

Swelling a Lamellar Diblock Copolymer with Homopolymer: Influences of Homopolymer Concentration and Molecular Weight

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ABSTRACT: The lamellar morphology in 14 binary blends of a lamellar diblock copolymer and various homopolymers was investigated as a function of homopolymer concentration and homopolymer molecular weight. The diblock copolymer was a poly(styrene-*b*-isoprene) diblock copolymer with a total molecular weight of 48 700 and a polystyrene block molecular weight of 26 600. The homopolystyrenes ranged in molecular weight from 2600 to 36 700 and were blended with the diblock copolymer up to a concentration of 24 wt %. A constant glass transition temperature for the PI microdomains established the presence of pure microdomains. Samples were characterized by small-angle X-ray scattering and transmission electron microscopy. As the homopolymer concentration increased, the PS layer thickness increased, the PI layer thickness decreased, and the area per junction increased. Increasing the homopolymer molecular weight at a fixed concentration increased the PS and PI layer thicknesses and decreased the area per junction. The symmetry of swelling in the PS layer was quantitatively evaluated by the ratio of the axial expansion to the lateral expansion. The swelling in the PS layer became dramatically asymmetric with an increase in the homopolymer concentration and/or the homopolymer molecular weight. The onset of asymmetric swelling is consistent with a proposed homopolymer concentration profile with a maximum in the center of the PS layer.

Introduction

The molecular weight dependence of the domain spacing and the chain conformations of the copolymer blocks relative to a Gaussian chain are of significant interest in diblock copolymer systems. The domain spacing, L , was theoretically determined assuming narrow interfaces between domains to scale as the two-thirds power of the diblock copolymer molecular weight.¹⁻³ This scaling law has been approximately experimentally confirmed in poly(styrene-*b*-isoprene) and poly(styrene-*b*-2-vinylpyridine) lamellar diblock copolymers,^{4,5} though another study has found a higher exponent.⁶ A scaling exponent greater than $1/2$ indicates that the chains are stretched relative to a Gaussian chain in the direction normal to the planar interface. Small-angle neutron scattering experiments have been used to investigate chain conformations of a deuterated block of the copolymer in the lateral (parallel to the interface) and axial (normal to the interface) directions.⁷⁻⁹ The polymer chain is found to be contracted laterally and extended axially as compared to a Gaussian chain. For example, in the case of a poly(styrene-*b*-isoprene) diblock copolymer having a total molecular weight of $\sim 75\,000$ and ~ 49 wt % PS, the deuterated polystyrene block is approximately 30% contracted in the lateral direction and approximately 20% extended in the axial direction.⁸

A lamellar diblock copolymer swollen by the addition of a homopolymer introduces the influence of the ho-

mopolymer molecular weight and the concentration of homopolymer in the blend. Ptaszynski et al.¹⁰ were the first to investigate the lamellar spacing and layer thicknesses of binary blends of a lamellar poly(styrene-*b*-isoprene) diblock copolymer, having a total molecular weight of $\sim 90\,000$ with ~ 44 wt % PS, swollen with up to 30 wt % homopolystyrene (hPS). The lamellar spacing and the PS layer thickness were found to increase with an increase in the hPS concentration for a homopolystyrene with a molecular weight about one-quarter that of the PS block of the copolymer. The PI layer thickness was found to decrease with an increase in the hPS concentration. Hashimoto et al.¹¹ recently studied the homopolymer molecular weight dependence of the lamellar morphology in blends at a single homopolymer concentration containing homopolystyrene and poly(styrene-*b*-isoprene) diblock copolymer with a total molecular weight of 31 600 and 48 wt % PS. Blends of 20 wt % homopolystyrene exhibited an increase in the lamellar spacing, the PS layer thickness, and the PI layer thickness as the homopolymer molecular weight was increased from 2300 to 16 700. In addition, the homopolymers were suggested to segregate more toward the center of the PS microdomains as the homopolymer molecular weight increases.^{11,12}

The present study is a part of an extensive investigation concerning the incorporation of homopolymers into diblock copolymers.¹³ In this paper we concern ourselves with the special case where the blend remains lamellar. The lamellar spacings of the neat poly(styrene-*b*-isoprene) diblock copolymer and the blends were measured as a function of homopolymer concentration and homopolymer molecular weight by small-angle X-ray scattering. Our

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primary focus is with homopolystyrenes with molecular weights comparable to or smaller than the polystyrene block of the copolymer. Transmission electron microscopy was used to confirm the lamellar morphology of the blend. The axial changes within the morphology are deduced from the PS and PI layer thicknesses, while the lateral changes between the block copolymers are illustrated by the area per copolymer junction. Chain conformations can be inferred in a limited manner from these data. The symmetry of swelling is quantitatively evaluated by comparing the axial and lateral changes in the PS layer, that is by comparing the percent change of the PS layer thickness and the percent change of the square root of the area per junction. The homopolymer molecular weight and the homopolymer concentration in the lamellar blends both influence the symmetry of swelling. Our experimental results suggest a nonuniform hPS concentration profile in the PS layer.

Experimental Methods

Materials. The anionic polymerization of the poly(styrene-*b*-isoprene) diblock copolymer was initiated with purified *sec*-butyllithium in a benzene/cyclohexane mixture (10/90, v/v) at 30 °C using a high-vacuum technique.¹⁴ The polystyrene block (PS) was polymerized first after which an aliquot was removed for characterization. A Waters 150C size-exclusion chromatograph (SEC) calibrated with polystyrene standards was used to determine the number-average molecular weight, 26 600, and the polydispersity index, 1.02, of the PS block. Isoprene monomer was subsequently added to the reaction mixture, and the reaction was terminated with methanol. The polystyrene molar composition (44 mol %) and the polydispersity index (<1.05) of the diblock copolymer were measured with 400-MHz ¹H NMR and by SEC, respectively. The polyisoprene block (PI) has an approximate microstructure distribution of 70% *cis*-1,4, 24% *trans*-1,4, and 6% 3,4 addition as determined by NMR. The number-average molecular weight of the PI block (22 100) and the PS weight percent (55 wt %) were calculated from the PS block molecular weight and the molar composition. The diblock copolymer is denoted as SI27/22 where the numbers refer to the molecular weights of polystyrene and polyisoprene blocks given in kilograms per mole.

The homopolystyrenes (hPS) were purchased from Pressure Chemical Co. The homopolystyrenes have the following number-average molecular weights and polydispersity indices (in parentheses) as determined by SEC: 2600 (1.11), 5900 (1.08), 14 000 (1.02), 36 700 (1.02). The homopolystyrenes are designated by their approximate molecular weight (in kg/mol) followed by hPS: 2.6 hPS, 6 hPS, 14 hPS, and 37 hPS. Prior to use the polystyrene homopolymers were treated at 160 °C under vacuum for 30 min to remove residual solvent, styrene monomer, dimers, and oligomers.

Blend Preparation. The casting protocol for blend preparation was designed to reproducibly prepare bulk binary blends at thermodynamic equilibrium characteristic of the annealing temperature, 125 °C. A 3 wt % polymer solution was first prepared in toluene (a nonselective solvent for polystyrene and polyisoprene). The solution was then placed in a glass casting dish, which has been coated with the mold release agent dichlorodimethylsilane. The solvent was slowly evaporated over a 7–10-day period at room temperature to form a ~1-mm-thick sample. The blend was further dried (2 weeks at 40 °C) and annealed (1 week at 125 °C) in a vacuum oven. The annealing procedure was more than sufficient to develop a well-ordered, equilibrium morphology in the blend.¹³ The casting dish with the sample was then removed from the oven and quenched in liquid nitrogen to end the heat treatment. Blends are identified by the homopolystyrene concentration in the blend given in weight percent and the homopolystyrene designation: 20% 14 hPS. These two parameters fully define the blend because the diblock copolymer and annealing temperature remain constant. Table I lists the 14 blends prepared for this study.

Transmission Electron Microscopy. Selected blends were imaged with transmission electron microscopy (TEM) to confirm

Table I
SAXS Results for Binary Blends of Diblock Copolymer SI27/22 and Homopolystyrene

designation	hPS in blend, wt %	Φ_{PS} ($\pm 1\%$)	L ($\pm 1\%$), Å
SI 27/22		51	387
10% 2.6 hPS	10.0	55	374
20% 2.6 hPS	19.8	60	382
10% 6 hPS	10.3	56	389
20% 6 hPS	20.0	60	397
5% 14 hPS	5.1	53	382
10% 14 hPS	10.0	55	389
15% 14 hPS	15.1	58	403
20% 14 hPS	20.0	60	422
22% 14 hPS	22.2	61	431
24% 14 hPS	24.0	62	451
5% 37 hPS	5.1	53	399
10% 37 hPS	10.0	55	399
15% 37 hPS	15.1	58	423
20% 37 hPS	20.0	60	464

that a lamellar model was appropriate for the SAXS analysis. Bulk samples were microtomed at low temperature (approximately -110 °C) using a diamond knife and a Reichert Ultracut microtome with a FC4 cryo temperature attachment. The sections, approximately 500 Å thick, were then stained with OsO₄ vapors. The sections were examined in the bright-field mode using a JEOL 100CX transmission electron microscope at 100 kV.

Differential Scanning Calorimetry. The glass transition of the PI microdomain was determined by differential scanning calorimetry (DSC). Thermal transition data were obtained with a Du Pont DSC 2910 differential scanning calorimeter. The calorimeter was calibrated with indium and was not calibrated with an additional low-temperature standard. Annealed blend samples of ~8 mg were sealed in aluminum pans. Each sample was quenched from room temperature to -120 °C and then heated at 20 °C/min to 150 °C under a dry-nitrogen purge. This procedure was performed three times on each sample, and the scans were indistinguishable. The microphase separation or the order-disorder transition temperature is certainly above the maximum temperature of the DSC scan, 150 °C, because the glass transitions were as well-defined in the second and third scans as they were in the first scan. A blend of diblock copolymer and homopolymer would be expected to have a single glass transition between the glass transitions of the two components, if the blend was in the homogeneous state. On the contrary, all the blends in this study exhibited two well-defined glass transitions attributed to the polystyrene and polyisoprene microdomains. The PS glass transitions were somewhat broader than the transitions observed for the PI microdomains. The glass transition temperatures were reported as the average inflection point of the three scans. The standard deviation was ≤ 0.5 °C for the PI glass transition temperature.

Small-Angle X-ray Scattering. The lamellar spacings of the binary blends were measured by small-angle X-ray scattering (SAXS) using Kratky slit collimation. The X-rays were generated by a sealed tube X-ray source with a copper anode using an accelerating voltage of 40 kV and a filament current of 7–10 mA. A Ni filter was used to reduce the Cu K β component and produce more monochromatic Cu K α X-rays, $\lambda = 1.542$ Å. The scattered intensities were collected by a Braun one-dimensional position-sensitive detector placed 50 cm from the sample and were corrected for wire sensitivity and parasitic scattering. The angular calibration of the SAXS system was accomplished with a duck tendon sample having a repeat distance of 640 Å and 9 orders of reflection. This calibration was repeated every 3 or 4 days while data were being collected. Desmeared scattered intensities were obtained by Vonk's scheme using a computer program originally provided by Vonk and modified by previous workers at the University of Massachusetts (Amherst).^{15–17}

Well-resolved peaks were obtained upon desmearing from which the interplanar spacings ($d_i = 1/s_i$) and order numbers (i) were obtained, where s_i is the magnitude of the scattering vector at the i th peak. Linear regression was performed by using all the observed reflections in the following equation: $d_i = m(1/i) + b$, where the y -intercept (b) is ideally zero. The lamellar spacing

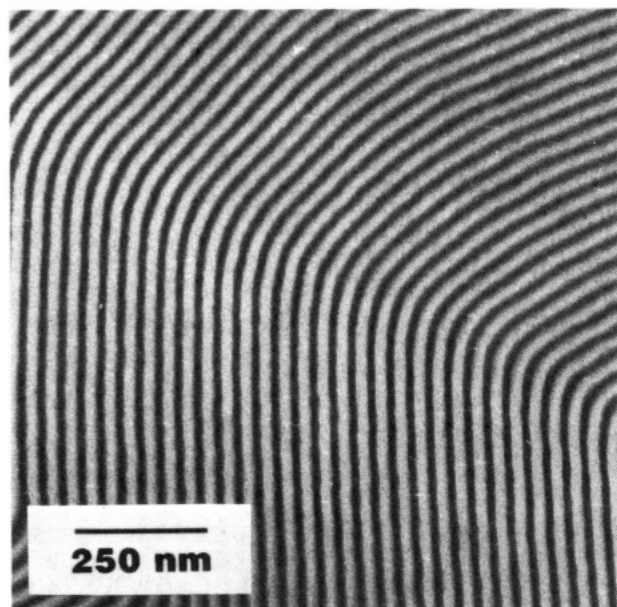


Figure 1. Transmission electron micrograph of the swollen lamellar morphology in a diblock copolymer and homopolymer blend of 10% 14 hPS.

(L) of the binary blends is defined as $m + b$. An alternative method would be to determine the lattice parameter from the first peak only. The one-peak method is less accurate, because an error of a single detector channel corresponds to a significant error in the interplanar spacing at small scattering vectors. The arrows on the desmeared scattered intensity versus scattering vector plot indicate the peak positions characteristic of the calculated lamellar spacing. Good agreement is found between the observed and the calculated peak positions. The lamellar spacing of SI27/22 was determined four times over the course of 16 months and found to vary less than 1%.

Results

All the binary blends of this study exhibit the lamellar morphology. Figure 1 shows a typical transmission electron micrograph of blend 10% 14 hPS where the dark regions indicate the osmium-stained polyisoprene domains. The lamellar morphology consists of alternating layers of polyisoprene and polystyrene. None of the blends studied exhibits separate domains of homopolystyrene or macrophase separation, thus indicating that all the homopolymers are solubilized into the microdomains. The extent of order in the lamellar morphology is comparable between the blends prepared for this study and neat, lamellar diblock copolymers.

The glass transition temperature (T_g) of the polyisoprene microdomains was used to establish the compositional uniformity of the microdomains. Figure 2 shows the differential scanning calorimetry (DSC) results for the neat diblock copolymer and four blends. The PI glass transitions of SI27/22 and the blends containing 20% hPS have the same inflection point (T_g) and breadth within experimental resolution. Specifically, the glass transition temperatures of the PI microdomains are -57 , -56 , -56 , and -56 °C for blends with 20% of 2.6 hPS, 6 hPS, 14 hPS, and 37 hPS, respectively, as compared to -56 °C for SI27/22. If homopolystyrene had mixed with the PI domain, the T_g of the PI layer would be expected to increase. For example, if the PI layer contained 5 wt % of 2.6 hPS, the Wood equation predicts a T_g increase from -56 °C for the neat diblock copolymer to -51 °C for the blend, which is a measurable difference.¹⁸ A constant T_g for the PI microdomains indicates approximately pure PI and pure PS microdomains for all the blends; essentially all the homopolystyrene resides in the PS microdomain.

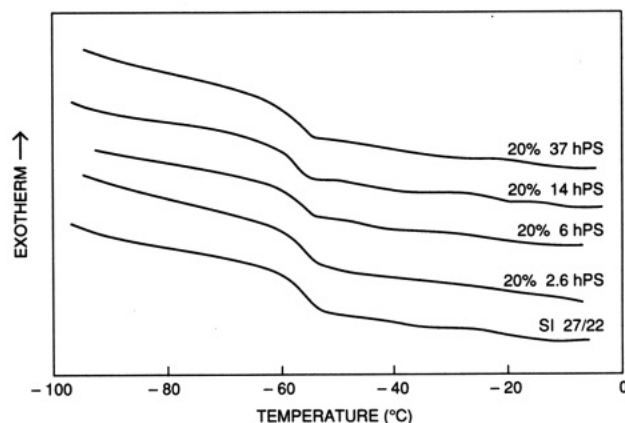


Figure 2. Differential scanning calorimetry results for the glass transition in the polyisoprene microdomain of the lamellar morphology of a neat diblock copolymer (SI27/22) and binary blends with 20% of 2.6 hPS, 6 hPS, 14 hPS, or 37 hPS.

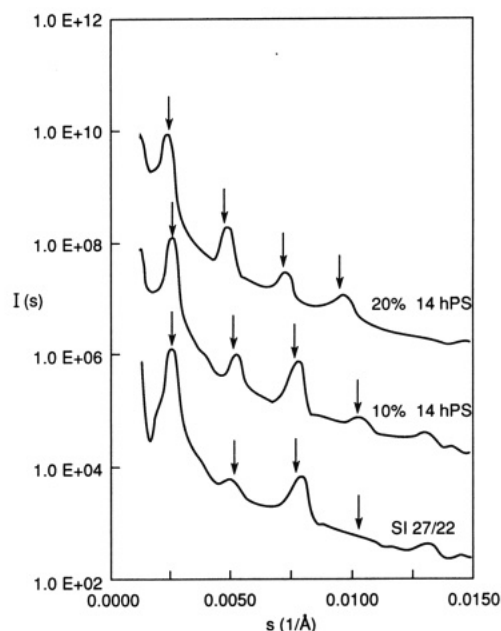


Figure 3. Desmeared small-angle X-ray scattering intensities as a function of scattering vector for SI27/22, 10% 14 hPS, and 20% 14 hPS. Peak orders of the lamellar microdomains are indicated with arrows. The intensity curves are offset vertically for legibility.

Lamellar Spacing. Lamellar spacings both larger and smaller than the neat diblock copolymer are observed in the binary blends (Table I). The lamellar spacings of SI27/22 and the binary blends were determined from desmeared small-angle X-ray scattering patterns to within an error of $\sim 1\%$. Figure 3 shows the desmeared scattered intensities as a function of the scattering vector for the blend system of 14 hPS and SI27/22 with increasing homopolymer concentration (0%, 10%, and 20%). As expected, the relative peak intensities change due to the increasing overall polystyrene composition in the blend. The even-ordered peaks are somewhat suppressed in the neat diblock copolymer, because the copolymer composition is near 50 vol % where the even-ordered interference peaks coincide with minima in the form factor scattering. Adding homopolystyrene to SI27/22 increases the compositional asymmetry producing more pronounced even-ordered reflections while weakening the odd-ordered reflections.

Increasing the homopolymer content in a blend typically causes a slight initial decrease followed by an increase in

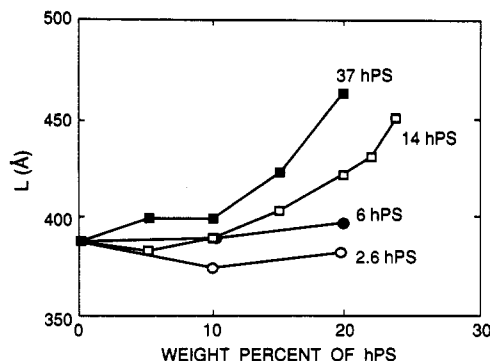


Figure 4. Lamellar spacing versus homopolymer concentration in blends of SI27/22 and various hPS. Homopolystyrene molecular weights are indicated.

the lamellar spacing (Figure 4). For example, the homopolymer concentration sequence with 14 hPS exhibits lamellar spacings of 382 (−1%), 398 (+1%), 403 (+4%), 422 (+9%), 431 (+11%), and 451 Å (+16%), as the homopolymer concentration of the blends increased from 5% to 24%. The percentages are relative to the pure diblock copolymer having $L = 387$ Å. The initial decrease in L is more pronounced and extends to larger homopolymer concentrations at lower homopolymer molecular weights. The blend with 10% 2.6 hPS displayed a lamellar spacing 3% smaller than that of SI27/22.

Previous studies with diblock copolymer/homopolymer blends have not reported a reduction in the lamellar spacing.^{10,11} However, Quan et al. do report contraction of the lamellar spacing in a triblock copolymer/homopolymer blend when 20 wt % of low molecular weight homopolymer was added to the midblock.^{19,20} In their case, as in ours, low molecular weight homopolymer is necessary to reduce the lamellar spacing relative to the neat block copolymer. Though the homopolymers used by Ptaszynski et al. and Hashimoto et al. were of sufficiently low molecular weight, the homopolymer concentrations employed were apparently too large to observe any lamellar contraction.

Increasing the homopolymer molecular weight (M_{hPS}) increases L at a fixed homopolystyrene concentration (see Figure 4). At 20% hPS, the lamellar spacing is 382 Å (−1%) for 2.6 hPS and 464 Å (+20%) for 37 hPS. If a simple power law expression is derived over the entire homopolymer molecular weight range, one finds $L \sim M_{hPS}^{0.02}$ at 10% hPS and $L \sim M_{hPS}^{0.07}$ at 20% hPS. The very weak homopolymer molecular weight dependence increases significantly as the homopolymer concentration increases from 10% to 20%. Such a universal molecular weight power law dependence is not appropriate for the lamellar spacing, because the resultant lamellar spacing is a combination of opposing responses in the PS and PI lamellar layers. The next section separates the influence of the homopolymer on the PS and PI layers for better understanding.

Layer Thicknesses and Interfacial Area per Copolymer Junction. The individual layer thicknesses and the average interfacial area per copolymer junction on the PS-PI interface are straightforward to calculate from the lamellar spacing and the overall blend composition assuming pure phases with zero interfacial thickness. Our DSC results indicate that the homopolystyrene has not penetrated the polyisoprene block; thus, the two microdomains are essentially pure as discussed above. Interfaces in neat SI diblock copolymers are known to be narrow (~20 Å) via X-ray scattering results in well-segregated samples.⁴ Justification for the assumptions of pure phases

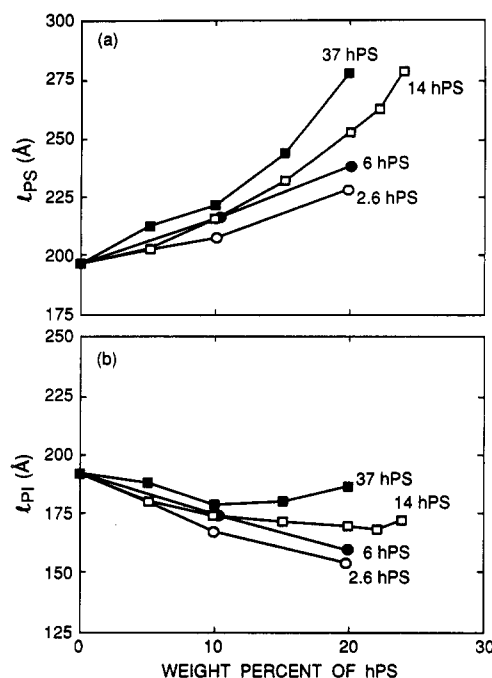


Figure 5. Polystyrene layer thickness (a) and polyisoprene layer thickness (b) versus homopolymer concentration in blends of SI27/22 and various molecular weight homopolystyrenes.

and narrow interfaces also comes from the work of Hashimoto et al.¹¹ with similar polymer blends. They found good agreement between the PS layer thickness calculated from a one-dimensional paracrystal analysis of SAXS data and the volumetric calculation which assumed pure phases.

The overall polystyrene volume fraction, Φ_{PS} , includes the polystyrene from the homopolymer and the block of the copolymer; see Table I. The homopolymer concentration in the blend, the composition of the copolymer, and the polymer densities are used to calculate Φ_{PS} . The densities used are characteristic of 125 °C, the annealing temperature, as determined by Dr. D. Walsh using pressure-volume-temperature measurements: $\rho_{PS} = 0.999$ g/cm³ and $\rho_{PI} = 0.856$ g/cm³.²¹ Note that if room temperature densities were used ($\rho_{PS} = 1.033$ g/cm³, $\rho_{PI} = 0.903$ g/cm³) the overall PS volume fraction only changes by less than 0.5 vol % PS. The polystyrene layer thickness (l_{PS}) and the polyisoprene layer thickness (l_{PI}) are given by

$$l_{PS} = \Phi_{PS}L \quad (1)$$

$$l_{PI} = L - l_{PS} = (1 - \Phi_{PS})L \quad (2)$$

The average area per junction (σ_j) on the PS-PI interface is given by

$$\sigma_j = \frac{2M_{PI}}{N_{Av}\rho_{PI}(1 - \Phi_{PS})L} \quad (3)$$

where M_{PI} is the molecular weight of the PI block and N_{Av} is Avogadro's number. These three values (l_{PS} , l_{PI} , σ_j) provide a measure of the morphological size changes of the system as homopolymer content and homopolymer molecular weight are varied. The layer thicknesses are a measure of the axial changes perpendicular to the PS-PI interface, whereas the area per junction is a measure of the lateral changes parallel to the PS-PI interface. The errors associated with Φ_{PS} and L result in an error of less than ~3% for the layer thicknesses and area per junction.

Figure 5 shows the axial changes in the PS and PI layers

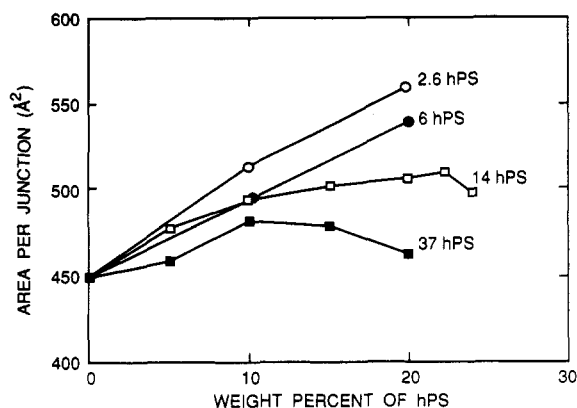


Figure 6. Area per copolymer junction versus homopolymer concentration in blends of SI27/22 and hPS for various homopolystyrene molecular weights.

as a function of homopolymer content in the blend for various molecular weight homopolymers. The PS layer thickness increases with the addition of homopolymer while the PI layer thickness decreases relative to the neat diblock copolymer. The overall lamellar spacing is a combination of an axial expansion in the PS layer and an axial contraction in the PI layer of the binary blends. This indicates the inappropriateness of a molecular weight power law to describe the lamellar spacing in blends.

The polystyrene layer thickness increases monotonically with increasing homopolymer concentration in the blend at a fixed homopolymer molecular weight. For instance, the blends containing 14 hPS exhibit PS layer thicknesses of 203 (+4%), 216 (+10%), 232 (+18%), 253 (+29%), 264 (+35%), and 279 Å (+42%), as the homopolymer concentration increases from 5% to 24%. The percentages are relative to the PS layer thickness in the neat diblock copolymer, 196 Å. The expansion in the PS layer thickness is considerably greater for higher homopolymer molecular weights; for example, blends containing 20% homopolymer have a l_{PS} of 229 Å (+17%) with 2.6 hPS and a l_{PS} of 278 Å (+42%) with 37 hPS.

On the other hand, the polyisoprene layer thickness decreases relative to the PI layer in SI27/22 (191 Å) as the homopolymer content in the blend increases. Once again consider the example of blends with 14 hPS, which have l_{PI} values of 179 (−6%), 173 (−9%), 171 (−10%), 169 (−12%), 167 (−13%), and 172 Å (−10%) as the homopolymer concentration increases from 5% to 24%. Note that a lower bound plateau is observed in l_{PI} for the blends with 14 hPS. Decreasing the homopolymer molecular weight produces a more pronounced contraction in the PI layer thickness as the homopolymer concentration increases; i.e., l_{PI} is 169 Å (−12%) for the blend with 14 hPS as compared to 153 Å (−20%) for the blend with 2.6 hPS at a fixed homopolymer concentration of 20%. Blends with the highest molecular weight homopolymer (37 hPS) exhibit an approximately constant PI layer thickness at all compositions.

The area per copolymer junction in a binary blend is always larger than that of the pure diblock copolymer, indicating lateral expansion between the copolymer chains (Figure 6). The area per junction at fixed homopolymer concentration increases with decreasing homopolymer molecular weight: for example, blend 20% 37 hPS had a σ_j of 462 Å² (+3%), while for blend 20% 2.6 hPS σ_j was 560 Å² (+25%), where the percentages are relative to a σ_j of 449 Å² for SI27/22. The area per junction also increases with the addition of homopolymer: for example, blend 10% 2.6 hPS exhibited a σ_j of 514 Å² (+15%), which

Table II
Comparison of Axial and Lateral Expansions in the PS Layer as a Function of the Volume Percent Increase in the PS Layer and the Homopolymer Molecular Weight

hPS in blend, wt %	vol % increase	axial:lateral			
		2.6 hPS	6 hPS	14 hPS	37 hPS
5	10			4%:3%	8%:1%
10	20	5%:7%	10%:5%	10%:5%	13%:4%
15	33			18%:6%	24%:3%
20	46	17%:12%	21%:10%	29%:6%	42%:1%

increases to 560 Å² (+25%) at 20% homopolymer in the blend. The one exception to this trend is the case of the blends with 37 hPS where σ_j remains approximately constant with increasing homopolymer concentration.

Swelling in the Polystyrene Layers. The comparison of the percent axial and the percent lateral increase in the PS layer provides a useful way to clarify and describe the swelling of a lamellar diblock copolymer by a selective homopolymer as a function of the homopolymer concentration and the homopolymer molecular weight. The asymmetry of swelling in the PS layer can be dramatic. The axial and lateral dilations in the PS layer were compared to the pure diblock copolymer to investigate quantitatively the asymmetry of swelling. The axial increase in the PS layer is given by the percent change in l_{PS} relative to SI27/22: $(l_{PS} - l_{PS}^0)/l_{PS}^0$, where l_{PS}^0 is the polystyrene layer thickness in SI27/22. The lateral expansion in the PS layer is given by comparing the square root of the area per copolymer junction: $(\sigma_j^{1/2} - \sigma_j^{0,1/2})/\sigma_j^{0,1/2}$, where σ_j^0 is the area per junction in SI27/22.

The results are summarized as "percent axial expansion to percent lateral expansion" in Table II. Given a fixed diblock copolymer and temperature, the binary blend system is fully defined by the homopolymer molecular weight and the homopolymer concentration in the blend. These two parameters are the horizontal and vertical designations in the chart, respectively. The total volume percent increase in the PS layer volume has been calculated and is also included in the chart. The PS layer volume percent increase is related to the percents of axial and lateral expansion as shown for the blend of 20% 6 hPS. This blend exhibits 21% axial and 10% lateral expansion in the PS layer to give an overall volume percent increase of 46% in the PS layer: $(1.21)(1.10)^2 = 1.46$. If only axial expansion occurs in the PS layer, the percent of axial expansion will equal the volume percent increase in the PS layer and the percent of lateral expansion will be zero; i.e., for the blend 20% 6 hPS, the result for entirely axial expansion would be 46%:0% instead of the observed 21%:10%.

The blend system of 14 hPS and SI27/22 shows symmetric swelling (4%:3%) at 5% hPS, asymmetric swelling (10%:5%) at 10% hPS, and significantly asymmetric swelling (29%:6%) at 20% hPS. The homopolymer induced swelling favors expansion in the axial direction as the lateral expansion appears to reach a limit of approximately 6% as the hPS concentration increases in blends of 14 hPS and SI27/22. Blends with lower molecular weight homopolymers exhibit the transition from symmetric to asymmetric swelling at higher homopolymer content. The PS layers in blends containing 2.6 hPS were swollen approximately symmetrically at 10% homopolymer (5%:7%) and became only slightly asymmetric at 20% homopolymer (17%:12%). A pronounced molecular weight dependence of the swelling asymmetry was observed in the blends with 20% homopolymer: 17%:12% with 2.6 hPS, 21%:10% with 6 hPS, 29%:6% with 14 hPS, and 42%:1% with 37 hPS. The 46 vol % increase

in the PS layer of the blend with 20% 37 hPS was almost entirely compensated for by axial swelling as indicated by the axial and lateral expansions, 42%:1%. The asymmetric nature of swelling in the PS layer increases with an increase in the homopolymer concentration in the blend and with an increase in the homopolymer molecular weight.

Discussion

Homopolystyrene mixes with the polystyrene blocks of the SI diblock copolymer and swells the PS layer both axially and laterally as evidenced by an increase in l_{PS} and σ_j . As the PS layer expands laterally, the PI layer must also expand laterally due to the connectivity between the PS and PI blocks of the copolymer. The PI layer thickness thus decreases as the area per copolymer junction increases in order to maintain constant density within the PI microdomain. The axial contraction of the PI layer indicates a relaxation of the PI chains from the perturbed conformation of the pure diblock copolymer (axially elongated and laterally contracted) to a more Gaussian-like conformation. The addition of homopolymer to the PS block of the copolymer thus reduces the conformational free energy of the PI block. The situation in the PS layer containing the PS block and the homopolystyrene is more complicated.

We propose that the homopolystyrene is not distributed uniformly throughout the polystyrene layer and a maximum in the homopolymer concentration profile is centered in the polystyrene domain. The homopolymer concentration profiles depend on both the homopolymer molecular weight and the homopolymer concentration (Figure 7). Homopolymers readily mix with the segments of the PS blocks near the center of the PS layer. However, mixing between the homopolymer and the PS block segments near the PS-PI interfaces is restricted due to the spatial constraints of the PS block and the loss of entropy for a homopolymer near a surface. In the absence of spatial constraints on the PS blocks, the mixing between the PS blocks and hPS would be complete and uniform because the entropy of mixing is positive and the enthalpy of mixing is zero. Limited experimental and theoretical evidence supports this nonuniform homopolymer concentration profile. Small-angle neutron scattering was used to evaluate the concentration of deuterated homopolystyrene added to the PS matrix of the spherical diblock copolymer; though a detailed concentration profile was not obtained, the homopolymer was clearly not distributed evenly.²² The spatial constraints of grafted polymer chains were sufficient to produce a nonuniform solvent concentration profile near a surface as calculated by Muthukumar et al. using a self-consistent-field theory.²³ These results support the proposed nonuniform homopolystyrene distributions in the PS layer for the case of athermal mixing in AB/hA blends.

While our results support the hypothesis of asymmetric swelling in the PS layer presented recently for diblock copolymer/homopolymer blends,^{11,12} we propose a qualitatively and quantitatively different homopolymer concentration profile than Hashimoto et al. They propose homopolymer concentration profiles with slight gradients in the homopolymer concentration across the PS layer and 40–50% homopolymer at the interface when the homopolymer has a low or medium molecular weight. We propose profiles with sharper gradations in the homopolymer concentration as well as lower homopolymer concentrations at the interface for comparable homopolymer molecular weights. Shull has recently developed a self-consistent-field theory for end-adsorbed polymer chains

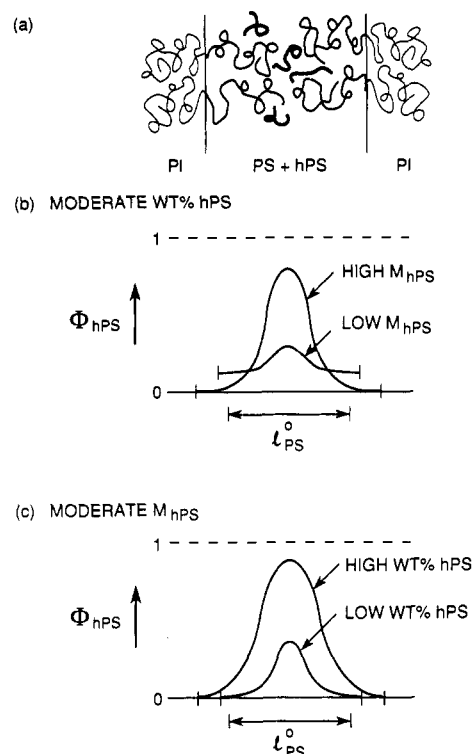


Figure 7. Schematics of the nonuniform homopolymer distribution in diblock copolymer/homopolymer blends. (a) A schematic showing the lamellar morphology with PI blocks (thin lines) and a PS microdomain containing PS blocks (medium lines) and hPS (thick lines). Note that homopolystyrene preferentially mixes with PS block segments away from the PS-PI interface. Homopolystyrene concentration (Φ_{hPS}) profiles across the PS microdomain are shown for a constant homopolymer concentration (b) and a constant homopolymer molecular weight (c). At fixed concentration, increasing the homopolymer molecular weight decreases the breadth and increases the maximum of the hPS profile. At a moderate homopolymer molecular weight, increasing the homopolymer concentration increases both the breadth and the maximum of the hPS profile. The polystyrene layer thickness of the neat diblock copolymer is indicated by l_{PS}^0 .

which has been used to develop our proposed homopolymer concentration profiles.²⁴

The PS block segments near the center of the PS layer are *preferentially* swollen due to a higher homopolymer concentration as compared to the PS block segments near the PS-PI interfaces. The chain swelling of these PS block segments in the axial direction is accommodated by separating the PS-PI interfaces, thus increasing l_{PS} . The lateral chain swelling of the PS block segments near the center of the PS layer separates the copolymer molecules, thus increasing σ_j . The increase in σ_j is also accomplished by the presence of hPS closer to the PS-PI interfaces when the homopolymer molecular weight is sufficiently low to allow hPS to penetrate toward the PS-PI interfaces. In either case, the PS block segments near the PS-PI interfaces fill the gaps at the PS-PI interfaces produced by the preferential lateral expansion of PS block segments in the middle of the PS layer. The chain segments near the copolymer junction in neat lamellar diblock copolymers are more perturbed relative to a Gaussian conformation than those in the centers of the lamellar microdomain.²⁵ These highly perturbed chain segments near the PS-PI interfaces (laterally contracted and axially elongated) assume a more Gaussian conformation to fill the gaps near the PS-PI interfaces. This chain relaxation reduces the free energy of the PS block by decreasing the conformational free energy of a portion of the PS block segments.

The penetration of homopolystyrene toward the PS-PI interfaces also reduces the system free energy by increasing the entropy of mixing. The conformational changes of the PS block induced by the presence of hPS are due to both chain swelling and chain relaxation.

The breadth of the homopolymer concentration profile decreases as the homopolymer molecular weight increases (Figure 7b). High molecular weight homopolymer chains penetrate the spatially constrained PS blocks to a lesser extent than low molecular weight chains at a fixed homopolymer concentration. Less mixing between hPS and the PS blocks of the copolymers produces less lateral expansion. For a fixed volume percent increase in the PS layer, that is, a fixed homopolymer concentration in the blend, increasing the homopolymer molecular weight reduces the extent of lateral expansion. Consequently, the axial expansion (the PS layer thickness) increases and the swelling becomes asymmetric as the hPS molecular weight increases at a fixed hPS concentration. The lower entropy of mixing between high molecular weight homopolymers and spatially constrained polymer chains produces asymmetric swelling which favors axial swelling in the PS layers.

Prior to block saturation the breadth and the maximum of the homopolymer concentration profile increase as the homopolymer concentration in the blend increases (Figure 7c). This trend indicates lateral and axial expansion. At higher homopolymer concentrations the onset of PS block saturation is not equivalent to macrophase separation, because a separate phase of hPS is not observed. At homopolymer concentrations just above the saturation limit of the PS block, the lateral swelling remains constant and any additional homopolymer is accommodated by separating the PS-PI interfaces without significantly altering the homopolymer concentration profiles near the PS-PI interfaces. The onset of macrophase separation would result in a fixed homopolymer concentration profile as excess homopolymer is expelled from the lamellar morphology. Therefore, while increasing the homopolymer concentration at a fixed homopolymer molecular weight initially increases the lateral and axial expansion, a limit to the lateral expansion eventually induces asymmetric swelling.

Conclusions

The swelling of a lamellar diblock copolymer with various homopolymers was studied as a function of both homopolymer concentration and homopolymer molecular weight. The layer thicknesses and area per junction provide insightful measures of swelling a diblock copolymer in the axial and lateral directions.

1. The PS layer thickness increases and the PI layer thickness decreases with the addition of homopolystyrene to a poly(styrene-*b*-isoprene) diblock copolymer. While the overall lamellar spacing (the sum of the two layer thicknesses) is typically greater than that of the pure diblock copolymer, blends with low homopolymer molecular weights at low homopolymer concentrations display a lamellar spacing *smaller* than that of the neat diblock copolymer.

2. The PI block exhibits chain relaxation upon the addition of homopolymer, as indicated by the decrease in the PI layer thickness and the increase in area per junction. This chain relaxation is relative to the perturbed chains found in neat diblock copolymers.

3. The PS layer swells asymmetrically as the homopolymer molecular weight increases and/or as the homopolymer concentration increases so as to favor axial expansion.

The ratio of the axial expansion to the lateral expansion in the PS layer has been introduced to describe the onset of asymmetric swelling. Increasing the homopolymer molecular weight decreases the lateral expansion due to a lower degree of penetration of the hPS into the PS blocks of the copolymer. This result is attributed to a less favorable entropy of mixing between high molecular weight homopolymers and spatially restricted polymer chains as compared to low molecular weight homopolymers. Increasing the homopolymer concentration increases the lateral expansion until the PS block is saturated, after which the addition of homopolymer induces asymmetric swelling.

4. A homopolymer concentration profile with a maximum in the center of the PS layer is proposed which is consistent with the observed nature of swelling in the PS layer. The effects of homopolymer molecular weight and homopolymer concentration on the homopolymer concentration profile are presented.

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Registry No. (PS)(PI) (block copolymer), 105729-79-1; hPS (homopolymer), 9003-53-6.