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Small-Angle X-ray Scattering Study of Micelle Formation in Mixtures of Butadiene Homopolymer and Styrene-Butadiene Block Copolymer. 3. Comparison with Theory

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ABSTRACT: The theory of block copolymer micelle formation formulated by Leibler, Orland, and Wheeler is compared with the experimental results of Rigby and Roe obtained with mixtures of styrene-butadiene diblock copolymer and butadiene homopolymer. To facilitate the comparison, the theoretical expressions are recast in terms of the molecular volume v and the root-mean-square end-to-end distance r , thereby avoiding the use of the concept of the segment size a and the number of segments N per molecule. The calculated radii of the micelles show excellent agreement with the observed values. The theory predicts correctly the trend of change in the critical micelle concentration with the change in temperature and in the relative lengths of the styrene and butadiene blocks. The theory predicts the micelle cores to consist predominantly of styrene blocks, whereas the experimental results indicate that above a certain temperature the micelle cores become increasingly swollen with polybutadiene as the temperature is raised toward the dissolution temperature.

Introduction

In the previous two papers,^{1,2} hereafter referred to as Part 1 and Part 2, we presented the result of investigation, by small-angle X-ray scattering, of the characteristics of spherical micelles formed when small amounts of styrene-butadiene block copolymer are dissolved in polybutadiene. The parameters evaluated include the critical micelle concentration (cmc), the radius of the micelle core, and the degree of swelling of the micelle core as a function of the temperature, the concentration of the block copolymer, and the relative lengths of the two blocks in the copolymer.

Theoretical investigation of block copolymer micelle formation in the medium of homopolymer was recently carried out by Leibler, Orland, and Wheeler³ and by Noolandi and Hong.⁴ The purpose of the present paper is to compute numerical results based on the theory of Leibler et al.³ and compare them with the experimental results presented in Parts 1 and 2.

Theoretical Expressions

Before setting out to make numerical computations, we at first introduce some minor modifications to the original expressions given in the paper³ by Leibler, Orland, and Wheeler (hereafter referred to as LOW). The modifications are of two kinds. The first is introduced in order to avoid the use of the concept of a "segment", which is often defined ambiguously. The second is to allow slight modification of the physical model on which the theory is based so that the possibility of swelling of the micelle core can be investigated.

In the theories in which configurational properties of polymer chains enter into consideration, a polymer molecule is often represented by a chain of N segments, each of length a . The exact size of the length parameter a is usually undefined, and this poses no problem as far as theoretical development is concerned. In fact, it can be

shown in a general term that, when the theory deals only with bulk properties and no surface phenomena are involved, the segment a can be chosen entirely arbitrarily without affecting the numerical predictions of thermodynamic functions by the theory. When the theory includes the consideration of surface phenomena, however, the numerical results obtained depend on the precise definition of a , as the depth of the surface effect predicted is proportional to the segment size a . The customary practice is to equate a to some dimension (e.g., length or cube root of volume) of the chemical repeat unit constituting the polymer molecule. However, there is really no theoretical basis for such a choice, and, moreover, the repeat unit itself is ill-defined for some polymers (for example, polyethylene). This introduces a degree of arbitrariness into the numerical results calculated from the theory. The solution to this dilemma is found by dispensing with the use of the concept of segment size altogether and, instead, by recasting the theoretical expressions in terms of quantities that can experimentally be determined unambiguously.

We propose that the configurational properties of polymer chains be expressed not in terms of N and a but instead in terms of the molecular volume v and the root-mean-square end-to-end distance r of the polymer molecules. These two sets of parameters can be related to each other (for Gaussian chains) by

$$r^2 = Na^2 \quad (1)$$

$$v = ca^3 \quad (2)$$

where c is a geometrical constant, usually taken equal to 1.

The Flory-Huggins free energy of mixing can then be written, in the same spirit, as follows:

$$\Delta G_M = kT[(\phi_1/v_1) \ln \phi_1 + (\phi_2/v_2) \ln \phi_2] + \Lambda \phi_1 \phi_2 \quad (3)$$

where ΔG_M is per unit volume of the mixture, ϕ_1 and ϕ_2

are the volume fractions, v_1 and v_2 are the molecular volumes, and Λ is the interaction energy density between components 1 and 2. The advantage of eq 3 over the more traditional expression was pointed out previously.^{5,6} Note that the numbers of segments N_1 and N_2 in the component molecules no longer appear in (3). The interaction energy density Λ is related to the usual χ parameter by

$$\chi = \Lambda V_{\text{ref}}/kT \quad (4)$$

where the volume of reference V_{ref} is customarily taken equal to the volume of a solvent molecule (if one is involved) or some average of volumes of repeat units of the two polymers involved. Obviously, numerical values of χ are meaningful only if the reference volume is clearly defined and specified.

We now rewrite some of the theoretical expressions given by LOW³ in order to display the explicit expressions utilized for the numerical computations in this work. In so doing, we also incorporate the consequence of minor modifications to the physical model originally employed. Whereas LOW³ assumed that homopolymer A is not penetrating into the micelle core consisting of the B blocks of the copolymer, we now allow swelling of the core by the homopolymer A and seek to determine the equilibrium degree of core swelling dictated by the minimization of free energy. LOW³ presented explicit expressions only for the case of symmetric diblock copolymers, whereas we now write expressions applicable also to nonsymmetric copolymers in order to be able to make comparison with experimental results given in Parts 1 and 2.

The system of study consists of a mixture containing homopolymer A of molecular volume v_h and diblock copolymer A-B of overall molecular volume v . The volume fraction of A (or B) units in the copolymer is equal to f_A (or f_B) so that the volume of an A block is $v_A = f_A v$ ($v_B = f_B v$, $f_A + f_B = 1$). We consider a spherical micelle of radius R containing p copolymer chains. The core, of radius R_B , contains B blocks of the copolymer and some number of homopolymer chains, so that the volume fraction of B monomers in it is equal to η_B . The spherical outer shell or corona, of thickness $R_A = R - R_B$, contains A blocks of the copolymer and some homopolymer chains. The corona contains only A monomers, and the volume fraction of these monomers that belong to copolymers is equal to η_A .

The free energy of a single micelle consists of the following contributions:

$$F = 4\pi R_B^2 \gamma + F_d + F_{mA} + F_{mB} \quad (5)$$

where γ is the interfacial tension at the boundary between the core and corona, F_d is the contribution due to deformation of copolymer chains, and F_{mA} and F_{mB} are the free energies of mixing the homopolymer molecules with the blocks of copolymer in the corona and the core, respectively. The interfacial tension can be written

$$\gamma = \gamma_0 \eta_B \quad (6)$$

where γ_0 is the interfacial tension between the corona and the unswollen core containing only the B blocks of the copolymer. Assuming that γ_0 is equal to the interfacial tension between two homopolymers A and B, we can write (see Appendix)

$$\frac{\gamma_0}{kT} = \frac{2 \left(\frac{\Lambda}{kT} \right)^{1/2} (r_A^2/v_A) + (r_A^2/v_A)^{1/2} (r_B^2/v_B)^{1/2} + (r_B^2/v_B)}{3 \left(\frac{\Lambda}{kT} \right)^{1/2} (r_A^2/v_A)^{1/2} + (r_B^2/v_B)^{1/2}} \quad (7)$$

The contributions F_d , F_{mA} , and F_{mB} can be written as

$$F_d = (3/2)kTp(R_A^2/r_A^2 + r_A^2/R_A^2 + R_B^2/r_B^2 + r_B^2/R_B^2 - 4) \quad (8)$$

$$F_{mA} = (4/3)\pi(R^3 - R_B^3)(kT/v_h)(1 - \eta_A) \ln(1 - \eta_A) \quad (9)$$

$$F_{mB} = (4/3)\pi R_B^3 [(kT/v_h)(1 - \eta_B) \ln(1 - \eta_B) + \Lambda \eta_B(1 - \eta_B)] \quad (10)$$

From the incompressibility conditions we also have

$$(4/3)\pi R_B^3 \eta_B = p v_B \quad (11)$$

$$(4/3)\pi(R^3 - R_B^3)\eta_A = p v_A \quad (12)$$

Combining eq 5-12, we have

$$F/kT = pf = B_1(\gamma/kT)(p v_B/\eta_B)^{2/3} + B_2(1 + C)p^{5/3}(v_B/\eta_B)^{2/3}/r_B^2 + B_3(1 + 1/C)p^{1/3}(\eta_B/v_B)^{2/3}r_B^2 + p\{(v_A/v_h)[(1 - \eta_A)/\eta_A] \ln(1 - \eta_A) + (v_B/v_h)[(1 - \eta_B)/\eta_B] \ln(1 - \eta_B) + (\Lambda/kT)v_B(1 - \eta_B) - 6\} \quad (13)$$

where $B_1 = 6^{2/3}\pi^{1/3}$, $B_2 = 3^{5/3}/2^{7/3}\pi^{2/3}$, $B_3 = 6^{1/3}\pi^{2/3}$, and

$$C = (r_B^2/r_A^2)[(v_A\eta_B/v_B\eta_A + 1)^{1/3} - 1]^2 \quad (14)$$

Next we consider the free energy F_M of the whole system of volume V . The overall volume fraction of the copolymer is ϕ , and of these only fraction ξ participates in the micelles, the remainder being molecularly dissolved in the continuous homopolymer phase. We then write

$$F_M = (V\phi\xi/v)fkT + F_{\text{mix}} - TS_m \quad (15)$$

where 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. They are given by

$$F_{\text{mix}}/kT = V\{(1 - \xi\phi\xi)\{(\phi_1/v) \ln \phi_1 + [(1 - \phi_1)/v_h] \ln(1 - \phi_1) + (\Lambda/kT)\phi_1 f_B(1 - \phi_1 f_B)\} \quad (16)$$

and

$$S_m/k = -V\{(\phi\xi/pv) \ln(\xi\phi\xi) + [(1 - \xi\phi\xi)/(p v)] \ln(1 - \xi\phi\xi)\} \quad (17)$$

where

$$\xi = (1/v)(v_A/\eta_A + v_B/\eta_B) \quad (18)$$

and

$$\phi_1 = \phi(1 - \xi)/(1 - \xi\phi\xi) \quad (19)$$

The equilibrium values of the parameters p , η_A , η_B , and ξ can then be obtained by minimizing F_M with respect to these quantities with ϕ fixed.

Numerical Results and Discussion

The value of Λ (in cal/cm³) as a function of temperature was calculated by

$$\Lambda = 0.718 \pm 0.051 - (0.0021 \pm 0.00045)(t - 150^\circ\text{C}) \quad (20)$$

which was obtained by averaging the values determined previously⁶ from the cloud points of mixtures containing a polystyrene and a polybutadiene or a styrene-butadiene copolymer. (The error limits denote the standard deviation.) The molecular volumes of the polymer chains were calculated from the molecular weight by using the following values of specific volume:

$$v_A = 1.1138 + 8.24 \times 10^{-4}t \quad (21)$$

for polybutadienes² and

$$v_B = 0.9217 + 5.412 \times 10^{-4}t + 1.687 \times 10^{-7}t^2 \quad (22)$$

Table I
Characterization of Polymers Used

	diblock copolymer			poly- butadiene
	25/75	50/50	75/25	
M_n	27 000	25 000	21 000	2350
M_w/M_n	1.04	1.04	1.05	1.13
styrene content, wt %	27.0	52.2	76.6	

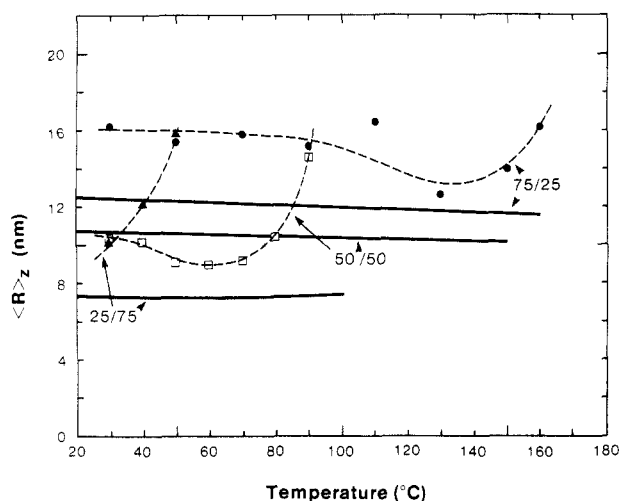


Figure 1. The radii $\langle R \rangle$ of the micelle core calculated from the theory (thick lines) are compared with the z -average radii $\langle R \rangle_z$ obtained experimentally: solid circles, 3% sample 75/25; open squares, 4% sample 50/50; solid triangles, 14% sample 25/75. The theoretical values were calculated for the same concentrations of the copolymers, but the concentration dependence is small in any case.

for polystyrenes,^{2,7} where v_A and v_B are in centimeters cubed per gram and t is in degrees Centigrade. The end-to-end distances were calculated from the molecular weight by $r = (\text{const})M^{1/2}$ with the constant⁸ equal to 0.9 Å for polybutadiene and 0.7 Å for polystyrene. The number-average molecular weights of the polymers, utilized for the computation, are listed in Table I. The minimization of the free energy F_M with respect to p , η_A , η_B , and ζ was performed on a PDP 11/34 minicomputer. (The Fortran program for this computation can be made available on request.)

In Figure 1 the calculated values of the core radius $\langle R \rangle$ are compared with the observed z -average radius $\langle R \rangle_z$. The agreement between the observed and calculated values is very good. The theory ignores the possible polydispersity of the core radius (in fact, it predicts the polydispersity to be very small), so that the calculated $\langle R \rangle$ does not distinguish different types of averages. If we had evaluated the number-average $\langle R \rangle_n$ instead of the z -average $\langle R \rangle_z$ from the experimental data, the agreement would probably have been better. The predicted temperature dependency of the core radius $\langle R \rangle$ is very small, whereas the experimental data show that over a temperature interval just below the dissolution temperature the observed radius $\langle R \rangle_z$ varies appreciably and goes through a minimum. The theory was developed to apply for the cases where the incompatibility between A and B units is high, and it is therefore not surprising that the features observed near the dissolution temperature are not predicted in detail.

In Figure 2 the observed and calculated values of the cmc are compared. In Figure 3 the same information is replotted, this time with the concentration on a logarithmic scale. The trend of increasing cmc with increasing compatibility between the copolymer and homopolymer, as the proportion of styrene block decreases, is correctly displayed by the calculated curves. The theory also correctly re-

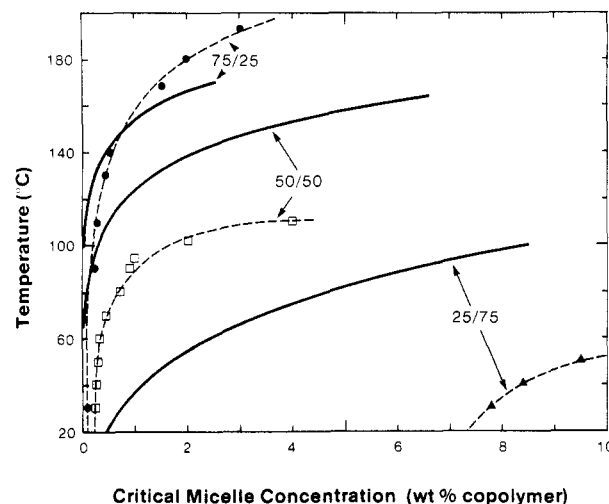


Figure 2. The observed and calculated values of the critical micelle concentration as a function of temperature are given for the three copolymers.

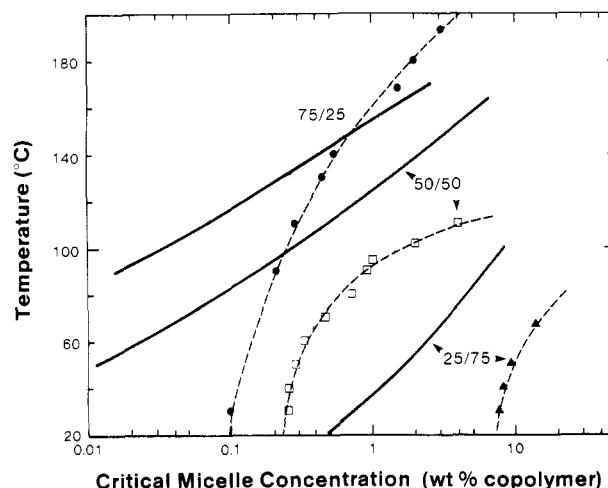


Figure 3. The same data as in Figure 2 are replotted with the concentration axis on a logarithmic scale.

produces the general trend of the cmc increasing very rapidly with temperature before approaching the final dissolution temperature. Quantitative agreement is less satisfactory, and this is more apparent in Figure 3 where the disagreement at low concentrations is greatly exaggerated.

The most important discrepancy between the observation and the prediction is with respect to the degree of swelling of styrene cores by the butadiene homopolymer. Figure 7 of Part 1 and Figure 6 of Part 2 show that the volume fraction η of styrene in the core (η there is equivalent to η_B of the present paper) decreases steadily from unity as the temperature is raised above a certain temperature (which in the case of sample 75/25 is about 90 °C). The value of η_B predicted from the theory, however, falls from unity to at most 0.96 with increasing temperature throughout the temperature ranges studied experimentally. The prediction of the very low degree of swelling of styrene core by polybutadiene basically reaffirms the incompatibility between the styrene and butadiene units, which was deduced from the miscibility study⁶ of mixtures of polystyrene and polybutadiene. The value of η falling as low as 0.3 before the micelles finally dissolve, as found experimentally, cannot therefore be explained within the framework of the model on which the LOW theory is based. To explain the observed values of η , some modifications may have to be introduced into the model, al-

lowing, for example, the possibility of a butadiene-rich inner core developing within the styrene-rich core or the possibility of the micelle core adopting shapes different from spheres.

Despite some of the discrepancies noted above, it would be fair to say that LOW theory predicts the semiquantitative behavior of the block copolymer micelles well, especially at temperatures far below the dissolution temperature, and should serve adequately as a basis for understanding the thermodynamics of mixtures containing a block copolymer and a homopolymer.

After this work was completed, a paper by Whitmore and Noolandi⁹ was published in which they extend the earlier theory of block copolymer micelles by Noolandi and Hong¹⁰ and compare its predictions with experimental results obtained by Selb et al.¹¹ on block copolymer-homopolymer blends very similar to ours. Their numerical results were calculated on the basis of the concept of a segment equal to the Kuhn statistical length and therefore cannot be compared directly with our results. Their calculated values of micelle core radii, however, agree approximately with our calculated values, and the overall trend of the cmc calculated by them also agrees with the prediction from LOW theory. In view of the close similarity between the models used in these two theories, we believe that the degrees of agreement with our experimental results offered by them are likely to be comparable.

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Appendix

Here we give a brief derivation of the interfacial tension γ_0 and the thickness d_{int} of the interfacial layer between two polymers in the long-chain limit and phrase the expressions in terms of v , r , and Λ rather than the customary set N , a , and χ .

Near the interface the local free energy density (per unit volume) can be given by

$$F/kT = (\phi/v_1) \ln \phi + [(1-\phi)/v_2] \ln (1-\phi) + (\Lambda/kT)\phi(1-\phi) + \text{gradient term} \quad (\text{A1})$$

To derive the gradient term, we consider the result of the random-phase approximation¹² applied to polymer mixtures

$$[\tilde{s}(q)]^{-1} = [\phi v_1 f_D(x_1)]^{-1} + [(1-\phi)v_2 f_D(x_2)]^{-1} - 2\Lambda/kT \quad (\text{A2})$$

where $\tilde{s}(q)$ is the Fourier transform of the correlation function, f_D is the Debye function

$$f_D(x) = 2(e^{-x} + x - 1)/x^2 \quad (\text{A3})$$

and

$$x_1 = q^2 r_1^2 / 6 \quad (\text{A4})$$

For $x \gg 1$, $f_D(x) \simeq 12/q^2 r^2$, so that

$$[\tilde{s}(q)]^{-1} \simeq (q^2/12)[(r_1^2/v_1)/\phi + (r_2^2/v_2)/(1-\phi)] - 2\Lambda/kT \quad (\text{A5})$$

The gradient term in (A1) comes from $(1/2)\sum_q [\tilde{s}(q)]^{-1} \delta\phi(q)\delta\phi(-q)$, and utilizing (A5), we find

gradient term =

$$(1/24)[(r_1^2/v_1)/\phi + (r_2^2/v_2)/(1-\phi)](\nabla\phi)^2 \quad (\text{A6})$$

In the limit of long chains, (A1) can therefore be written as

$$F/kT \simeq (\Lambda/kT)\phi(1-\phi) + (1/24)[(r_1^2/v_1)/\phi + (r_2^2/v_2)/(1-\phi)](\nabla\phi)^2 \quad (\text{A7})$$

Next we derive the density profile at the interface boundary. Applying the Lagrange-Euler relation

$$\partial F/\partial\phi = (\partial/\partial x)(\partial F/\partial\dot{\phi}) \quad (\text{A8})$$

(where $\dot{\phi} = \partial\phi/\partial x$) to (A7), we find

$$(\Lambda/kT)(1-2\phi) = (\dot{\phi}^2/12)[(r_1^2/v_1)/\phi + (r_2^2/v_2)/(1-\phi)] + (\dot{\phi}^2/24)[-(r_1^2/v_1)/\phi^2 + (r_2^2/v_2)/(1-\phi)^2] \quad (\text{A9})$$

Multiplying both sides of (A9) by $\dot{\phi}$ and integrating with respect to x , we obtain (for a very incompatible case where $\phi \rightarrow 0$ and $\phi \rightarrow 1$ as $x \rightarrow \pm\infty$)

$$(\Lambda/kT)\phi(1-\phi) = (\dot{\phi}^2/24)[(r_1^2/v_1)/\phi + (r_2^2/v_2)/(1-\phi)] \quad (\text{A10})$$

The density profile can be derived by integrating $\partial\phi/\partial x$ obtainable from (A10). In particular, the thickness d_{int} of the interface layer, defined as the reciprocal of the gradient at $\phi = 1/2$, is found to be

$$d_{\text{int}} = \left(\frac{2kT}{3\Lambda}\right)^{1/2} \left(\frac{r_1^2/v_1 + r_2^2/v_2}{2}\right)^{1/2} \quad (\text{A11})$$

The interfacial tension γ_0 is obtained by integrating the free energy F given by (A7) (with the density profile given by (A10) substituted in it) for the whole range of x between $-\infty$ and ∞ . The result is

$$\gamma_0/kT = (\Lambda/kT)^{1/2}(2/3)[(r_1^2/v_1)^{3/2} - (r_2^2/v_2)^{3/2}]/(r_1^2/v_1 - r_2^2/v_2) \quad (\text{A12})$$

Equations A11 and A12, when reinterpreted in terms of N , a , and χ , agree with the results given by Helfand et al.¹³

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