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A scaling model for the prediction of micellization of diblocks in polymer melts

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Abstract

A scaling model is proposed for A–B diblock copolymers in homopolymer melts based on the minimization of free energy. Competition between the migration of block copolymer to the A and B homopolymer interface and formation of micelles in the B phase has been modeled. Sample calculations done for polystyrene (PS), polybutadiene (PB), and PS–PB diblock copolymers support experimental observation for the onset of micellization and for the aggregation number of a micelle. The model is relatively simple and testable. It can be used as a predictive tool, once knowledge of three scaling factors is obtained. This would allow a priori calculation of the block copolymer concentration needed for full coverage of the homopolymer interface. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Micelle; Diblock; Interface

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1. Introduction

Incompatible polymers are often blended to obtain required properties. Block copolymers provide a simple and a versatile means for achieving interfacial adhesion in such blends [1,2]. The tendency of the block copolymers to adsorb at the interface or self assemble into micelles or other structures can be judged by the minimization of free energy. Several features need understanding, such as the amount of block copolymer present at the interface, the interfacial concentration at which micellization takes place, the aggregation number of the micelles and other parameters. From a practical standpoint, the amount of block copolymer required to just cover an interface would lead to optimal usage, as block copolymers are expensive compared to the homopolymers.

Studying the effect of block copolymers in blends or grafting in blends produced by polymerization or extrusion is not easy because of confounding factors. It is more easily done by compositional quenching [3]. A single phase solution in a good solvent is prepared for two incompatible polymers, say polystyrene (PS) and polybutadiene (PB), and their diblock copolymer. This polymer solution is then flash devolatilized to give a solvent-free blend with the diblock copolymer at the interface [3]. The mechanism of morphology formation is spinodal decomposition. If the minor phase has a content less than 33%, spherical particles are formed [4,5]. The particle size can be controlled by varying the depth of flash and by post-flash ripening.

Simple correlations exist for the prediction of block requirements to saturate the interface in the blend [6]. These are based on the molecular weight of the block and particle size of the minor phase, and many approximations have been made. However, conformational restrictions will prohibit filling the interface with block copolymer and may reduce the amount of block copolymer calculated by an order of magnitude [7,8]. Also, because of the large differences in cohesive and chemical bond energies, adequate adhesion may sometimes result in much lower surface occupation densities [9]. Thus, predicting the optimal amount of block to be added for adequate interfacial adhesion and impact strength in commercial blends remains a challenge. If excess block is added or if the quantity added becomes excessive as a result of ripening of the particles, micelles can be formed in either major or minor phases, depending on the relative block lengths in the copolymer. The appearance of micelles or lamella in both phases was observed when block lengths were commensurate [10]. The present paper is concerned with the case where the block length corresponding to the B phase is much longer than that corresponding to the A phase, $N_B > N_A$. It is then observed that

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essentially spherical micelles form preferentially within the B phase.

Noolandi and Hong [11] employed mean field theory (MFT) to estimate the critical micelle volume fraction, for a quaternary system of two homopolymers, a solvent and a 50/50 diblock copolymer of varying degrees of polymerization. Their results focussed on the emulsifying effect at the homopolymer interface and the reduction of interfacial tension. The trade-off in copolymer free energy between an interface and micellization was not studied. Later, Leibler et al. [12] published their work on critical micelle concentration (cmc) for a block dispersed in a single homopolymer using both the scaling approach and MFT. It was found that, for a high Flory–Huggins interaction parameter, the concentration of free copolymer outside the micelles was small, $<1\%$. Shull and Kramer [13] developed a comprehensive MFT to describe the broadening of the homopolymer interface and reduction of interfacial tension as a result of the presence of block copolymer at homopolymer interfaces. Shull et al. [14] did experiments in a simple geometry to describe the effects of the diblock at the homopolymer interface and compared results to MFT. A theory of micelle formation was stated to calculate the chemical potential for micellization [14], based on the work of Leibler [36] and Semenov [22].

The success of scaling theories in describing solutions of homopolymers, their mathematical simplicity and clarity of physical interpretation make them a useful tool for the analysis of more complex systems [15]. Scaling theories have been widely applied to model dilute and semidilute polymer solutions [16–18]. These have been incorporated into theories dealing with block copolymer adsorption from solutions [19,20]. Micelle formation in melts by diblock copolymers has been modeled using mean field theory [21,22]. Leibler [36] calculated the free energy of a micelle for the dry brush case, which corresponds to copolymer blocks being much shorter than the homopolymer. In this paper we postulate a simple, testable model for systems containing both homopolymer melts and a block copolymer of commensurate length. We study the competition between the adsorption at the interface and micellization in one of the homopolymer phases. This provides insight into maximum surface coverage, the onset of micellization, and the aggregation number of a micelle as a function of copolymer properties. We are restricted to the case where the copolymer block length and homopolymer lengths are similar, which is typically the case for copolymers used for interfacial adhesion and toughness improvement. The model assumes that like polymers can be modeled as θ solvent in melts. Experimental results [23,24] obtained from neutron scattering show that in the amorphous state the conformation of the polymer molecule is indistinguishable from that in θ solvent. The model is tested by varying parameters and looking at trends for the PS/PB/diblock system. Finally, the model prediction for coverage of the interface at the onset of micellization is tested against experimental results.

2. Theory

The system consists of homopolymer phases A and B in a fixed volumetric ratio and the A–B diblock copolymer which is added to varying extents. The block lengths, N_A and N_B are monodisperse. The polymers A and B are also monodisperse having lengths P_A and P_B, amorphous, non-electrolytes and non-polar, so that intermolecular forces are the van der Waals type. It is assumed for this theoretical treatment that, $N_A \sim P_A$, and $N_B \sim P_B$. The polymers are incompatible with a high Flory–Huggins interaction parameter ($n\chi > 2$). At low copolymer concentrations, the block copolymer migrates to the interface between the two incompatible homopolymers. At higher block concentrations, the interface becomes crowded and the excess copolymer forms micelles. Our model attempts to predict the crossover point using a scaling approach.

The thermodynamic reference state is a fully phase separated system with homopolymer A, homopolymer B, and a clean interface between them. The diblock copolymer is present as free chains in the B phase. With $N_A \ll N_B$, the concentration of diblock in the A phase will be ignored. As the like–like interactions are more favorable, the B portion of the diblock is a gaussian chain while the A portion collapses into a spherical ball. This configuration minimizes the A block and B homopolymer interactions. The radius of the sphere containing A segments of the diblock is determined by the bulk density of the A homopolymer.

The reference state is not an equilibrium state. Reductions in free energy per diblock molecule and for the system as a whole will occur as copolymer molecules migrate to the interface or combine to form micelles. The change in free energy for the diblock going to the interface has three contributions. The interface between the A blocks and the B homopolymer is minimized, and the unfavorable elastic energy in the A core is released. These are favorable changes with a negative free energy. However, the long B blocks cause crowding at the interface. This is a positive contribution to the free energy which ultimately limits the interfacial density of the copolymer. Micellization also makes three contributions to the free energy. The collapsed chains aggregate in the core of the micelle. This reduces the enthalpic contribution to the free energy. The segments in the A core go from compression to stretching. This causes a negative change in free energy for low aggregation numbers (n_m), but ultimately becomes positive and can limit the size of the micelle. The third contribution because of crowding of the B blocks in the corona of the micelle is always unfavorable and may also limit the aggregation number.

In this model, a quasi-steady state has been assumed with respect to the interface. Micellization or migration of the blocks to the interface is assumed fast compared to any changes in interfacial area because of ripening. Thus, predictions are made at equilibrium. Theoretically, micelles form after a certain minimum bulk concentration. However, this concentration is small [11,12,25], and has been

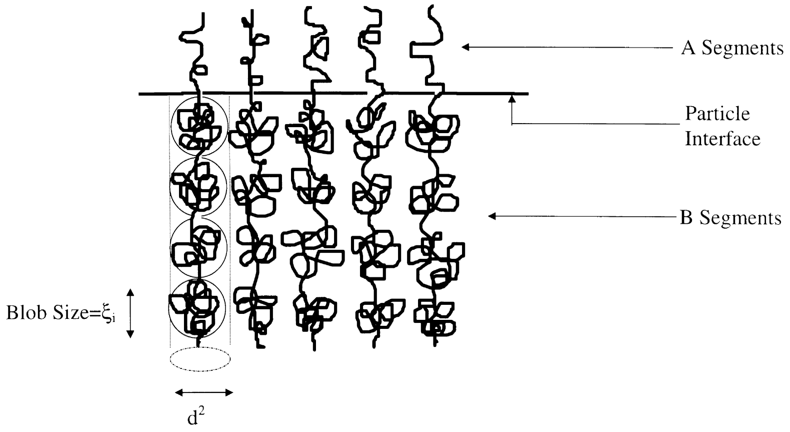

Fig. 1. Application of blob scaling model to block copolymer chains at a flat interface.

neglected in our treatment. It is assumed that, in the presence of an interface, all the copolymer goes to the interface until the free energy of the last molecule added to the interface equals the free energy of a molecule in a micelle. The free energy per diblock molecule at the interface is a monotonically increasing function of interfacial concentration, with a minimum at the extreme (zero concentration of the diblock).

Implicit is the concept of a unique saturation concentration at the interface. This saturation limit at the interface is imposed by crowding of the B-block. Beyond this concentration, a greater reduction in free energy relative to the reference state is achieved through micellization. Thus, all additional diblock will go into micelles. Below the saturation concentration, all diblock goes to the interface and there are no micelles. Thus, we assume a sharp transition between saturation of the interface and formation of micelles. Real diblocks will be polydisperse and there may be a region of overlap where short blocks go to the interface and long blocks form micelles. Experiments suggest this region of overlap to be small [14]. Although one can imagine situations where there is a jump discontinuity in free energy upon micellization, this possibility will not be addressed here.

A second region of overlap may occur at very high diblock concentrations where interactions between micelles in the B phase or between micelles and the interface become important. Such high concentrations are not considered here.

2.1. Free energy at the interface

Fig. 1 shows a schematic of the diblock copolymer chains at the homopolymer interface. Each chain is assumed to be perfectly placed at the interface with the A portion of the diblock being in the homopolymer A phase and the B portion of the diblock within the B phase. When the copolymer chains are far apart, they occupy a space corresponding to the radius of gyration of the B block. However, on further addition of diblock, crowding of the B segments occurs. To explain this behavior, the free energy per chain at the interface can be given as the sum of three terms

$$F_i = F_\mathrm{A} + F_\mathrm{interface} + F_\mathrm{B} \tag{1}$$

where F_A is the conformational free energy change caused by A segments, $F_\mathrm{interface}$ the enthalpic change as a result of A–B interactions and F_B the conformational free energy change as a result of the B segments.

The A portion of the diblock is a tightly coiled chain, of radius R_S, in the reference state. Thus

$$\frac{4}{3}\pi R_\mathrm{S}^3 = N_\mathrm{A} v_A \tag{2}$$

where N_A is the total number of A segments in the diblock copolymer chain and v_A the volume of the A segments of the diblock copolymer.

The A segments at the interface occupy a radius at least equal to that of the radius of gyration of the A block, R_gA, because $R_\mathrm{gB} > R_\mathrm{gA}$. Hence, the energy is given by the difference in free energy between a terminally anchored chain [26], which is normally negligible, and the elastic free energy of the collapsed A block in the reference state:

$$F_\mathrm{A} = -\frac{3}{2}\left[\frac{R_\mathrm{S}^2}{R_\mathrm{gA}^2} + \frac{R_\mathrm{gA}^2}{R_\mathrm{S}^2} - 2\right]kT \tag{3}$$

where k is Boltzmann constant and T the absolute temperature.

Substituting $R_\mathrm{gA}^2 = N_\mathrm{A} l_\mathrm{A}^2/6$, and R_S from Eq. (2), gives

$$F_\mathrm{A} = -\frac{3}{2}\left[\left(\frac{3}{4\pi}\right)^{2/3}\frac{6}{N_A^{1/3}}\left(\frac{v_A^{2/3}}{l_A^2}\right) + \left(\frac{4\pi}{3}\right)^{2/3}\frac{N_\mathrm{A}^{1/3}}{6}\left(\frac{l_\mathrm{A}^2}{v_\mathrm{A}^{2/3}}\right) - 2\right]kT \tag{4}$$

where l_A is the length of a statistical A segment.

Eq. (4) corresponds to a favorable interaction. The A segments in the reference state are under compression. This energy is released when the segments come to the interface and behave essentially ideally.

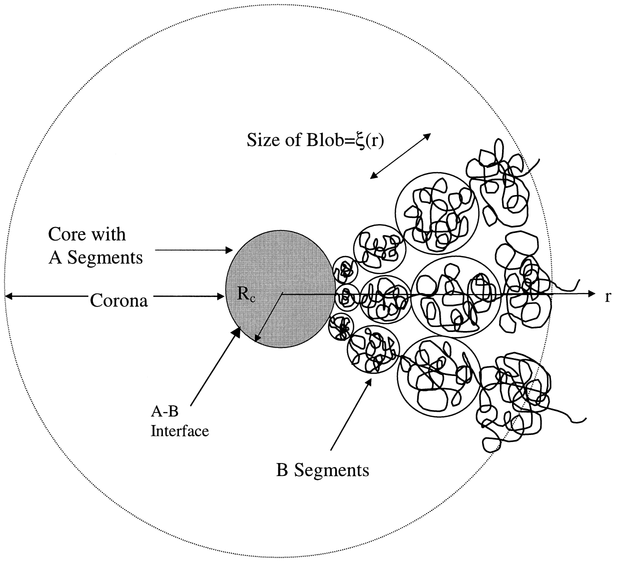

Fig. 2. Application of blob scaling model to block copolymer chains in a micelle.

The interfacial free energy per chain is given by [12,27]:

$$F_{\text{interface}} = -4\pi R_S^2 \gamma_{AB} \tag{5}$$

where γ_{AB} is the interfacial tension between the A segments and the B segments.

The interfacial tension can be related to the Flory–Huggins interaction parameter, χ, using a well known approximation which is valid for large χ [11,12,14,36]:

$$\gamma_{AB} = \frac{kT}{l_m^2}\sqrt{\frac{\chi}{6}} \tag{6}$$

where l_m is the monomer length.

Thus, Eq. (5) becomes

$$F_{\text{interface}} = -4\pi\left(\frac{3}{4\pi}\right)^{2/3} N_A^{2/3} v_A^{2/3} \frac{kT}{l_m^2}\sqrt{\frac{\chi}{6}}. \tag{7}$$

As stated before, the A segments occupy an area at the interface which corresponds to the radius of gyration. This conclusion holds for all copolymer concentrations at the interface, as $N_B > N_A$.

The blob model has been applied to semi-dilute regimes by de Gennes [28], and will be used to calculate the free energy of the B segments. For application of the blob scaling model, no entanglement between diblock chains is assumed. Thus, each blob has segments from a single diblock molecule [28], and possibly from the B homopolymer. The scaling models applicable to good solvents, and extended to θ solvents [28,29], can be used when the solvent is replaced by the B homopolymer. Ideal interactions should exist between the segments of the copolymer and homopolymer [30], and also between blobs. This approach is different from that of deGennes [31] who considers a screened excluded volume ν/P, in the regime $N^{1/2} < P < N$. The screened excluded volume is negligible for the regime when the concentration is less than $PN^{-3/2}$. Our treatment is restricted to low concentrations at the interface where the ideal chain assumption is correct.

The concept of blob is illustrated in Fig. 1 for a flat interface. The long B-block forms a succession of blobs, each of size ξ. The size of the blobs, $\xi = \xi_i$, is not a function of distance from the interface [31], but does depend on the diblock concentration, σ. The number of segments per blob, $N\xi_i$, can be related to the size of a blob via an ideal chain argument [28]:

$$\xi_i = N_{\xi_i}^{1/2} l_B \tag{8}$$

where l_B is the length of a statistical B segment.

The size of blobs, ξ_i, in the B phase is the distance between graft points [32] for tightly packed B chains, $\xi_i < R_g$, of the diblock copolymer. However, when the concentration of the chains at the interface is low, $\xi_i = R_g$. Thus, the area occupied by each copolymer chain at the interface, $\sim d^2$, is proportional to the blob size, $\sim \xi_i^2$,

$$d = s_i \xi_i \tag{9}$$

where s_i is the scaling constant $O(1)$.

The concentration of copolymer chains at the homopolymer interface, σ, is scaled by l_B,

$$\sigma = \frac{l_B^2}{d^2}. \tag{10}$$

Conserving the total number of B segments per diblock copolymer chain, N_B, gives

$$N_B = N_b N_{\xi_i} \tag{11}$$

where N_b is the number of blobs of B segments in a diblock copolymer chain.

The free energy per blob scales as kT [33,34] thus

$$F_B = s_e kT N_b \tag{12}$$

where s_e is a scaling constant $O(1)$.

Substituting Eqs. (8)–(11) for N_b in Eq. (12),

$$F_B = s_i^2 s_e N_B \sigma kT = s_1 N_B \sigma kT. \tag{13}$$

This results in a positive contribution to free energy, because of steric hindrance. The layer thickness of B blocks scales as $N_B\sigma$. This is because of the fact that energy lowered from A blocks coming to the interface would alter the blob size. Previous results [35] for end tethered chains show that a constant thickness of $N_B^{1/2} l_B$ would be obtained.

The overall free energy per copolymer chain at the interface becomes

$$\frac{F_i}{kT} = -\frac{3}{2}\left[\left(\frac{3}{4\pi}\right)^{2/3}\frac{6}{N_{\mathrm{A}}^{1/3}}\left(\frac{v_{\mathrm{A}}^{2/3}}{l_{\mathrm{A}}^2}\right) + \left(\frac{4\pi}{3}\right)^{2/3}\frac{N_{\mathrm{A}}^{1/3}}{6}\left(\frac{l_{\mathrm{A}}^2}{v_{\mathrm{A}}^{2/3}}\right) - 2\right] - 4\pi\left(\frac{3}{4\pi}\right)^{2/3} N_{\mathrm{A}}^{2/3}\frac{v_{\mathrm{A}}^{2/3}}{l_{\mathrm{m}}^2}\sqrt{\frac{\chi}{6}} + s_1 N_{\mathrm{B}}\sigma. \tag{14}$$

2.2. Free energy of a micelle

The micelles are assumed to be spherical, monodisperse with respect to aggregation number, and to consist only of A–B diblock copolymer. Scaling models have been developed for diblock copolymers in solvents by previous authors [18,15,36]. We now extend these results to melts of component B. In the model, micelles of aggregation number n_{m} consist of three distinct regions as shown in Fig. 2: a core region consisting of A segments, with radius R_{c}, a corona having B segments from the A–B diblock copolymer together with chains of homopolymer B, and a thin boundary region where the A–B junctions are concentrated. A high interaction parameter has been assumed, which guarantees a sharp interface between the homopolymers, and a correspondingly negligible thickness of the boundary of the micelle compared to the core size, R_{c}. It is also assumed that there is no penetration of the core by homopolymer A. Thus, ripening of a micelle is not allowed. The total free energy of the micelle within phase B is

$$F_{\mathrm{m}} = F_{\mathrm{core}} + F_{\mathrm{boundary}} + F_{\mathrm{corona}} \tag{15}$$

where F_{core} is the conformational free energy change of the A segments in the core of the micelle, F_{boundary} the enthalpic change as a result of the A and B interaction segments and F_{corona} the conformational free energy change as a result of the corona of B segments radiating outward from the core.

The core has a uniform melt density. Thus, the radius of the core can be related to the number and size of copolymer chains in the micelle

$$\frac{4}{3}\pi R_{\mathrm{c}}^3 = n_m N_{\mathrm{A}} v_A. \tag{16}$$

The free energy contribution of the core stems from the stretching of the A segments which arises from constraining the A–B junction to a sharp interface and from space filling requirements for the core. A quantitative expression was derived by Semenov [22]. The elastic free energy can be restated, accounting for the reference state, as

$$F_{\mathrm{core}} = \frac{3}{2} n_{\mathrm{m}}\left[\frac{R_{\mathrm{c}}^2}{R_{\mathrm{gA}}^2} + \frac{R_{\mathrm{gA}}^2}{R_{\mathrm{c}}^2} - \frac{R_{\mathrm{S}}^2}{R_{\mathrm{gA}}^2} - \frac{R_{\mathrm{gA}}^2}{R_{\mathrm{S}}^2}\right]kT. \tag{17}$$

In the aforementioned expression the second term is the compressive free energy for the core. As the chains are stretched in the micelle and $R_{\mathrm{c}} > R_{\mathrm{g}}$, the second term can be neglected. Substituting for R_{gA}, $R_{\mathrm{gA}}^2 = N_{\mathrm{A}} l_{\mathrm{A}}^2/6$, and R_{c} from Eq. (16) in Eq. (17) the core free energy is obtained. Thus, the free energy per chain of the core is given by

$$F_{\mathrm{core}} = \frac{3}{2}\left[\left(\frac{3}{4\pi}\right)^{2/3}\frac{6}{N_{\mathrm{A}}^{1/3}}\left(\frac{v_{\mathrm{A}}^{2/3}}{l_{\mathrm{A}}^2}\right)n_{\mathrm{m}}^{2/3} - \left(\frac{3}{4\pi}\right)^{2/3}\frac{6}{N_{\mathrm{A}}^{1/3}}\left(\frac{v_{\mathrm{A}}^{2/3}}{l_{\mathrm{A}}^2}\right) - \left(\frac{4\pi}{3}\right)^{2/3}\frac{N_{\mathrm{A}}^{1/3}}{6}\left(\frac{l_{\mathrm{A}}^2}{v_A^{2/3}}\right)\right]kT. \tag{18}$$

The free energy change is negative when n_{m} is low as a result of releasing compression in the collapsed core. For large n_{m}, the free energy contribution becomes positive, as a result of stretching of the A block. This would ultimately limit R_c to the length of a fully stretched chain. However, in what follows, a crowding limit on the B side of the boundary will usually occur at lower n_{m}.

For the boundary, the free energy per chain can be written as [37]:

$$F_{\mathrm{boundary}} = \left[\frac{4\pi R_{\mathrm{c}}^2}{n_{\mathrm{m}}} - 4\pi R_{\mathrm{S}}^2\right]\gamma_{\mathrm{AB}}. \tag{19}$$

Substituting for known values gives

$$F_{\mathrm{boundary}} = 4\pi\left(\frac{3}{4\pi}\right)^{2/3} N_{\mathrm{A}}^{2/3} v_{\mathrm{A}}^{2/3}\left[n_{\mathrm{m}}^{-1/3} - 1\right]\frac{kT}{l_{\mathrm{m}}^2}\sqrt{\frac{\chi}{6}}. \tag{20}$$

The corona of the micelle consists of B chains of the diblock copolymer grafted to the core and entangled with homopolymer B chains. We treat the homopolymer chains as a θ solvent. The assumptions for modeling B copolymer chains in the previous section apply. Daoud and Cotton [29] modeled star polymers by dividing the volume into three regions: a core composed of polymer melt, an unswollen θ solvent regime, and a swollen good solvent regime. To account for the radially decaying segment density, they developed a spherical blob model. We shall follow their approach in the intermediate θ solvent regime to derive the free energy density of the micellar corona. A different approach has been stated for star polymers in a chemically identical high molecular weight solvent by Raphael et al. [38]. Fig. 2 depicts their model with blobs of size $\xi(r)$ each containing $N\xi_{\mathrm{m}}$ segments. The scaling dependence of ξ on r can be obtained by a simple geometric consideration that the sum of the cross sectional areas from all the blobs is equal to the total surface area

$$\frac{s_{\mathrm{b}} n_{\mathrm{m}}\pi\xi^2}{4} = 4\pi r^2 \tag{21}$$

where s_{b} is the scaling constant $O(1)$.

The size of a blob can be related to the number of

Table 1
Molecular parameters used for the PS/PB biblock copolymer

Parameter	Symbol	Value
Statistical segment length of PS	l_A	12.7 Å
Statistical segment length of PB	l_B	8.3 Å
Segment volume for PS	v_A	1800 Å^3
Flory–Huggins interaction parameter	χ	0.08
Number of statistical PS segments	N_A	80
Number of statistical PB segments	N_B	1100
Scaling constant	s_1	0.4
	s_2	1.0
	s_3	1.0

segments via an ideal chain argument [28]:

$$\xi(r) = N_{\xi m}^{1/2} l_B. \tag{22}$$

Thus, the number density, $c(r)$, of the B segments at a given position r is

$$c(r) = \frac{N_{\xi m}}{(4/3)\pi(\xi/2)^3} = s_b^{1/2}\frac{3}{2\pi}\left(\frac{n_m^{1/2}}{l_B^2 r}\right). \tag{23}$$

The concentration of the B segments of the diblock decreases with incraeasing distance from the core. The space is filled by homopolymer B. The interactions with the homopolymer are treated as ideal, and thus make no contribution to the free energy.

The location of the outer extremity of the corona (radius R) is obtained by conservation of the B segments of the diblock copolymer. Thus, the total B segments are

$$n_m N_B = \int_{R_c}^{R} 4\pi r^2 c(r)\, dr. \tag{24}$$

Substituting for $c(r)$ gives

$$R = R_c\left[1 + \frac{1}{3s_b^{1/2}} n_m^{1/2} N_B \left(\frac{l_B}{R_c}\right)^2\right]^{1/2}. \tag{25}$$

As before, the energy per blob scales as kT [33,34]. Substituting for ξ from Eq. (21), the free energy is integrated over the corona to give

$$F_{\text{corona}} \sim kT\int_{R_c}^{R} \frac{4\pi r^2}{(4/3)\pi(\xi/2)^3}\, dr = \frac{3}{8} s_b^{3/2} kT n_m^{3/2} \ln\left(\frac{R}{R_c}\right). \tag{26}$$

Substituting for R from Eq. (25), and then for R_c from Eq. (16), gives

$$F_{\text{corona}} = \frac{3}{16} kT s_3 n_m^{3/2} \times \ln\left[1 + \frac{1}{3}\left(\frac{4\pi}{3}\right)^{2/3} s_2 n_m^{-(1/6)} N_B N_A^{-(2/3)} \left(\frac{l_B^2}{v_A^{2/3}}\right)\right]. \tag{27}$$

The scaled free energy of the micelle is obtained by combining Eqs. (18), (20) and (27):

$$\begin{aligned}\frac{F_m}{kT} = \frac{3}{2}&\left[\left(\frac{3}{4\pi}\right)^{2/3} \frac{6}{N_A^{1/3}}\left(\frac{v_A^{2/3}}{l_A^2}\right)\left(n_m^{2/3} - 1\right)\right.\\ &\left.-\left(\frac{4\pi}{3}\right)^{2/3}\frac{N_A^{1/3}}{6}\left(\frac{l_A^2}{v_A^{2/3}}\right)\right]\\ &+ 4\pi\left(\frac{3}{4\pi}\right)^{2/3} N_A^{2/3}\frac{v_A^{2/3}}{l_m^2}\left[n_m^{-1/3} - 1\right]\sqrt{\frac{\chi}{6}}\\ &+ \frac{3}{16} s_3 n_m^{1/2} \ln\left[1 + \frac{1}{3}\left(\frac{4\pi}{3}\right)^{2/3} s_2 n_m^{-1/6} N_B N_A^{-2/3}\left(\frac{l_B^2}{v_A^{2/3}}\right)\right]\end{aligned} \tag{28}$$

2.3. System equilibrium

In the reference state, all the copolymer molecules are in the B phase and the interface is clean. The system free energy is decreased as block copolymer migrates to the interface. The first few molecules are uncrowded, and the free energy change per molecule at the interface is negative and large in magnitude. Crowding causes a decrease in the magnitude of the free energy change per molecule although the change remains negative relative to the reference state. The interface saturates when the change in free energy for a diblock molecule going from the B phase to the interface equals that for a diblock molecule going from the B phase to a micelle. Thus, the free energy change for the system is a monotonically decreasing function of σ while the free energy change per molecule is a monotonically increasing function of σ.

The change in interfacial free energy as a function of σ is characterized by three parameters. The first is the energy of the first molecule, F_0, absorbed, which remains constant until crowding begins:

$$\begin{aligned}\frac{F_0}{kT} = -\frac{3}{2}&\left[\frac{6v_A^{2/3}}{N_A^{1/3} l_A^2}\left(\frac{3}{4\pi}\right)^{2/3} + \frac{N_A^{1/3} l_A^2}{6v_A^{2/3}}\left(\frac{4\pi}{3}\right)^{2/3} - 2 - s_3\right]\\ &- 4\pi\left(\frac{3}{4\pi}\right)^{2/3} N_A^{2/3} v_A^{2/3}\frac{1}{l_m^2}\sqrt{\frac{\chi}{6}}.\end{aligned} \tag{29}$$

The second is the crowding point, σ_c, where the slope of the curve changes:

$$\sigma_c = \frac{6}{4N_B}. \tag{30}$$

The third parameter is the slope of the crowded region, obtained from Eq. (14)

$$\frac{\partial F_i}{\partial \sigma} = s_3 N_B. \tag{31}$$

Table 2
Effect of various parameters on free energy and surface concentration. Note the symbols in the table qualitatively represent, −− large negative effect, − negative effect, 0 no effect, + positive effect, ++ large positive effect

Parameter	Effect with increasing parameter value			
	F_i	F_m	σ_c	σ_s
l_A	−	−−	0	−
l_B	0	+	0	+
v_A	−	−	0	+
$(v_A^{2/3}/l_A^2)$	−−	++	0	++
χ	−−	−−	0	−−
s_1	++	0	0	−−
s_2	0	++	0	++
s_3	0	++	0	++
N_A	−	−	0	+
N_B	+	+	−−	−

The aggregation number, n_m, for micelles is found from

$$\frac{\partial(F_m/n_m)}{\partial n_m} = 0. \tag{32}$$

The value obtained from Eq. (32) is substituted in Eq. (28), to give the free energy change per molecule going to a micelle. This minimized free energy per chain, F_m*, is simply the chemical potential of the copolymer. Thus, F_m* is a measure of the equilibrium tendency of the copolymer chains to aggregate. The point where the value of F_m crosses F_i determines the interface saturation value, σ_s. This is much lower than a concentration that would be obtained when F_i is positive.

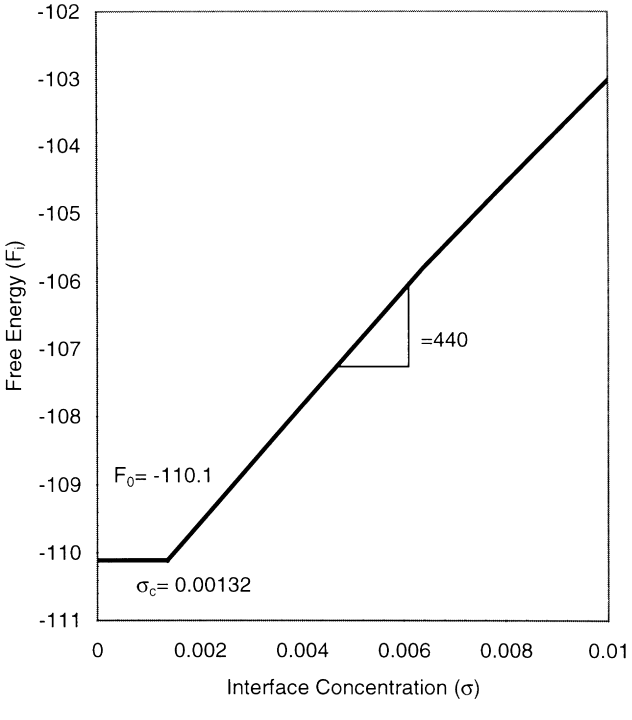

Fig. 3. Interfacial free energy as function of copolymer concentration σ.

An overall balance on the number of copolymer chains relates micelle and interface concentration to the total amount of copolymer added.

$$N_T = N_m n_m + \frac{A_p \sigma}{l_B^2} \tag{33}$$

where N_T is the total number of copolymer chains in the system, N_m the number of micelles and A_p the interfacial area between the homopolymer. Note that A_p can be varied in a particulate system by ripening the particles.

3. Model predictions

Table 1 shows the molecular parameters used for the example PS/PB system. The characteristic ratio, c_∞, relates the length of a statistical segment, l, to the average bond length, l_0, by the relationship $l = c_\infty l_0$ [39]. The c_∞ value is typically insensitive to changes in surroundings [41] and is mainly dictated by the architecture of the polymer backbone. For polystyrene the bond length corresponds to a single carbon–carbon bond, and is taken to be 1.27 Å. The value of 1.29 Å is used for polybutadiene, which corresponds to the average of three single bonds and a double bond. The values for c_∞ are 10.0 for PS [40,41] and 6.5 for PB [41]. The segment volume for A can be obtained from density calculations or be backed out from cell dimensions [41]. The number of segments is obtained by preserving the contour length, L_c, of the chain, $N = L_c/l$.

The model contains three independent scaling parameters, s_1, s_2, and s_3, which are assumed to be ~1. The other scaling parameters are dependent, $s_i = s_1^{1/2} s_2^{3/4} s_3^{-1/2}$, $s_b = s_2^{-2}$, and $s_e = s_2^{-3/2} s_3$. The actual values of, s_1, s_2, and s_3 can of course be expected to vary between 0.1 and 10. Table 2 shows the sensitivity of model predictions to assumed parameters. Numerical partial derivatives were used to estimate the trends in this table. The base parameters used are given in Table 1.

Fig. 3 shows the results for the change in interfacial free energy as a function of σ. This curve is characterized by three parameters as stated before. The first is the scaled free energy of the first molecule going to the interface, −110.108. The crowding point where the slope of the curve changes is $\sigma_c = 0.00132$, and the slope of the curve is 440.

Fig. 4 shows F_m/n_m as obtained from Eq. (28). The free energy decreases rapidly at low n_m but achieves a broad minimum. This is because the change in interfacial area at the boundary is insensitive at high n_m, i.e. ~ $(1/n_m^{1/3} - 1)$. The broad minimum suggests that the micelles will be polydisperse with respect to the aggregation number for this example system. The exact minimum, $n_m = 60$, was found numerically and used in subsequent results. The optimal n_m depends on N_A and N_B. Increasing N_A leads to an almost linear increase in n_m. With increasing N_B, n_m decreases. Some calculated numbers are given in Table 3.

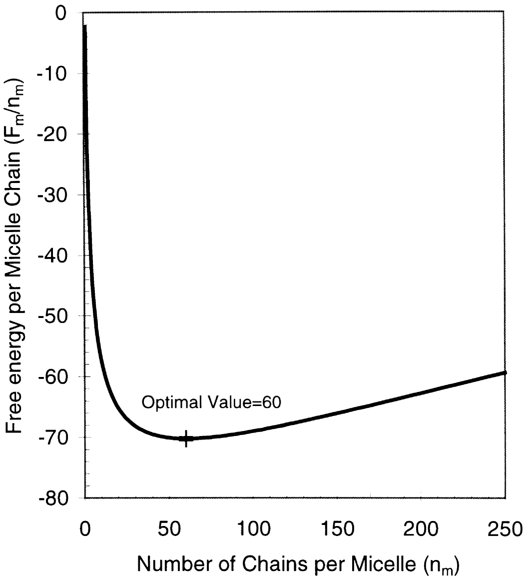

Fig. 4. Free energy of diblock copolymer chain in a micelle as a function of number of chains per micelle.

Fig. 5 shows the system free energy, F_s, as a function of the fraction of diblock molecules which have left the bulk B phase, x. The plot is linear until the onset of crowding at $\sigma_c = 0.00132$ (or an abscissa value of 0.0078). This is because the free energy change per molecule at the interface is constant. It becomes linear again after the onset of micellization at $\sigma_m = 0.0914$. This is because of the fact that the interface is saturated ($F_i\ \sigma$ is constant) and F_m is constant.

The model has been developed for flat interfaces. However, if one of the phases has a volume less than 33%, the geometry may be particulate. In our case we consider spherical particles consisting of the minor B phase. The radius of these particles, $d_p/2$, is assumed to be of the order of microns, hence orders of magnitude larger than the radius of gyration, R_g, of the polymer. For $R_g/d_p \ll 1$, the system is modeled as a flat interface [33,34,42].

In Fig. 6 the amount of polybutadiene added to the system is held constant at 16% of the total volume. The amount of block copolymer is varied from 1%–23%, and the amount of polystyrene homopolymer is adjusted accordingly. Fig. 6 shows the expected trend that large particles and high

Table 3
Change of micelle aggregation number, n_m, with segment length

N_A	N_B	n_m
40	400	32
40	4000	28
40	40 000	24
80	400	66
80	4000	56
80	40 000	47
120	400	101
120	4000	84
120	40 000	70

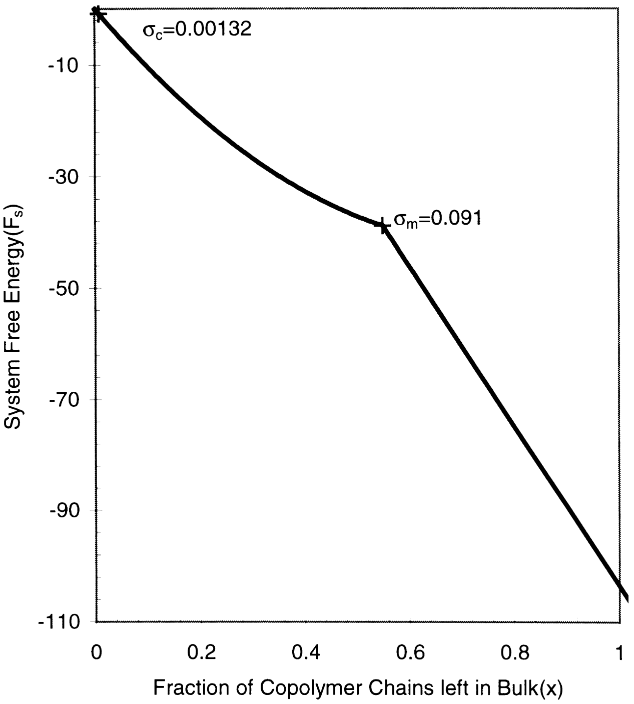

Fig. 5. Free energy of the system as function of fraction of copolymer chains which have left the bulk B phase.

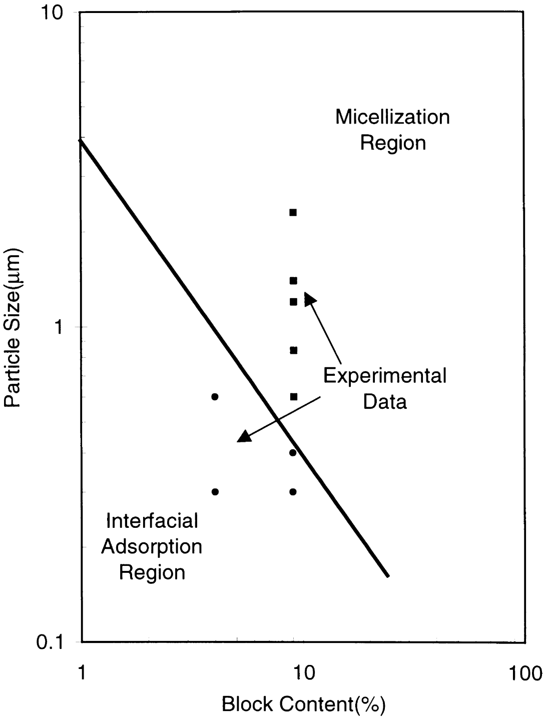

Fig. 6. Phase diagram showing the self micellization and adsorption regimes of the diblock copolymer as a function of particle size and copolymer content: ■ micelles, ● no micelles.

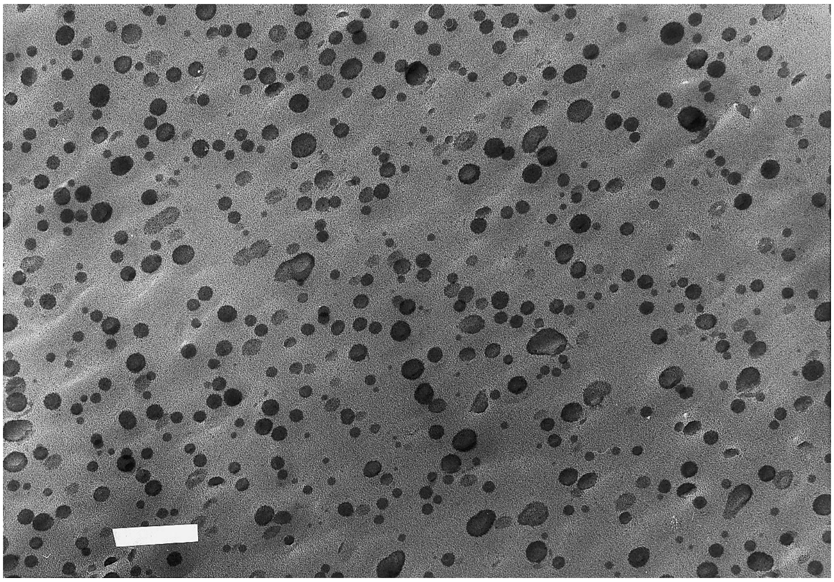

Fig. 7. TEM of PS/PB/730 A-diblock blend showing no micelles at a mean particle size of 0.3 μm. Scale bar: 1 μm.

diblock contents lead to micellization. Thus, below a particle size of 0.43 μm, for 16% rubber and 9% diblock, the copolymer adsorbs at the particle interface. Scaling parameters 0.4, 1.0, and 1.0 were chosen which gave results consistent with experimental observation. However, if s_1 were 1.0, much smaller particle sizes would be predicted, with $d_p = 0.17$ μm for the aforementioned concentration.

4. Experimental

Polymer A was general purpose polystyrene obtained from Novacor, with a molecular weight, M_n, of 82 000 and polydispersity of 2.2. Polymer *B* was polybutadiene (Diene55NR®) from Firestone with $M_n = 132\ 000$, and a polydispersity of 2.4. The A–B diblock copolymer was obtained from Firestone. It had a $M_n = 140\ 000$ and a polydispersity of 1.1, with 30% polystyrene. The segments had a molecular weight of 33 000 and 98 000 for PS and PB respectively. Calculated values of the number of segments in the diblock copolymer are $N_A = 80$ and $N_B = 1100$.

The polymer mixture consisted of 75% PS, 16% PB, and 9% diblock which gives a total butadiene volume fraction of 23%. A 5% polymer solution of this mixture in xylene was single phase. This solution was heated to 220°C–240°C, and

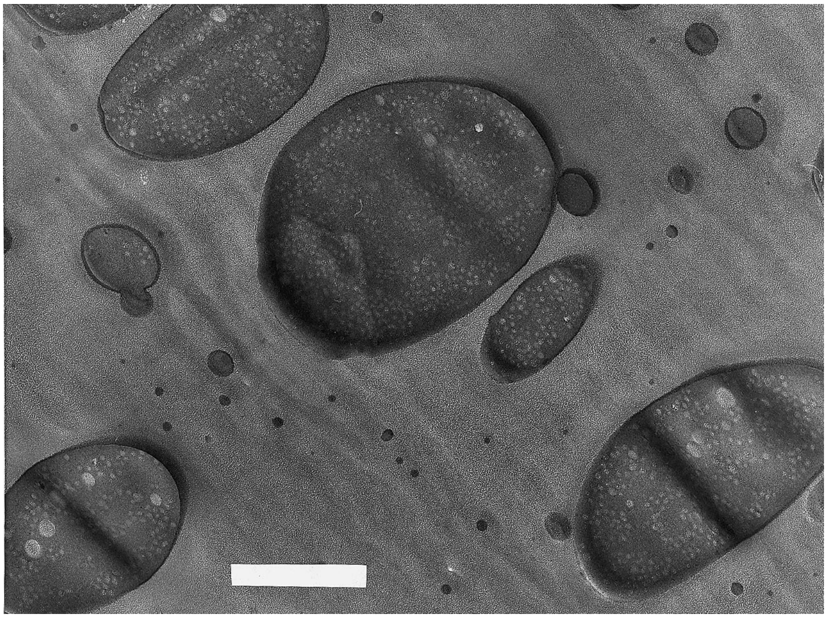

Fig. 8. TEM of PS/PB/730 A-diblock blend showing micelles at a mean particle size of 1.4 μm. Scale bar: 1 μm.

compositionally quenched using a vacuum of 5 Torr. Molding time at 200°C was used to ripen the particles. The molded blends were cut, shaped to form a sharp pyramid, and stained with osmium tetraoxide [43]. Thin sections (approx. 800 Å) were cut with a diamond knife and observed under a 100 kV electron beam using a Philips CM12 Transmission Electron Microscope. The material after compression molding for 3 min at 200°C had a particle size of approximately 0.3 μm as shown in a representative TEM in Fig. 7. No micelles are apparent.

Fig. 8 is a representative micrograph showing numerous micelles formed in the ripened PB particles. This fact, along with other data, are shown in Fig. 6. It is seen that the predicted crossover is consistent with the experimental observations, and previous results [44]. Rough estimates of micelle size made from the TEM's show that the micelles grow as the particulate phase ripens. They start as small as 250 Å for the micelle core, which corresponds to ~57 copolymer chains, and grow to 3500 Å, which corresponds to occluded micelles with homopolymer PS in the core. These results are similar to those obtained in films by Polance et al. [45] in the PS phase with the diblock composition being 70/30 (PS/PB) and the micelles grow in size from 240 to 520 Å when annealed at 200°C for 2 h.

5. Conclusions

This article has demonstrated application of scaling theory to diblock copolymers in homopolymer melts. We have made simplifying assumptions, particularly for the interactions between the homopolymer and the copolymer brush. The result is a testable theory supported in part by experimental observations. Specifically considered is the existence of an interface between incompatible homopolymers. The theory contains three adjustable scaling parameters, all $O(1)$. Using crude estimates for these parameters (0.4,1,1), the theory predicts a crossover from adsorption at the interface to micellization which is consistent with experiments. The model also predicts a plausible value for the aggregation number of a micelle. The model can be used as a predictive tool to obtain optimal surface coverage of the homopolymer interface. The model can be further expanded for different copolymer and homopolymer lengths by using more rigorous models for their interactions. For interfaces the work of deGennes [31] and Aubouy et al. [35] can be expanded, and for micelles the work of Raphael et al. [38] be applied. It appears possible to relax the assumptions made and include free copolymer solubility in the A and B phases, and equality of segment lengths $N_A \sim N_B$. The assumption of high segregation might also be removed. However, this model cannot handle structured aggregates of micelles i.e. when the micelles cease to be a gas.

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