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Morphological Studies of Micelle Formation in Block Copolymer/Homopolymer Blends. Comparison with Theory

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ABSTRACT: The predictions of the Leibler, Orland, and Wheeler (LOW) theory of micelle formation in block copolymer/homopolymer blends, as modified by Roe, are compared to experimental results for a series of poly(styrene-butadiene) diblock copolymer/homopolystyrene blends. The LOW-Roe theory predicts the observed trends in spherical micelle structures as a function of copolymer concentration and the molecular weights of the homopolymer and copolymer blocks. Semiquantitative agreement between the LOW-Roe predictions and the experimental results is observed. The most notable discrepancies are as follows: (1) The theory predicts critical micelle concentrations that are 1-2 orders of magnitude less than those determined for the blends studied. (2) The theory underestimates the amount of copolymer that does not aggregate into micelles for copolymer concentrations greater than the critical micelle concentration.

Introduction

We previously presented[2] the results of a study of the spherical micellar structure in blends of poly(styrene-butadiene) diblock copolymers and low molecular weight homopolystyrene. The structure of such blends is shown schematically in Figure 1. At copolymer concentrations above the critical micelle concentration (cmc), micelles form, which consist of a core region of radius R_c, containing mostly the polybutadiene block of the copolymer, and a corona region of thickness L, comprised of polystyrene segments highly swollen with homopolystyrene. In addition, the homopolystyrene matrix surrounding the micelles contains dissolved block copolymer, while the micelle core region may contain a small amount of homopolystyrene. The structural parameters characterizing such blends (the critical micelle concentration, micelle core radius, polydispersity in the core radius, corona thickness, fraction of unaggregated copolymer, concentration of homopolymer in the micelle corona region, and amount of homopolymer in the micelle cores) were determined at a temperature range of 115 °C as a function of block copolymer concentration and the molecular weights of the homopolymer and copolymer blocks. These experimental results will be critically compared to the predictions of the Leibler, Orland, and Wheeler (LOW) theory[3] of spherical micelle formation in diblock copolymer/homopolymer blends, as extended by Roe[4] (hereafter referred to as LOW-Roe) to allow for the case of asymmetrical copolymers and the possibility of homopolymer residing in the micelle core. Whitmore and Noolandi[5] and Mayes and Olvera de la Cruz,[6] as well as Semenov,[7] have presented similar theories for spherical micelle formation in block copolymer/homopolymer blends, which are expected to yield predictions similar to that of the LOW-Roe theory.

It should be noted that the formation of nonspherical (e.g., cylindrical or lamellar) micelles has also been observed in blends of poly(styrene-butadiene) diblock copolymers and polystyrene homopolymers by Kinning, Winey, and Thomas.[8] In addition, cylindrical or lamellar micelle geometries have been predicted to occur, under certain conditions, by the theories of micelle formation presented by Mayes and Olvera de la Cruz[6] and Munch and Gast.[9] This paper, however, is concerned only with those blends exhibiting spherical micelles.

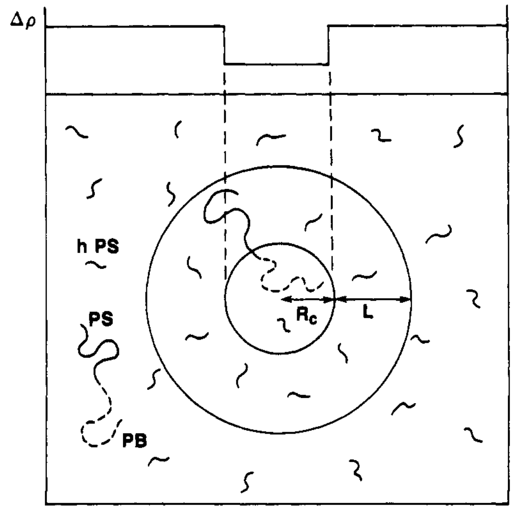

Figure 1. Scheme showing the structure of the spherical micelles in blends of poly(styrene-butadiene) diblock copolymer and polystyrene homopolymer (hPS). The micelle core radius is R_c, and the thickness of the micelle corona region is L. Also shown is the electron density profile assumed in the analysis of the experimental small-angle X-ray scattering curves.

Experimental and Theoretical Methods

The synthesis and characterization of the poly(styrene-butadiene) diblock copolymers and polystyrene homopolymers used in our studies are described elsewhere.[2] The characteristics of these block copolymers and homopolymers are listed in Tables I and II, respectively. The block copolymer/homopolymer blends were prepared by solvent casting from a 3% solution in toluene; a relatively nonpreferential solvent for polystyrene and polybutadiene. The solvent was evaporated over a period of about 1 week. The films were subsequently annealed at 115 °C (i.e., at least 20 °C above the polystyrene T_g) for 1 week. This sample preparation technique was designed to provide, as near as possible, equilibrium morphologies. The films were quenched in liquid nitrogen so that the polystyrene structure present is characteristic of the blends at 115 °C.

The experimental methods used to characterize the micellar structure included transmission electron microscopy and small-angle X-ray scattering. The SAXS data were modeled via the Percus-Yevick hard-sphere fluid approximation to obtain the interparticle interference contribution to the scattered intensity. Details of the modeling can be found elsewhere.[2,10]

The equations used in the LOW-Roe theory have been presented previously[3,4] and will not be repeated in detail here.

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Table I
Poly(styrene–butadiene) Diblock Copolymer Characteristics

sample	PS M_n	PB M_n	PS, wt %
SB 60/10	56.6	10.9	83.9
SB 40/10	42.0	10.3	80.3
SB 23/10	22.2	9.0	71.2
SB 10/10	12.0	10.0	54.7
SB 20/20	20.5	20.5	50.0
SB 40/40	41.3	45.0	48.2
SB 80/80	81.0	74.5	52.1

Table II
Polystyrene Characteristics

sample	M_n	M_z/M_w	M_w/M_n
2100 PS	2.10	1.07	1.09
3900 PS	3.90	1.05	1.08
7400 PS	7.40	1.05	1.08
17000 PS	17.0	1.04	1.05
35000 PS	34.1	1.03	1.05

Briefly, the free energy of the system is given by

$$F_M = N_m F + F_{mix} - TS_m \qquad (1)$$

where N_m is the total number of micelles in the system, F is the free energy of a single micelle, F_{mix} is the free energy of mixing homopolymers and copolymers in the bulk phase outside the micelles, and S_m is the translational entropy of the gas of micelles. The loss in entropy associated with requiring the junction between the blocks in the copolymer to be located at the interface between the core and corona regions has been neglected in the LOW–Roe theory. The free energy of a single micelle is given as

$$F = 4\pi R_c^2\gamma + F_d + F_{mA} + F_{mB} \qquad (2)$$

where γ is the interfacial tension at the boundary between and core and corona, R_c is the radius of the core, F_d is the contribution due to deformation of the copolymer chains from their Gaussian conformations, and F_{mA} and F_{mB} are the free energies of mixing the homopolymer molecules with the blocks of copolymer in the corona and core regions, respectively. For the sake of simplicity, it is assumed that the core, corona, and homopolymer matrix regions are homogeneous and that all micelles have the same dimensions. The free energy of mixing terms (F_{mix}, F_{mA}, and F_{mB}) are all of the form described by the Flory–Huggins theory, and the interfacial tension can be related to the interaction parameter, χ, by the relation

$$\gamma = (kT/a^2)(\chi/6)^{1/2} \qquad (3)$$

where a is the monomer or segment size. In the original treatment by Leibler et al.,[3] a was assumed to be the same for all polymer molecules in the blend.

Roe[4] recast the original free energy equations of the LOW theory[3] in terms of molecular volumes and root-mean-square end-to-end distances of the individual homopolymer chains and copolymer blocks, thereby avoiding the ambiguous concept of segment size and the number of segments per molecule. Roe has also replaced the interaction parameter, χ, with the interaction energy density, Λ, defined by

$$\Lambda = \chi[V_{ref}/kT]^{-1} \qquad (4)$$

where V_{ref} is taken to be an average of the volumes of the repeat units of the two polymer segments. The possibility of homopolymer mixing with the copolymer blocks in the micelle core region was introduced by Roe in his revision of the LOW theory.

At a fixed volume fraction of copolymer and temperature (i.e., a constant polystyrene–polybutadiene interaction parameter) the parameters that characterize the structure of the micellar system are (1) p, the number of copolymer chains per micelle, (2) ζ, the fraction of copolymer chains that aggregate into micelles, (3) η_A, the fraction of PS monomers in the corona that belong to copolymer chains, and (4) η_B, the fraction of the micelle core that is made up of PB monomers. The equilibrium values of p, ζ, η_A, and η_B can be found by minimizing the total free energy of the system with respect to these quantities. Roe has written a computer program (kindly provided to the authors) to perform the free energy minimizations from which the equilibrium values of p, ζ, η_A, and η_B can be obtained for a given copolymer/homopolymer blend as a function of copolymer concentration and temperature. The parameters that must be added to the program include the temperature, the volume fraction of copolymer, the molecular weights of the homopolymer and copolymer blocks, the PS and PB specific volumes as a function of temperature, the PS–PB interaction energy density as a function of temperature, and the root-mean-square end-to-end distances and molecular volumes of PS and PB chains.

The specific volume of PB as a function of temperature[11] is

$$V_{PB}\ (\text{cm}^3/\text{g}) = 1.0968 + (8.24 \times 10^{-4})T \qquad (5)$$

The specific volume of PS as a function of temperature, above its glass transition temperature, has been determined by Richardson and Savill[12] to be

$$V_{PS}\ (\text{cm}^3/\text{g}) = 0.9217 + (5.412 \times 10^{-4})T + (1.678 \times 10^{-7})T^2 \qquad (6)$$

where T is in degrees Celsius. The polystyrene–polybutadiene interaction energy density as a function of temperature has been determined by Roe and Zin[13] to have the functional form

$$\Lambda\ (\text{cal/cm}^3) = A - B(T - 150\ ^\circ\text{C}) \qquad (7)$$

where $A = 0.718 \pm 0.051$ and $B = 0.0021 \pm 0.00045$, which was obtained by averaging the values determined by cloud-point measurements of several different mixtures containing polystyrene and polybutadiene or a poly(styrene–butadiene) block or random copolymer. The compositional dependence of Λ was found to be negligible. The unperturbed root-mean-square end-to-end distances of PB and PS have the following form:[14-19]

$$\langle R^2\rangle_{0,PB}^{1/2}\ (\text{Å}) = 0.93M_{PB}^{1/2} \qquad (8)$$

$$\langle R^2\rangle_{0,PS}^{1/2}\ (\text{Å}) = 0.70M_{PS}^{1/2} \qquad (9)$$

These relations are designed to reflect the chain dimensions for the two polymers at 115 °C, the temperature for which most of the calculations were performed. However, in some instances, calculations were also performed at higher temperatures. Since $\text{d} \ln \langle R^2\rangle_0/\text{d}T$ is small[20-22] over the temperature range used, it was neglected. The molecular volumes, v_i, of the PS and PB chains are given by the relation

$$v_i\ (\text{Å}^3) = M_i\ (\text{kg/mol}) \times V_i\ (\text{cm}^3/\text{g})/0.602 \qquad (10)$$

The comparison of our results to the predictions of the LOW–Roe theory is divided into four sections. The first section examines the critical micelle concentration, the second section examines the radii of the micelle cores, the third section examines the thickness of the micelle coronae, and the last section examines the different types of phase mixing occurring (η_B and ξ), as a function of copolymer concentration and the molecular weights of the homopolymer and copolymer blocks.

Results and Discussion

I. Critical Micelle Concentration. LOW–Roe predicts that the cmc should decrease with increasing homopolystyrene molecular weight. Also, the cmc is predicted to increase with either decreasing copolymer molecular weight (for constant copolymer composition) or increasing polystyrene block length. These qualitative trends were confirmed by the results of our previous study.[2] For example, Figure 2 compares the experimentally determined (solid lines) and theoretically predicted (dashed lines) cmc values for blends containing copolymers SB 10/10, SB 40/10, and SB 20/20 as a function of homopolystyrene molecular weight (at 115 °C). Although the aforementioned qualitative trends predicted by theory are observed for the experimental data, it is immediately apparent that the LOW–Roe theory predicts cmc values

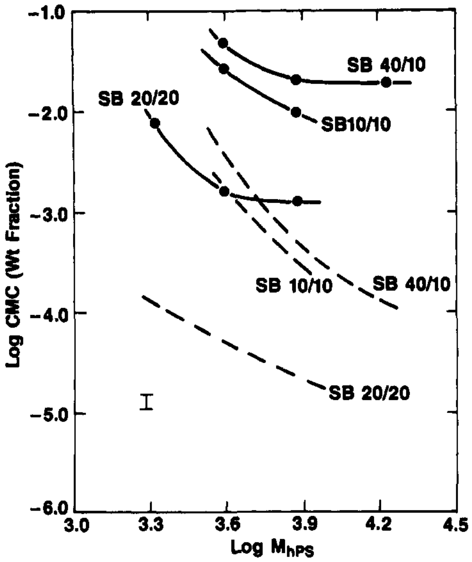

Figure 2. Comparison of experimentally determined (solid lines) and theoretically predicted (dashed lines) critical micelle concentrations at 115 °C for blends containing copolymers SB 10/10, SB 40/10, and SB 20/20, as a function of homopolystyrene molecular weight.

that are 1–2 orders of magnitude smaller than those observed. Similar comparisons were found for the other blends we studied. This discrepancy had been observed previously by Roe,[4] who compared the predictions of the LOW–Roe theory to experimental results presented by Rigby and Roe[23,24] for blends of poly(styrene–butadiene) diblock copolymer in low molecular weight polybutadiene homopolymer. One possible explanation for this discrepancy is that the values of the polystyrene–polybutadiene interaction energy densities used in both Roe's and our calculations are somewhat larger than the actual values. This would lead to lower predicted cmc values. The cmc is very sensitive to small changes in the interaction energy density. For example, decreasing the value of Λ from 0.79 to 0.72 cal/cm^3 (corresponding to an increase in temperature from 115 to 150 °C according to eq 7), which is within the error in the measurement of the interaction energy density, results in a calculated cmc of 0.8 wt % SB 20/20 in 2100 PS homopolymer (compared to a cmc value of 0.013 wt % at 115 °C). This prediction is now in agreement with the experimental observations. However, in order to correctly predict the experimental cmc values for other blends, much larger corrections to the interaction energy densities are required. For example, for blends of SB 10/10 in 7400 PS and SB 40/10 in 17000 PS, interaction energy densities of 0.61 cal/cm^3 (corresponding to a temperature of 200 °C) and 0.50 cal/cm^3 (corresponding to a temperature of 225 °C) are required. This change in the interaction energy density is well outside the error of Roe and Zin's[13] measurements. Alternatively, one or more of the other expressions used in the LOW–Roe theory for calculating the various contributions to the free energy of a single micelle (see eq 2) could be inexact. If these expressions lead to a calculated micelle free energy that is too large, the theory would predict cmc values that are too small.

II. Micelle Core Radius. It was observed in our previous work[2] that the micelle core radius increased slightly with increasing copolymer concentration. For example, in blends of SB 20/20 in 3900 PS homopolymer, the core radius increased from 128 Å at 2.66 wt % copolymer to 139 Å at 30.3 wt % copolymer. The LOW–Roe theory and Whitmore and Noolandi theories predict a relatively constant value of R_c, independent of copolymer concentration. A recent theory of micelle formation in block copolymer/homopolymer blends presented by Mayes and Olvera de la Cruz[7] predicts a very slight increase in the number of chains per micelle (i.e., R_c) as the copolymer concentration increases. The predictions of these theories are based on the assumption of a composition-independent interaction energy density between the two different polymer segments. If the PS–PB interaction energy density were to increase with an increasing concentration of polybutadiene (i.e., with increasing copolymer concentration), this could explain the slight increase in core radius observed, since a larger interaction energy would cause smaller surface to volume ratios, or larger cores, to be energetically favored. However, Roe and Zin's results[13] indicate that the compositional dependence of the interaction energy density between polybutadiene and polystyrene is negligible, within the error of their measurements.

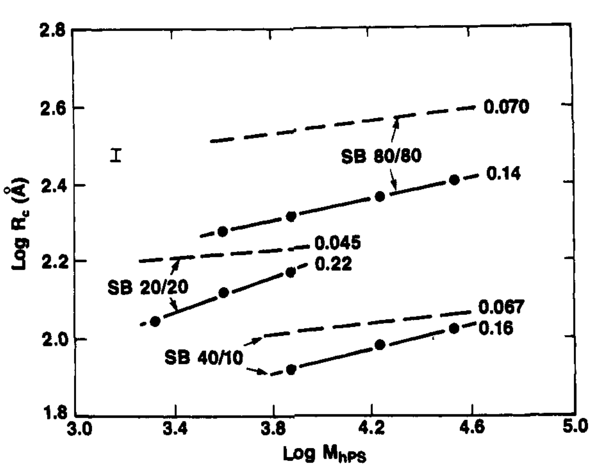

Figure 3. Comparison of experimentally determined (solid lines) and theoretically predicted (dashed lines) micelle core radii at 115 °C for blends containing copolymers SB 40/10, SB 20/20, and SB 80/80, as a function of homopolystyrene molecular weight.

The LOW–Roe theory predicts that the micelle core radius should decrease as the homopolymer molecular weight is decreased. The reasons for this trend have been discussed previously.[2,3,5] Briefly, as the ratio of homopolystyrene to PS block molecular weight decreases, the entropy of mixing effects, tending to drive the homopolymer density toward a more uniform value, increase. A more uniform value of homopolymer density can be obtained by maximizing the volume fraction of the corona region. This may be accomplished, in part, by decreasing the core radius, resulting in a larger number of smaller cores. The micelle core radii determined experimentally for blends containing copolymers SB 40/10, SB 20/20, and SB 80/80 (at 10% concentration) as a function of homopolystyrene molecular weight are compared to the predictions of the theory in Figure 3. In all cases, the experimental core radii are slightly smaller than predicted, with the difference between the predicted and experimental values decreasing with increasing homopolystyrene molecular weight. For example, in the case of copolymer SB 20/20, the experimental core radii range from 70% (2100 PS homopolymer) to 86% (7400 PS homopolymer) of the predicted value. The fact that the experimental core radii are smaller than those predicted by the theory could be due, in part, to using too high a value for the interaction energy density in the calculations. Another fact to consider is that the LOW–Roe theory neglects the entropy of localizing the block copolymer segment joints to the interface between the micelle core and corona regions. This entropy factor favors smaller core radii.

The dependence of the core radius on homopolymer molecular weight is seen to be larger than that predicted theoretically. For example, the predicted values of the scaling exponent γ ($R_c \propto M_{hPS}^{\gamma}$) are 0.067, 0.045, and 0.070, compared to the experimental values of 0.16, 0.22, and 0.14 (±0.04) for copolymers SB 40/10, SB 20/20, and SB 80/80, respectively. While the theory does not predict universal scaling laws for dependencies of core radii or corona thickness with the molecular weights of homopolymer or copolymer blocks, it nevertheless predicts fairly straight log–log plots over the limited range of molecular parameters studied. This relatively rapid increase of core radius with increasing homopolystyrene molecular weight is thought to be an equilibrium effect and not an artifact of the sample preparation technique. It has been found consistently that the spherical domains in poly(styrene–diene) diblock copolymer systems having high molecular weights and/or large polystyrene contents (i.e., factors that favor nonequilibrium structures) are smaller than those predicted by equilibrium theories of domain formation.[25-28] Therefore, it is expected that nonequilibrium effects, associated with increasing homopolystyrene molecular weight, would cause the micelle core radii to increase more slowly with increasing homopolystyrene molecular weight than predicted by theory. This is, however, opposite to what is found. In addition, the values of γ determined from our data agree fairly well with that determined by Whitmore and Noolandi[5] ($\gamma = 0.19$) from the data of Selb et al.,[29] who studied micelles in blends of poly(styrene–butadiene) diblock copolymer in low molecular weight polybutadiene homopolymer. (It should be noted, however, that the scaling exponents derived from the data of Selb et al. were determined with only two data points; therefore, there is a larger degree of uncertainty in their scaling exponents.) Evidently, the effect of homopolymer molecular weight on micelle core size (i.e., aggregation number) is appreciably greater than that predicted by the LOW–Roe theory. This may be due to inaccuracies in the expression used in calculating the deformation energies, F_d, of the copolymer segments.

The LOW–Roe theory predicts that the micelle core radius will decrease slightly as the molecular weight of the polystyrene block increases, as was previously explained. If the ratio of homopolystyrene to polystyrene block molecular weight decreases, the entropy of mixing (which drives the homopolymer density toward a more uniform value) increases. This leads to a larger number of smaller micelles. This qualitative trend was also observed in our experiments. Figure 4 shows a comparison of the micelle core radii as a function of the polystyrene block length, utilizing the data for blends of copolymers SB 10/10, SB 23/10, SB/40/10, and SB 60/10 (10 wt %) in 7400 PS homopolymer, to that predicted theoretically. Again, the experimental core radii are slightly smaller (14–27%) than predicted, with the difference increasing with increasing PS block molecular weight. In addition, the scaling exponent α ($R_c \propto M_{PS}^{\alpha}$) predicted by the LOW–Roe theory (−0.048) has a significantly smaller absolute value than that found experimentally (−0.16). A similar dependency of micelle core size on the molecular weight of the copolymer block located in the corona ($\alpha = -0.17$) was determined by Whitmore and Noolandi[5] from the data of Selb et al.[29] Therefore, the effect of the molecular weight of a block copolymer segment located in the corona region (polystyrene for our blends) on the micelle core size appears to be greater than theoretically predicted. This is in accord with the larger than predicted dependence of core radius on the ratio M_{hPS}/M_{PS} indicated previously by the data in Figure 3. This is believed to be an equilibrium effect. Again, the most likely cause for this discrepancy is the approximations used in the expressions for calculating the deformation energy.

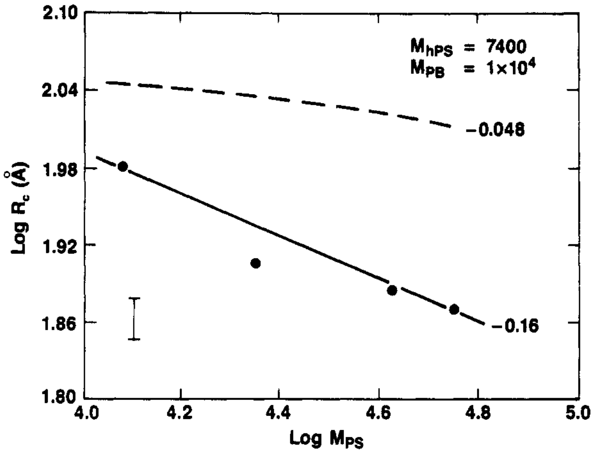

Figure 4. Comparison of experimentally determined (solid lines) and theoretically predicted (dashed line) micelle core radii at 115 °C for blends of copolymers SB 10/10, SB 23/10, SB 40/10, and SB 60/10 in 7400 PS homopolymer, as a function of polystyrene block molecular weight.

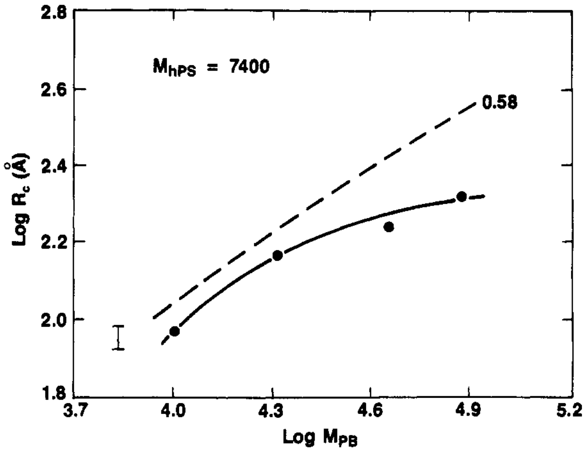

Figure 5. Comparison of experimentally determined (solid lines) and theoretically predicted (dashed line) micelle core radii at 115 °C for blends containing copolymers SB 10/10, SB 20/20, SB 40/40, and SB 80/80 in 7400 PS homopolymer, as a function of polybutadiene block molecular weight.

As would be expected the LOW–Roe theory predicts that increasing the molecular weight of the polybutadiene block will increase the core radius. Figure 5 shows a log–log plot of the core radius versus polybutadiene block molecular weight for blends containing copolymers SB 10/10, SB 20/20, SB 40/40 and SB 80/80 (at 10 wt %) in 7400 PS homopolymer. Also included in Figure 5 are the predictions of the LOW–Roe theory. Once again, the experimentally determined core radii are somewhat smaller (15–40%) than predicted. In addition, the difference is seen to increase with increasing polybutadiene (or polystyrene) block molecular weight. This is a direct result of the larger than predicted dependence of the core radius on polystyrene block molecular weight found experimentally. Figure 6 shows a log–log plot of the core radius versus polybutadiene block molecular weight for these same blends, in which the core radii have now been scaled by M_{PS}^{α} to eliminate the effect of PS block length on the core radius. The values of α used are those determined previously in Figure 4 (−0.16 for experimental data and

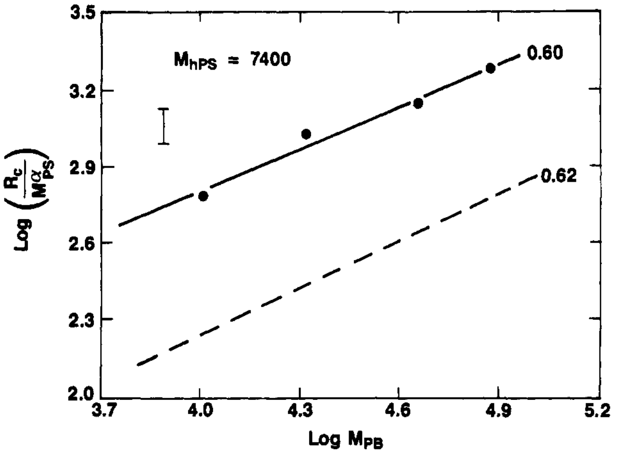

Figure 6. Comparison of experimentally determined (solid line) and theoretically predicted (dashed line) core radii at 115 °C for blends containing copolymers SB 10/10, SB 20/20, SB 40/40, and SB 80/80 in 7400 PS homopolymer, as a function of polybutadiene block molecular weight. The core radii have been scaled by M_{PS}^{α} in order to account for the effect of polystyrene block molecular weight on the core radius.

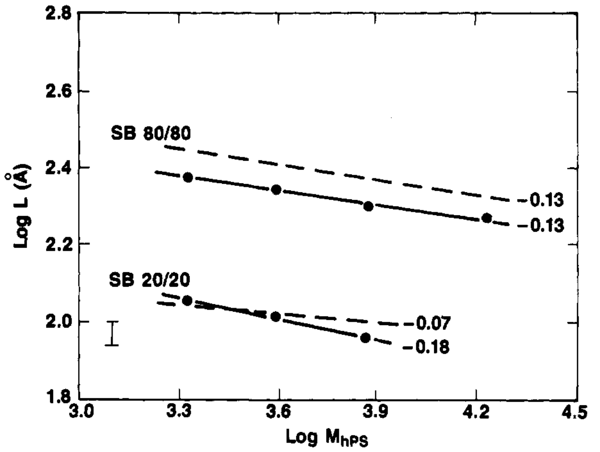

Figure 7. Comparison of experimentally determined (solid lines) and theoretically predicted (dashed lines) micelle corona thickness at 115 °C for blends containing copolymers SB 20/20 and SB 80/80, as a function of homopolystyrene molecular weight.

−0.048 for theoretical predictions). This allows the scaling exponent β ($R_c \propto M_{PB}^{\beta}$) to be determined. Values of 0.62 and 0.60 are calculated from experimental results and theoretical predictions, respectively, indicating that the predicted dependence of the core radius on the molecular weight of the copolymer block located within the core agrees quite well with the experimental findings.

III. Corona Thickness. The LOW–Roe theory predicts that as the ratio of homopolystyrene to polystyrene block molecular weight increases toward unity, the entropy of mixing homopolystyrene and polystyrene blocks in the corona region decreases. This causes less mixing of homopolymer in the corona region, resulting in a decreased corona thickness. This trend was also observed in our previous study.[2] A comparison of the experimentally and theoretically predicted effects of homopolystyrene molecular weight on the micelle corona thickness is shown in Figure 7 for blends of copolymers SB 20/20 and SB 80/80 in various molecular weight homopolystyrene matrices. In the case of blends containing SB 80/80, the theory predicts the corona thickness fairly well, with the experimental values being slightly smaller (approximately 15%) than predicted. In addition, the values of the scaling exponent ϵ ($L_c \propto M_{hPS}^{\epsilon}$) determined experimentally and theoretically are both −0.13. For blends containing SB 20/20, the experimentally and theoretically predicted values of the corona thickness also agree quite well, although the experimental data show a larger dependence of the corona thickness on homopolystyrene molecular weight than that predicted by theory. The scaling determined from the experimental data is −0.18, while that predicted by theory is −0.07. However, it must be kept in mind that there is a relatively large error in the experimentally determined value of ϵ (±0.07).

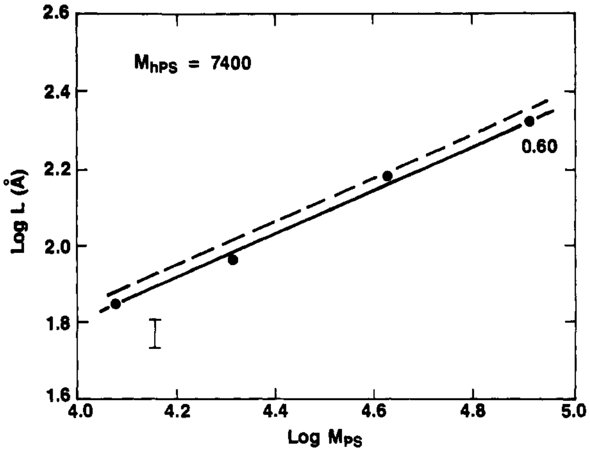

Figure 8. Comparison of experimentally determined (solid line) and theoretically predicted (dashed line) micelle corona thickness at 115 °C for blends containing copolymers SB 10/10, SB 20/20, SB 40/40, and SB 80/80 in 7400 PS, as a function of polystyrene block molecular weight.

Figure 8 shows a comparison of the experimentally and theoretically predicted corona thicknesses for blends containing copolymers SB 10/10, SB 20/20, SB 40/40, and SB 80/80 in 7400 PS homopolymer as a function of the polystyrene block length. Very good agreement is seen in both the magnitude of the corona thickness and the scaling of the corona thickness with polystyrene block molecular weight. The experimental corona thickness values are virtually identical with those predicted by the LOW–Roe theory. In addition, the scaling exponent δ ($L \propto M_{PS}^{\delta}$) is found to be 0.60 both experimentally and theoretically.

The experimentally determined volume fractions of homopolystyrene in the micelle corona for blends containing copolymer SB 80/80 (wt %) in various molecular weight homopolystyrenes are compared to the predictions of the LOW–Roe theory in Figure 9 (see ref 2 for a discussion of the method used to obtain this volume fraction experimentally). The concentration of homopolymer in the corona determined experimentally is greater than that predicted, even though the experimentally determined corona thickness is approximately the same as that predicted. This is a result of the experimental core radii (i.e., the number of copolymer chains per micelle) for SB 80/80, being appreciably smaller than that predicted by the theory. Similar comparisons are observed for other blends.

IV. Phase Mixing. In our previous study,[2] SAXS invariant analysis indicated that there was, in some cases, additional mixing of polystyrene and polybutadiene chains beyond that due to the cmc. For the blends where this additional mixing occurred, it was determined from a combination of SAXS invariant analysis and Percus–Yevick modeling of the SAXS patterns that the main type of mixing was due to having free (unaggregated) copolymer dissolved in the homopolymer matrix at a concentration in excess of the cmc. For the blends studied, it was concluded that the amount of homopolymer dissolved in the micelle core was quite small (<10%). This additional

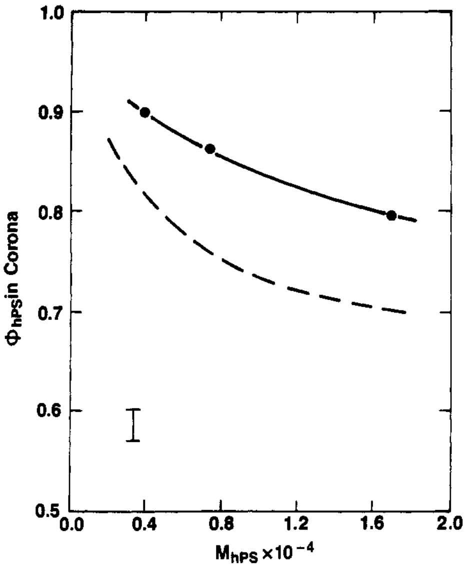

Figure 9. Comparison of experimentally determined (solid line) and theoretically predicted (dashed line) volume fraction of homopolystyrene in the micelle corona region at 115 °C for blends containing copolymer SB 80/80, as a function of homopolystyrene molecular weight.

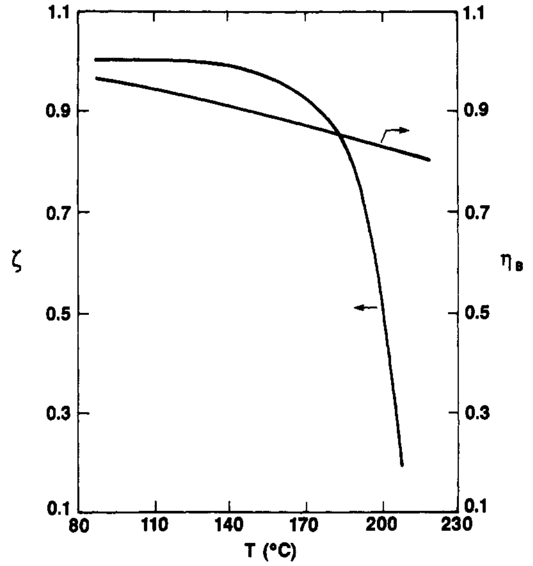

Figure 10. Theoretically predicted values of ζ (the fraction of copolymer chains that aggregate into micelles) and η_B (the fraction of the micelle core made up of polybutadiene blocks) for 12.5 wt % SB 20/20 in 2100 PS as a function of temperature.

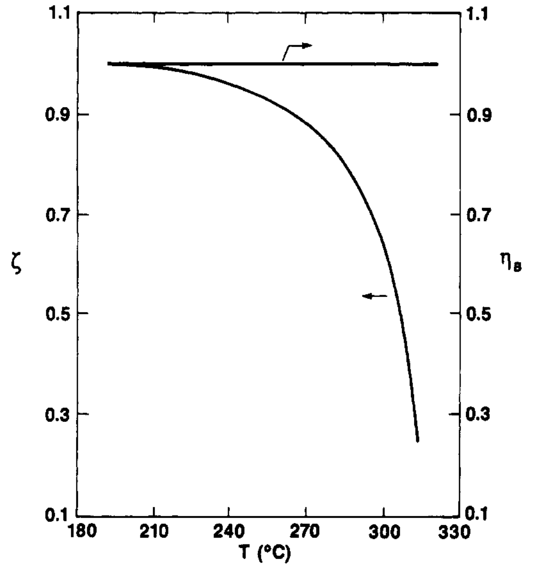

Figure 11. Theoretically predicted values of ζ (the fraction of copolymer chains that aggregate into micelles) and η_B (the fraction of the micelle core made up of polybutadiene blocks) for 17.6 wt % SB 40/10 in 17000 PS as a function of temperature.

matrix mixing was observed to be most prevalent for blends comprised of lower molecular weight homopolystyrene matrices, lower molecular weight block copolymers, or copolymers with larger polystyrene contents. For example, for a blend of SB 20/20 in 2100 PS the cmc was determined to be 0.8 wt % copolymer, while the amount of free copolymer, at 12.5 wt % total copolymer concentration, was determined to be 3.5 wt %. Blends containing copolymer SB 20/20 in higher molecular weight homopolystyrene matrices (3900 PS, 7400 PS) did not exhibit this additional mixing. However, a blend of SB 40/10 in 17000 PS exhibited a cmc of 2.0 wt % copolymer, while the amount of free copolymer, at 17.6 wt % total copolymer concentration, was determined to be 9.5 wt %.

If the cmc transition is a true first-order phase transition, then the volume fraction of free copolymer in the homopolymer matrix should be independent of the copolymer concentration for copolymer concentrations above the cmc. However, the experimental results indicate that for some blends the volume fraction of free copolymer in the homopolymer matrix can increase markedly beyond the cmc as the overall concentration of copolymer increases. This leads one to the conclusion that the cmc transition observed for these blends is not a true first-order phase transition. Therefore, phase diagrams of block copolymer/homopolymer blends such as those proposed by Roe and Zin,[30] which are based on first-order phase transitions, may not be valid in the micellar region. Indeed, Leibler et al.[3] point out that, because only finite-sized micelles occur at the cmc, the properties only exhibit rapid continuous variations through the cmc instead of discontinuous changes at a sharp transition point. The LOW–Roe theory predicts an increasing volume fraction of dissolved copolymer in the homopolymer matrix with increasing overall copolymer volume fraction, especially when the product χN is small (i.e., high temperatures or low molecular weight copolymers), when the molecular weight of the homopolystyrene is small, or when the block copolymer has a high polystyrene content. In other words, as the copolymer concentration is increased beyond the cmc, some additional copolymer chains remain free, increasing the entropy of the surrounding homogeneous solution. The theories of micelle formation presented by Whitmore and Noolandi[5] and Mayes and Olvera de la Cruz[6] also predict that, as the copolymer concentration is increased beyond the cmc, there is a gradual increase in the concentration of free copolymer in the homopolymer matrix.

It is interesting to examine the relative amounts of mixing of copolymer into the homopolymer matrix and mixing of homopolymer into the micelle cores predicted by the LOW–Roe theory. Figures 10 and 11 show the values of ζ, the fraction of copolymer chains that form micelles, and η_B, the fraction of micelle core consisting of polybutadiene blocks, predicted by the theory as a function of temperature for blends containing 12.5 wt % SB 20/20 in 2100 PS and 17.6 wt % SB 40/10 in 17000 PS, respectively. For the blend of SB 20/20 in 2100 PS, it is apparent that η_B is predicted to decrease very gradually from unity with increasing temperature, while ζ decreases quite suddenly as the temperature is increased above 170 °C. At 115 °C, the amount of copolymer dissolved in the homopolymer matrix is predicted to be virtually identical with the cmc value (0.013 wt % copolymer), giving a predicted ζ value of nearly unity. Recall that the experimental results for a blend containing 12.5 wt % SB 20/20 in 2100 PS indicated that, at 115 °C, the concentration of free copolymer was 3.5 wt %,[1] giving a value for ζ of 0.72. The theory predicts that this amount of free copolymer is not obtained until the temperature is increased to about 190 °C. Therefore, the experimentally observed structure of this blend at 115 °C corresponds to the structure predicted for a significantly higher temperature (or conversely a lower interaction energy density). This is consistent with the results of section I, which showed that the experimentally determined cmc values at 115 °C also corresponded to the predictions of a higher temperature.

For the blend of SB 40/10 in 17000 PS, the amount of homopolymer in the micelle cores is predicted to be essentially zero ($\eta_B = 1.0$) at all temperatures, while the fraction of copolymer chains forming micelles is again predicted to decrease rather abruptly as the temperature is increased above about 270 °C. The amount of homopolymer in the micelle core for this blend is predicted to be much smaller than that for the previous blend because of the higher homopolystyrene and polybutadiene block molecular weights, which causes a higher degree of incompatibility. This higher degree of incompatibility also accounts for the fact that higher temperatures must be reached before the blend of SB 40/10 in 17000 PS exhibits an abrupt increase in the fractions of unaggregated copolymer chains. At 115 °C, the theory predicts that the fraction of copolymer chains that do not aggregate into micelles is extremely small. Recall that it was determined[2] that the amount of free copolymer for a blend containing 17.6 wt % SB 40/10 in 17000 PS was 9.5 wt %. The theory predicts that this amount of free copolymer ($\zeta = 0.46$) is not obtained until the temperature is increased to about 300 °C. Once again, the experimentally determined micelle structure at 115 °C is found to correspond to a structure predicted for a much higher temperature. As discussed in section I, this discrepancy could be due to using too high a value of the interaction energy density in the calculations and/or the free energy expressions used in the theory could be inexact. At the present time it is not possible to determine which of these factors is responsible. It also might be argued that nonequilibrium structures, characteristic of a higher temperature, could somehow be frozen in during solvent casting. However, it is expected that the subsequent annealing treatment, in addition to the relatively low copolymer and homopolymer molecular weights employed, allows equilibrium structures (for 115 °C) to be obtained.

The blends shown in Figures 10 and 11 are meant to demonstrate the extremes in the predicted amount of mixing of homopolystyrene into the micelle cores for the block copolymer/homopolymer blends examined in our experimental studies. It should be noted that, even for the blends containing the lowest molecular weight homopolystyrenes studied (2100 PS), the LOW–Roe theory predicts that the type of phase mixing that should occur as the dissolution temperature is approached is predominantly an increase in the amount of free copolymer. Our experimental results indicate that, for all blends exhibiting additional mixing beyond that due to the cmc, the additional mixing is due predominantly to an increase in the amount of free copolymer above the cmc value and not due to mixing of homopolymer into the micelle cores, in agreement with the theoretical predictions. Rigby and Roe[4,23,24] concluded that, for the block copolymer/homopolymer blends they studied, the main type of mixing occurring, as the temperature was increased, was a swelling of the micelle cores with homopolymer. However, their analysis assumed that the amount of copolymer dissolved in the homopolymer matrix did not increase above the cmc as the overall copolymer concentration was increased. Our results indicate that this assumption is apparently not always valid.

Summary

In conclusion, we have found that the LOW–Roe theory qualitatively predicts all of the experimentally determined trends of spherical micelle structure, as a function of the molecular weights of the homopolymer and copolymer blocks, for blends of poly(styrene–butadiene) diblock copolymers in polystyrene homopolymer. However, quantitative agreement is not always seen. Although the theory predicts the dimensions of the micelle core and corona regions fairly well, these dimensions could have been predicted equally as well simply from the unperturbed dimensions of the copolymer blocks.[2] The most notable discrepancies between the experimental results and the predictions of the theory are the values of the cmc and the fraction of copolymer chains aggregating into micelles at the temperature of 115 °C. For example, although the qualitative dependence of the cmc on homopolymer and block molecular weights observed experimentally is correctly predicted, the theory predicts cmc values at 115 °C that are at least 1 order of magnitude smaller than those determined experimentally. In addition, for some blends the theory also underestimates the amount of free copolymer dissolved in the homopolymer matrix at overall copolymer concentrations above the cmc. In effect, the micelle structures observed experimentally at 115 °C correspond to structures predicted for significantly higher temperatures. These discrepancies could be attributed, in part, to using too high a value for the interaction energy density in the calculations. In addition, one or more of the expressions used in the LOW–Roe theory to describe the contributions to the free energy of the micellar phase could be inexact. Since the cmc and the amount of unaggregated copolymer are determined by a delicate energy balance, small inaccuracies in the model, or in the interaction energy density used in the model, could result in large errors in the model predictions.

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References and Notes

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Registry No. SB (block copolymer), 106107-54-4; PS (homopolymer), 9003-53-6.