy F_{el} and the mixing free energy F_{mix}. F_{el} is determined by the populations and conformational entropies of the bridge and loop/tail, while F_{mix} reflects the combinatorial number for distributing the chains in the bridge and tail/loop configurations. The bridge fraction is obtained by minimizing F_{chain}. For our PS−PI−PS/PS−PI blends, we modified this ZH model to calculate ratios of the bridge fraction in the blends to that in the bulk PS−PI−PS system, $r_{\text{f}}(w_{\text{SIS}}) = f_{\text{b}}^{\text{ZH}}(w_{\text{SIS}})/f_{\text{b}}^{\text{ZH}}(1)$ and $r_{\phi}(w_{\text{SIS}}) = \phi_{\text{b}}^{\text{ZH}}(w_{\text{SIS}})/\phi_{\text{b}}^{\text{ZH}}(1)$. Some details of the ZH model and our modification are described in Appendixes A1 and A2, respectively.

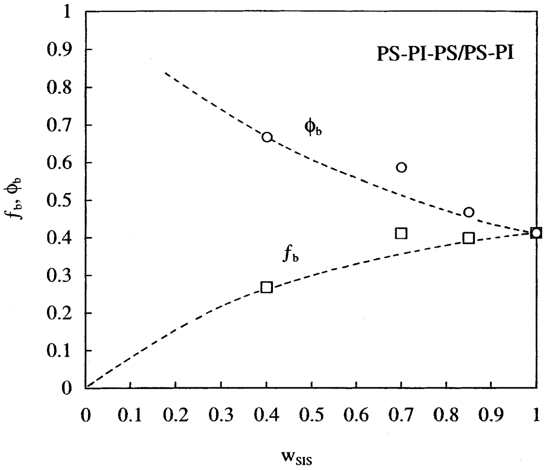

Figure 3. Plots of dielectrically estimated bridge fractions against the PS−PI−PS weight fraction w_{SIS}. The dotted curves indicate the fractions evaluated from ZH model. For further details, see text.

In Figure 3, the dotted curves indicate the bridge fractions obtained from the these ratios, $f_{\text{b}}(w_{\text{SIS}}) = r_{\text{f}}(w_{\text{SIS}})f_{\text{b,SIS}} = r_{\text{f}}(w_{\text{SIS}})\phi_{\text{b,SIS}}$ and $\phi_{\text{b}}(w_{\text{SIS}}) = r_{\phi}(w_{\text{SIS}})\phi_{\text{b,SIS}}$ with $\phi_{\text{b,SIS}}$ ($= f_{\text{b,SIS}} = 0.41$) being the dielectrically estimated bridge fraction in the bulk PS−PI−PS system. Namely, the ZH model is utilized here to calculate relative changes of the bridge fraction on blending, not the $f_{\text{b}}(w_{\text{SIS}})$ and $\phi_{\text{b}}(w_{\text{SIS}})$ values themselves. The f_{b} and ϕ_{b} data are in close agreement with the calculated f_{b} and ϕ_{b}, suggesting that the dielectrically detected changes in the bridge fraction are consistent with the changes expected from a balance of the conformational and mixing entropies of the bridge/loop/tail chains (incorporated in F_{el} and F_{mix} of the model).

In relation to this agreement, we should point out that the ZH model is formulated in the strong segregation limit under an approximation of exclusive occupancy of the central region of the lamellar domain by the bridge-type blocks. The $\phi_{\text{b,SIS}}$ calculated from the ZH model ($\phi_{\text{b,SIS}} = 0.36$ for our PS−PI−PS lamella; cf. Appendix A2) is a little different from the dielectrically estimated $\phi_{\text{b,SIS}}$ ($= 0.41$), possibly because our PS−PI−PS/PS−PI lamella is not in the strong segregation limit and the above approximation is not fully satisfied for this lamella. (Because of this moderate difference, only the ratios r_{f} and r_{ϕ} calculated from the model were utilized for the dotted curves in Figure 3.) However, the above approximation would not significantly affect the *relative* changes of ϕ_{b} calculated from the model, and the agreement seen in Figure 3 strongly suggests that the dielectrically observed changes of ϕ_b are consistent, in magnitude, with the changes expected from the balance of the conformational and mixing entropies.

For our PS−PI−PS/PS−PI lamellar blends, a complete theoretical analysis (without the above approximation of full occupancy) can be achieved by extending the self-consistent mean-field lattice calculation of Matsen and Schick.[11] This analysis is an interesting subject of future work.

Concluding Remarks

For the mixed PS−PI−PS/PS−PI lamellar blends, we have conducted dielectric measurements to estimate the bridge fraction ϕ_b for the PS−PI−PS chains therein. ϕ_b was found to increase with decreasing PS−PI−PS weight fraction w_{SIS}. This result suggests that the loop-type PI block of PS−PI−PS is thermodynamically similar to the tail-type PI block of PS−PI and the blending is equivalent to addition of loops to the bulk PS−PI−PS system. The changes of ϕ_b with w_{SIS} were consistent, in magnitude, with those expected from a balance of the conformational and mixing entropies of the bridge/loop/tail chains. These results in turn lend support to the molecular picture underlying the dielectric estimation of ϕ_b, the thermodynamic/kinetic similarity between the loop and tail and the difference between bridge and tail.

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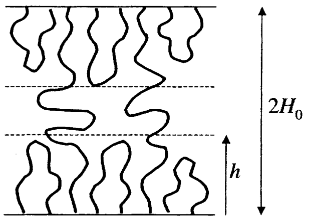
Appendix. Modification of the Zhulina−Halperin Model

Zhulina and Halperin[10] (ZH) developed a self-consistent-field model for A−B−A triblock lamellae in the strong segregation limit. Although our PS−PI−PS/PS−PI mixed lamellar blends are not in this limit, it is informative to modify the ZH model for these blends and compare the calculated bridge fraction with the dielectrically obtained estimate. The ZH model is briefly reviewed below, and then its modification is explained.

A1. ZH Model. The middle B blocks of the A−B−A triblock chains have either the bridge-type or the loop-type conformations, as schematically shown in Figure 4a. The ZH model regards the loop to be equivalent to two tails (the half fragments of the loop; cf. Figure 4b) and formulates an average free energy per middle block. The fundamental parameters of the model are the thickness of the lamellar domain $2H_0$, the number of segments per middle block $2N$ ($2N$ for the bridge and N for the tail), the segmental step length a, the lamellar surface area per block $\sigma = Na^3/H_0$, and the bridge fraction f_b in the ensemble of the bridge/loop chains. Because of the symmetry of the block conformations with respect to the midplane of the lamella, the analysis of the ZH model is made for the portion of the blocks below this midplane.

A key concept in the ZH model is the nonuniformity of the chain stretching in the direction normal to the lamellar surface: The end of the tail (corresponding to the midpoint of the loop) is distributed in a boundary region of a thickness $h < H_0$, and a stretch ratio E_t of the tail segment at a height $y \le h$ is determined by y as well as the end height y_e; see the unfilled circle shown in Figure 4b. (This stretch ratio is defined to give the local tension $3k_BTE_t/a^2$, with k_B being the Boltzmann constant.) Similarly, the bridge segment in the boundary region has a position-dependent stretch ratio E_b.

(a) bridge/loop lamella



(b) bridge/tail lamella

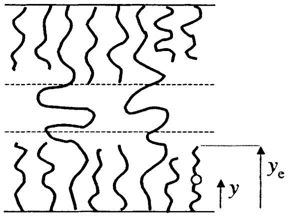


Figure 4. Schematic illustration of (a) bridge/loop mixed lamella and (b) bridge/tail mixed lamella.

The remaining, central region (with the half thickness $H_0 - h$) is filled only with the bridge segments. Among the $2N$ segments of the bridge, a fraction θ occupies this region. Equating the volumes of the central region and the occupying segments, we find an expression of θ in terms of h, H_0, and f_b:

$$\theta = \frac{1}{f_b}\left(1 - \frac{h}{H_0}\right) \tag{A1}$$

The bridge segments in the central region have a constant stretch ratio, $E_b' = (H_0 - h)/\theta N$.

Under the incompressible constraint ensuring the uniform segment density, the ZH model requires the matching of the E_b and E_b' at the border between the boundary and central regions to calculate E_b, E_t, and a distribution function of the position of the tail end $g(y_e)$. The average elastic energy F_{el} per block is calculated from these E's and g as

$$F_{el} = F_{el}^{\circ}\left[(1 - \theta f_b)^3 + \frac{12}{\pi^2}f_b^{\,2}\right] \quad \text{with } F_{el}^{\circ} = \frac{\pi^2 N a^4 k_B T}{8\sigma^2} \tag{A2}$$

Here, F_{el}° is the elastic free energy calculated for the diblock lamella ($f_b = 0$). The incompressible condition and matching requirement lead to a relationship between f_b and θ

$$f_b = \frac{1}{\theta + \left(\frac{2}{\pi}\right)\cot\left(\frac{\pi\theta}{2}\right)} \tag{A3}$$

Equations A2 and A3 give an explicit expression of F_{el} in terms of f_b.

The total free energy averaged per block chain, F_{chain}, is given by

$$F_{chain} = F_{el} + F_{mix} \tag{A4}$$

where the mixing free energy F_{mix} is written in a standard form:

$$F_{mix} = k_BT\{f_b \ln f_b + \beta(1 - f_b)\ln(1 - f_b)\} \tag{A5}$$

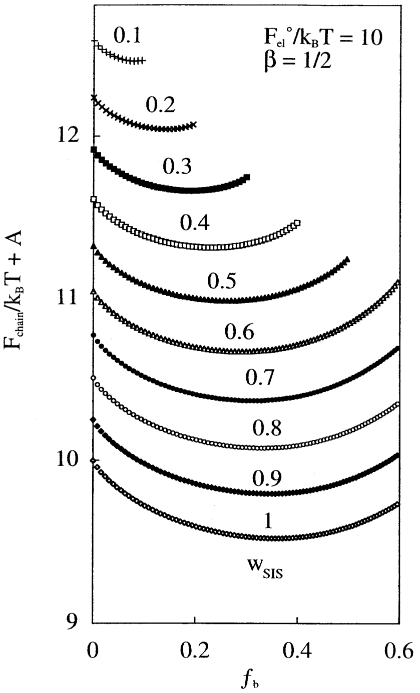


Figure 5. Normalized free energy per chain in the PS−PI−PS/PS−PI mixed lamella calculated from the ZH model. The model parameters were evaluated from structural data of bulk PS−PI−PS and PS−PI lamellae.[8] The free energy is plotted against the bridge fraction. The plots for different w_{SIS} values are vertically shifted by different factors *A* so as to avoid heavy overlapping of the plots.

Here, β is a parameter specifying a correlation of the positions of the two anchoring ends of the loop; $\beta = 1$ and $^1/_2$ for the cases of no correlation and perfect correlation, respectively, and $^1/_2 < \beta < 1$ for intermediate cases. Minimizing F_{chain} with respect to f_b, we can calculate the equilibrium bridge fraction f_b^{eq}. An example is shown later in Figure 5.

A2. Modification for PS−PI−PS/PS−PI Mixed Lamella. We consider the mixed PS−PI−PS/PS−PI lamella having the PS−PI−PS weight fraction w_{SIS}. The PI domain of this lamella contains the loop- and bridge-type PI blocks of the triblock chains and the tail-type PI blocks of the diblock chains. Within the ZH model, this mixed lamella is equivalent to the bridge/tail lamella (Figure 4b), and F_{el} is given by eqs A2 and A3 with f_b therein being redefined as the bridge fraction in the whole ensemble of the bridge, loop, and tail chains (with two tails being counted as one loop). This f_b is related to the bridge fraction for the PS−PI−PS triblock chains, ϕ_b, as

$$\phi_b = f_b/w_{SIS} \qquad \text{(A6)}$$

The mixing free energy for the mixed lamella is not given by eq A5. Considering a combinatorial number for dividing the $n_{SIS}w_{SIS}$ triblock chains (with n_{SIS} being the number of the chains in bulk triblock lamella) into $n_{SIS}f_b$ bridges and $n_{SIS}(w_{SIS} - f_b)$ loops, we find that the mixing free energy averaged per chain in the mixed lamella is written as (cf. eq A5)

$$F_{mix} = k_BT\{f_b \ln f_b + \beta(w_{SIS} - f_b)\ln(w_{SIS} - f_b)\} \qquad \text{(A7)}$$

Here, we have omitted a combinatorial term for the mixing of the triblock and diblock chains because the f_b value of our interest is not affected by this term.

The total free energy F_{chain} averaged per chain in the mixed lamella is given as a sum of F_{el} (eq A2 with f_b being redefined by eq A6) and F_{mix} (eq A7). For various w_{SIS} values, Figure 5 shows plots of a normalized free energy F_{chain}/k_BT against f_b. The correlation parameter β was set to be $^1/_2$, and the $F_{el}°$ value ($= 10k_BT$) in eq A2 was evaluated from the effective step length *a* (= 6.7 Å) of the PI block and the *N* (= 170) and σ (≅ 200 Å^2/chain) data[8] for our PS−PI−PS and PS−PI lamellae. The equilibrium $f_b^{\ eq}$ and ϕ_b^{eq} values are obtained from the f_b value giving the minimum of F_{chain}. As seen in Figure 5, f_b^{eq} gradually decreases from 0.36 to 0.08 (and ϕ_b^{eq} increases from 0.36 to 0.79 accordingly) on the decrease of w_{SIS} from 1 to 0.1. The ratios $r_f(w_{SIS}) = f_b(w_{SIS})/f_b(1)$ and $r_\phi(w_{SIS}) = \phi_b(w_{SIS})/\phi_b(1)$ evaluated from these f_b^{eq} and ϕ_b^{eq} values are utilized to obtain the dotted curves in Figure 3.

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(17) At $T < T_g^{PS}$, the global motion of the PI block of PS−PI−PS cannot be observed dielectrically in the absence of the dipole inversion in this block. The inversion serves as a label that enables us to observe the midpoint motion at $T < T_g^{PS.}$

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